

Production, trade and maritime transport of colouring materials based on Early Modern Gnalić shipwreck finds

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POSILIJEDIPLOMSKI SVEUČILIŠNI STUDIJ
ARHEOLOGIJA ISTOČNOG JADRANA



Katarina Batur

**PRODUCTION, TRADE AND MARITIME
TRANSPORT OF COLOURING MATERIALS
BASED ON EARLY MODERN GNALIĆ
SHIPWRECK FINDS**

Doktorski rad

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Ja, **Katarina Batur**, ovime izjavljujem da je moj **doktorski** rad pod naslovom **Production, trade and maritime transport of colouring materials based on Early Modern Gnalčić shipwreck finds** rezultat mojega vlastitog rada, da se temelji na mojim istraživanjima te da se oslanja na izvore i radove navedene u bilješkama i popisu literature. Ni jedan dio mojega rada nije napisan na nedopušten način, odnosno nije prepisan iz necitiranih radova i ne krši bilo čija autorska prava.

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FOREWORD

When I joined the excavation of the Gnalić shipwreck as an undergraduate student, I could not brag on my experience as a diver-archaeologist. Indeed, being a second-year undergraduate student and having only two dives deeper than 20 meters, my archaeological and diving skills were very poor. I could not even neutralize my buoyancy, I had extra-large diving equipment, and I really did not feel comfortable when I jumped in the water. Seeing the pieces of wood, broken glass, ingots and stones on the seabed did not look spectacular in the given moment, but as the artifacts were being recovered and the outlines of the wooden hull became clear, my curiosity was aroused. As the excavation period was getting close to the end, I knew that in the future I would put all my effort to reveal the stories behind these artifacts. Soon, I was given the responsibility to catalogue the artifacts by the director of the project Irena Radić Rossi.

‘Those were colours? What are they made from?’ were my questions posed to other archaeologists when I looked the remains of red powder and conical heavy objects that seemed to be made of lead. ‘How they were traded? Why did they make the lead conical? Look at this – the lead is actually not black, it has a white core!’, were my questions and exclamations when I first looked at these materials. At the beginning I knew nothing about colouring materials and I had no idea which sources to consult, or whom to ask particular questions. For several years it remained only a curiosity.

The moment that changed my mind happened when I reached for a book on the shelf in the University of Malta library. The book, titled ‘Trade in Artists’ Materials – Markets and Commerce in Europe to 1700’, was published as the proceedings of a conference held in London and was edited by Jo Kirby, Susie Nash and Joanna Cannon. The book is composed of articles presenting brilliant research case studies, where scholars revealed the histories of pigments and dyes through characterization analyses, or by thoroughly studying historical sources. Both avenues seemed very distant based on the knowledge I had then about trade with colouring materials, but the book helped me shape the idea for this dissertation. I was keen to decipher the composition of the Gnalić cargo, and to study how those items were produced, traded and used, and this book provided a roadmap for how to do it.

During the period of my research, I received the support of two persons who played important roles in this dissertation – my supervisor Irena Radić Rossi, who was the one who restarted the Gnalić project and from the very beginning emphasised how significant and rare these colouring finds are, and Adelphine Bonneau, who showed great enthusiasm about the

topic and agreed to teach me – from a distance – how to characterize archaeological materials. Learning about characterization analyses opened a whole new world of questions and possibilities to test my hypotheses, and introduced me to many interesting colleagues from the fields of art history, geochemistry, conservation science, archaeological science, geology and chemistry. Learning about their research project gave me a broad view on the potential of the instrumental analyses within the conservation and archaeological science – such as identification and characterization, dating, provenance studies, studies of the production and preparation of the materials. Besides working on my research, during the time I spent visiting research centers for conservation and restoration of the cultural heritage, I was pleased to have a look into case studies and the methodology applied during investigations of specific questions within the pigments and dyes studies.

This dissertation is not written by an expert, but by a person who is still learning how to characterize materials. The results obtained by this dissertation are the consequence of mutual forces of all the people who were fascinated by these finds and gave me support during underwater excavations, work on cataloguing artefacts, analysing samples, reading my papers, helping me with the interpretations and correcting my mistakes.

Numerous people were involved in the project of identifying colours from *Gagliana grossa*, and I am tremendously grateful to all the experts, professors and colleagues who contributed to this work. Underwater excavations were supported by funding from the FUWA eV. association from Koblenz, Germany, and the Ministry of Culture of the Republic of Croatia. The identification process of colouring materials was first initiated by Professor Vladimir Bermanec from the Department of Geology, Faculty of Science of the University of Zagreb. Further help was provided by Interdisciplinary Centre for the Conservation of Cultural Heritage (*Centre Interdisciplinaire de Conservation et de Restauration du Patrimoine - CICRP*) in Marseille, which accepted me for internship under the direction of Jean-Marc Vallet. The help provided by Dutch institutions in Ateliergebouw (University of Amsterdam, Cultural Heritage Agency of Netherlands, Rijksmuseum) was crucial to gain the results which, step by step, constructed and shaped this dissertation. For networking with Ateliergebouw I am greatly indebted to Maartje Stols-Witlox, who invited me for a visit, organized a lecture and performed analyses with me, and Birgit Reissland, who introduced me to a team Cultural Heritage Agency of Netherlands and helped me to develop the plan for characterization of some groups of samples.

During all four years, my friend David Ruff has made enormous contribution in editing all my English written reports, articles, grant applications, and had a major role in editing this

PhD. His great patience, expertise in maritime archaeology and background in chemistry helped make this dissertation readable. It would have been impossible to get the dissertation done without his friendship and support.

When I made my first interpretations within this research topic, I was privileged to consult with Mauro Bondioli, who corrected my hasty conclusions several times. He helped me to see how complex, but crucial it is to understand the complex historical questions and prior to doing any archaeological research. Further historical questions were discussed during correspondence with Julia DeLancey and Sabine Florence Fabijanec.

This research would have been impossible to complete without the 'whole army' of experts behind the characterization instruments. SEM-EDX was done with the help of Ineke Joosten (RCE, Amsterdam), Maartje Stols-Witlox (UvA, Amsterdam), and Alain Tonneto (UvAM, Marseille); XRD with Jean-Marc Vallet; RS with Ludovic Antonelli (CICRP, Marseille), Frederique Broers (Rijksmuseum, Amsterdam) and Inez van der Werf (RCE, Amsterdam); help with FTIR was provided by Fanny Baucheu (CICRP, Marseille) and Suzan de Groot (RCE, Amsterdam); UHPLC was done by Maarten van Bommel (UvA, Amsterdam); XRD by Victor Gonzales (Rijksmuseum, Amsterdam).

I am also grateful to have a chance to consult with Jo Kirby Atikson whose discussions helped me to raise new hypotheses based on interpretation of analysis results of the red lake pigments. Special gratitude goes to CICRP team members Odile Guillon, for working with me to gain the valuable skills needed for photography under different wavelengths, and Vincent Mercurio for teaching me how to make epoxy resin thin and then take cross sections. These two showed special patience for explaining the process and methods, especially as we did not speak a common language. The maps in the chapter about historical context are made by effort of Valerija Butorac.

Some analyses that were performed go beyond the research aims, but they demonstrate how fruitful results can be obtained when archaeology meets physics and geochemistry. Radiocarbon dating of lead carbonates with Accelerated Mass Spectroscopy was done by Lucile Beck and Cyrielle Messenger (Laboratory for radiocarbon 14 measurements, Paris), and lead isotope analyses with Multiple-Collector Inductively Coupled Plasma Mass Spectrometry were performed by Gareth Davis and Paolo d'Imporzano (VU, Amsterdam). It is very motivating to know that other research projects benefited from the samples provided by the Gnalić project.

I must recognize my colleagues and friends, who were there for me, helping me personally, giving the words of support, and providing irreplaceable help during projects of underwater excavations: Anamarija Belošić, Lea Boulogne, Filipe Castro, Matko Čvrljak, Chris

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My research required an extensive amount of both underwater work and laboratory analysis, especially as it was done in phases. It was especially difficult as within the project AdriaS I was responsible for many other project activities, as well as teaching classes at the Department of Archaeology. During my four years of PhD I travelled to Australia, Canada, Cyprus, Denmark, France, Germany, Italy, Poland, Spain, and the United States of America for analyses, workshops, studying visits and conferences. Consulting abroad, meeting experts and

gaining new skills helped to complete this dissertation. It was a privilege to walk through Piazza Navona or climb the Scalinata di Trinità dei Monti in Rome on the way to libraries, to cycle through Museumplein and pass through the middle of the Rijksmuseum when going to Ateliergebouw, or to work until late night hours in the Singel library of UvA in Amsterdam.

I hope this research demonstrates how much information can be extracted from neglected minerals kept in the storage of a museum, or covered with sand at 26 to 30 meters' depth. The results are a modest contribution to the studies of trade, provenance, and transport of Venetian colouring materials. I hope this work will emphasize the fact the colouring materials are present on shipwreck sites, bearing valuable information for colouring materials studies.

1. Introduction

Colours are an indispensable part of human existence. From the early beginnings, humans exploited natural sources for colour, using minerals, earths, charcoal, animals and plants to produce paint, cosmetics, medicine, or to use them in rituals. At a certain point, the resources of mineral deposits were not sufficient to satisfy consumption and demands for colours. Soon, our ancestors started to understand the physical and chemical properties of the materials, and realized that substances could be synthetically created or converted. Materials could gain new forms through processing and refining. Techniques such as burning, grinding or exposure to reactions under specific conditions, such as heating, resulted in new colours with different quality or hue. At this stage, humans started to experiment, which resulted in the development of different synthesis procedures. Invention of new procedures reflected the level of technological knowledge in colour production. In the late Middle Ages, the knowledge of colouring materials processing improved, based on the experiments of alchemists, painters and apothecaries; in short – if the profession involved the creation of metals, paint, or medicine, it was required to have a certain experience in mixing, refining, and converting raw materials. The Medieval compilation of the recipes for pigment preparation and processing was not a product of experiments made at one time, but was collected and copied from multiple earlier sources, while at the same time adding new recipes and the author's personal notes (Clarke 2011, p. 14). For this reason, the questionable dates of some manuscripts of painting treatises are the issue of debate, as the recipes could belong to a wider range of time.

In the Bronze Age, improvement of shipbuilding techniques made distance a less formidable obstacle, and highly appreciated exotic minerals began to be traded overseas. Skilful seafarers sailed long distances inside of the Mediterranean basin with vessels large enough to carry merchandise (Waschsmann 1998). The earliest example of colouring materials being present in the cargo of a ship appears in the Late Bronze Age (the fourteenth century BC). The ship found next to the island of Ulu Burun on the south-western shore of Turkey carried a considerable amount of raw materials, including arsenic sulphide / orpiment (Bass 1986). Written sources prove the Eastern Mediterranean was, as well, a place of active trade with colouring materials in Classical Antiquity.¹ Realgar, orpiment and antimony sulphide were

¹ Authors from Classical Antiquity provide information that the colouring materials were traded and transported most frequently on the Eastern Mediterranean. As an example, Theophrastus (4th c. BC), mentions red earth is extracted from the deposits in Cappadocia, and transported through Sinopia. Vitruvius, (1st c. AD), explains that

among commodities traded with Egypt and India, according to *The Periplus of the Erythraean Sea* from the first century AD (Casson 1989, pp. 208-209). The need to possess exotic minerals is often supported by descriptions of Marco Polo's traveling ventures in the late thirteenth century. He describes a precious stone, lapis lazuli, used for making the valuable pigment ultramarine, being extracted from the mines of Mount Badakshan in today's Afghanistan (Bucklow 2009, p. 44).

While taking overview of the maritime trade with colouring materials, it can be suggested that two major technological changes enhanced the availability of colouring materials, pigments, and dyes. The first was the invention of synthetically produced substances, which enabled control of the production process to create specific materials. The second change happened gradually, when, with the development of shipbuilding and the establishment of maritime connections, colouring materials and dyes began to be traded and exchanged over long distances.² Unfortunately, there is no abundance of historical sources and archaeological evidence which would enable the study of trade with colouring materials during history and help to draw a clear picture on how the need for their possession and use has grown within society.

With the idea to contribute to the knowledge on aforementioned questions, this dissertation gathers evidence of the production, trade and transport of colouring materials in the second half of the sixteenth century, looking through the prism of the archaeological site of the sunken *Gagliana grossa* (Gnalić shipwreck). The ship sunk on the depth from 26 to 30 metres on the slope of islet Gnalić, positioned at the entrance to the Pašman Channel, in the middle coast of Croatia. In addition to having uncertainties on how the colouring materials were employed, produced and traded, there are a number of matters which were not studied. Issues for further studies include: what amount of colouring materials were traded; what sort of packaging was used for transport; what types of ships were used for transport; what were the specific uses planned for the colouring materials carried on *Gagliana grossa*; and, which colours were in the greatest demand in the East.

The story about the last venture of *Gagliana grossa* has been told through research done on archival documents. It was late October 1583 when the ship *Gagliana grossa* got underway from the port of Venice and headed towards the Eastern Mediterranean sailing on the common

rubica, probably referring to red earth, originates from Sinope, Egypt, Lemnos and the Balearic Islands (Heldwig 2007, p. 41; Eastaugh et al. 2008, p. 334).

² See Appendix 1 for the full list of sunken ships testifying to the presence of cargo with pigments and colouring materials.

route through the Adriatic Sea. The ship was loaded with various cargo, including glass products from Murano workshops, from fabulously decorated chandeliers to small objects for everyday use, and both raw materials and semi-processed products. Products were made in European cities and imported to Venice, as well as products made in local workshops. Among loaded cargo were the colouring materials; the wide spectra of finds present on board testifies the versatile offerings of the sixteenth-century Venetian markets.

The ship was discovered in 1967, and continued to be excavated through 1968, 1972 and 1973, with short excavation organized in 1996. The colouring materials were noticed among the cargo already in 1967 and 1968 excavation campaign and published in *Vrulje – Glasilo Narodnog Muzeja u Zadru*, vol. 1 (1970). Unfortunately, for a long time it remained the only scientific reference to this valuable finds. According to the state of research done on the colouring materials is 1970, the ship transported mercury, cinnabar, lead white, antimony sulphide and sulphur (Kelez 1970).

This shipwreck and its artefacts attest that the trade in colouring materials could be executed in a large scale, sufficient to satisfy the demands of the markets in Constantinople. The possibility of reaching the markets of Asia Minor, the Levant, or South-eastern Europe is not excluded, as during this period three caravan routes were passing through Constantinople. Since this is the first archaeological evidence of massive amounts of colouring materials export, it finally gives the possibility of visualizing data that was once available only in the historical documents.

In order to investigate the trading of colouring materials in the Late Renaissance based on the Gnalić shipwreck finds, this dissertation objective is to merge archaeological data, historical data and the data from the characterization analyses.

The dissertation is composed of the following chapters.

After introduction, the second chapter entitled *Where can we expect to find colour?* *A brief overview of selected archaeological sites with attested presence of colouring materials, pigments and medicines* will introduce the reader to the testimonies of use of the colouring materials, pigments and dyes during history, based on selected examples of archaeological sites. The aim of the chapter is to give an idea of the presence of colouring materials in various archaeological context, discussing examples preserved from both terrestrial and underwater sites, and highlighting the most important.

The third chapter, *History of the research and terminology*, is composed of three sections. *The history of the research in sixteenth-century Venetian colouring materials and pigments* is represented in brief strokes, and is based on development of the research within two

main streams of studies – art history, and history. Both are exploring the colouring materials, pigments, and dyes, but from different sources. The results overlap, complementing each other, thus providing us an insight into materials, techniques, and preparation methods. Following two sections are devoted to terminology, where the fundamental terms are explained and their use justified. Each colouring material attested on the Gnalić shipwreck site was assigned a nomenclature according to the results of characterization analyses coupled with comparisons to historical sources. Different types of historical sources were used depending upon the colouring material, including metallurgy treatises, inventories and contracts attached to colour sellers, insurance documents and painting treatises.

In **the fourth chapter** *Methodology* sets a foundation for the research on colouring materials from the Gnalić shipwreck. The research proceeded in phases, starting from the research of secondary sources, including the research of reports and old documentation stored in the Conservation office in Zadar, then to both underwater and museum artefact sampling, and finally to the use of analytical instruments for colouring material characterization and identification. The characterization analyses allow determination of chemical composition, mineral structures, and molecular bonds. These analytical results combined with published results of studies on archival documents related to colour sellers and manufacturers of Venice, and the maritime insurance, provide new insight into the terminology used for these materials during the Renaissance.

The fifth chapter, *Gagliana grossa – Venetian merchant ship in the light of historical sources*, is composed of four sections. The first section presents geographical position of the Gnalić shipwreck. The second, *The discovery and excavations of the shipwreck*, presents a brief history of the excavations done on the site, including the phases 1967-1973, 1996, and the present-day excavations after the project was restarted in 2012. The current results of the research at the site are presented. The third section, entitled *Identification of the ship*, explains a research history conducted in the State Archives of Venice. The fourth section *The lifetime of the ship: from the construction to the depths of the Adriatic*, is a reconstruction of the story of the ship, an overview of the complex story of the *Gagliana grossa*, including the people involved in its building, its adventures at sea, and finally its sinking and salvage operations. This section is based on the archival research conducted over the past decade in the State Archives of Venice (Radić Rossi & Nicolardi 2019).

The sixth chapter, *Historical context of the Gnalić shipwreck*, is composed in four sections, explaining the historical events which shaped the late sixteenth century

Mediterranean, with Venetians and Ottomans as the main protagonists. The emphasis is placed on the Adriatic Sea, as not only the main trading corridor, but also a theatre of contacts and conflicts between two powerful regents. The end of the chapter is placing the ship in the historical context of the late sixteenth century.

The seventh chapter, *Production and trade with colouring materials in Venice* is separated into two sections. The first, *Manufacture, processing and colouring material refining* is an introduction to colouring material production and processing. The second part, *Colour sellers (vendecolori)*, explains how this unique profession emerged in Venice, and highlights its role in the development of the colour seller industry. The formation of the profession colour seller, *vendecolori*, at the end of the fifteenth century helped to create a wide array of artists' materials, binding mediums and painting tools. The inventories of the colour sellers, as well as the various contracts and wills, provide a vast amount of information to explore how the colouring materials, pigments and lakes were traded.

The eighth chapter, *International trade with colouring materials: cargo, trade, shipping* describes the flow of the colouring materials internationally, by land and sea routes. The emphasis is given on the colouring materials shipments listed in Alberto Tenenti's *Naufrages, corsaires et assurances maritimes à Venise, 1592-1609*.

The ninth chapter, *Colouring materials from the Gnalić shipwreck*, delivers the results of the identification, explaining the situation at the site, including the position of the colouring materials within the ship's hull, as well as their packaging and preservation. Although we cannot be sure about the origins of the materials, the variety present on board the *Gagliana grossa* gives us an overview of the raw materials available and offered in Venice. The archaeological data from the Gnalić shipwreck delivers quantitative evidence about the colouring material export capacity that could be provided by the Venetian colour production industry.

In the continuation of the text, each colouring material is individually presented, following the order of colour scale from white to black, starting with whites: lead carbonate (cerussite and hydrocerussite / lead white); then reds: red ochre, mercury (II) sulphide, and lead (II, IV) oxide (minium); then oranges and yellows: arsenic-sulphide based realgar; and finally blacks: antimony (III) sulphide (stibnite). Mercury is then included as a raw material, as it is used to create vermilion. The last colouring material covered is red lake pigment. It is positioned at the end of the list as it is the only partly organic-made material; all of the previous materials are inorganic.

The colouring materials section includes the following categories:

- general information about the colouring material and its use, properties and alterations;
- description of raw material and explanation of archaeological context;
- interpretation of chemical analyses;
- processing and preparation methods;
- trading with colouring material;
- discussion of the results.

Appendix 21 in the end of the dissertation, exported from *Filemaker* software, contains all results of the chemical analyses which support the interpretations.

The discussion is the compilation of the historical, archaeological and chemical data, and the elaboration of the results in the context of Early Modern Period trading connections.

As happened during the development of many dissertations, the author struggled with the question of whether the research is too broad. Including three different sorts of data – archaeological, historical and the results of chemical analyses – with the aim of studying production, trade and maritime transport became simply impossible to complete within the deadline constraints. The application of proper characterization techniques and consultations with conservators, geologists, archaeological and conservation scientists made it easier to define which materials were present on board. Thus, becoming familiar with the characterization of the materials and gaining knowledge of present-day instrument capabilities has enhanced the author's ability to examine recovered materials. Instead of typical qualitative questions posed by archaeologists, in-depth knowledge of data that can be provided by the instrumental analyses allows us to ask precise questions and make the examinations efficient, less expensive and less time consuming. Unfortunately, many 'samples' taken decades ago, labeled only with the name of the site, will never be analyzed because their context has been lost. Knowledge of the characterization techniques, proper sampling techniques, and best practices in sample packaging, coupled with a detailed site plan, allows observation of the situation on the site in a different light. Having more knowledge about physical and chemical properties of the materials, including their alterations over time in the marine environment, affords improved sampling technique, better sample preparations before their analyses, and more insightful data interpretation.

By writing this dissertation, the author desires to raise awareness of the existence of colouring materials at archaeological sites and to present the full potential of their research. The data from the Gnalić shipwreck site, when precisely dated and identified with the help of archival sources, have similar value to the inventories of the Venetian colour sellers, as they are material testimonies of the co-existence of different tools and artists' materials in the given moment. When combined, this information forces a re-evaluation of the colouring material timeline in the sixteenth century Venice, as well as clarifying which materials were available in the different levels of trade. As colouring materials prove to be a rare find on shipwrecks, this dissertation addresses current findings and tests methods for characterizations of materials from underwater sites, to identify the materials as accurately as possible.

2. ‘Where can we expect to find colour?’ A brief overview of selected archaeological sites with attested presence of colouring materials, pigments and medicines

Human beings, as creative and spiritual creatures, have always been inspired to make their surrounding environments colourful, and pleasant for living. The growing demand for paint resulted in the exploitation of various raw materials, which, after being ground and mixed with a binding medium, yielded delightful colours used to paint bodies and objects of everyday life. The raw materials, in this dissertation addressed as colouring materials, could have more than one use; the main purpose was usually as pigment, but historical and archaeological research has provided numerous examples of the same materials being used as a medicine or cosmetic supply (Velo 1896; Jones and MacGregor 2002; Hardy et al. 2006).³ Thus, the colouring materials were an inevitable component of common human activities.

To illustrate the importance and variety of colouring material finds in the archaeological context, this chapter will describe selected examples of terrestrial and underwater sites, and cultural heritage collections. The most remarkable finds of the colouring materials occur in localities with unique preservation conditions at the site, such as the natural catastrophe at Pompeii, or in instances of site abandonment, like in the case of the Prehistoric caves in South Africa (Henshilwood, d’Errico & Watts 2009; Dayet et al. 2013) and Europe (Clottes 2008; Hoffman et al. 2018). Archaeological records of these sites contain credible datasets of human activities stopped at a certain moment, then preserved as a result of cultural and natural formation processes (Renfrew & Bahn 2004, pp. 58-59). With respect to well-preserved and undisturbed archaeological sites, shipwrecks have full credibility to be considered as time-capsules. When hidden at deeper depths, shipwreck sites are difficult to access and therefore protected from potential salvage (Bass 1983; Bass 2013). A date range for the ship’s last sailing venture is suggested by the items of the inventory, and if possible, a precise date could be proposed based on archival research. Taking into consideration these dating limitations, shipwrecks are reliable testimony of the material culture of a certain period. Studying the inventory of a shipwreck is an opportunity to have direct insight into objects that co-existed, creating reference collections with precise dates. As ships are a medium for cultural exchange,

³ Due to the wide possibilities of potential consumption, such as pigment, medicine, cosmetics, etc., the term “colouring materials” was chosen. The terminology chapter explains the difference of terms applied in this dissertation.

studying these remains provides an insight into the flow of merchandise, demonstrating what types of objects were of interest, or about to be adopted in other nation.

Within the studies of colouring materials, a great deal of attention is given to pigment and dye processing, which in fact represent the level of technological development. Colouring materials used during history are studied on archaeological objects, paintings or in the historical sources, then elaborated in comprehensive publications (Eastaugh et al. 2008). The colouring materials from shipwreck inventories are not included in the well-known timeline of historical pigments and dyes. Systematic studies and analyses would yield plentiful information about production process, provenance and the trading mechanism. This study has the aim to address the importance of colouring materials studies from the shipwreck sites (Appendix 1 & 2).

Studies focused on the characterization of colouring materials have strongly substantiated the presence of colouring materials at numerous Prehistoric archaeological sites. Colouring materials have been in use from the earliest periods of human development, as shown by excavation of sites in South Africa (Barham 2002, p. 188; Henshilwood, d'Errico & Watts 2009; Dayet et al. 2013). The earliest archaeological finds of colouring material to date are recoveries of hematite and limonite lumps from the Twin Rivers archaeological site in central Zambia (Barham 2002). These minerals were collected by human ancestors from the surrounding environment as early as 270 000 – 170 000 BP. Their exact purpose is still unknown, although researchers suggest application in cosmetic or ritual purposes as early as the Middle Pleistocene (Barham 2002, p. 188; Eastaugh et al. 2008, p. 285). Some studies focus on the application of colourants to demonstrate understanding and comprehension of the world, based on various examples, including representations on the walls of the caves, as well as burials and associated artefacts. In many of these studies, the authors address the symbolical meaning of colours (Clottes 2008; eds Jones & MacGregor 2002).

A particularly interesting site is the Blombos Cave, South Africa, where numerous flaked red ochre pieces were recorded as evidence of raw material processing. These flaked pieces scraped from the original lump were intended to be ground and turned into pigment. Besides the evidence of pigment processing, scholars are fairly convinced this site holds one of the earliest-dated finds of colouring material used to postulate cognitive behaviour (Henshilwood, d'Errico & Watts 2009). This interpretation is based on engraved pieces of red ochre found in three of the Middle Stone Age Layers, dating to 75 000 – 100 000 BP (Fig. 2-1.). These engravings were made intentionally; smoothing the surface and creating repetitive lines required attention and deliberate effort. It has even been suggested that the lines were specifically made to produce a geometric-like template or pattern for decoration of the surface

of the object or a wall. The authors theorize that the inhabitants of the Blombos Cave were capable of processing pigments and drafting the decoration pattern, a significant process advancement in comparison with the colouring material attested on other archaeological sites (Henshilwood, d’Errico & Watts 2009).

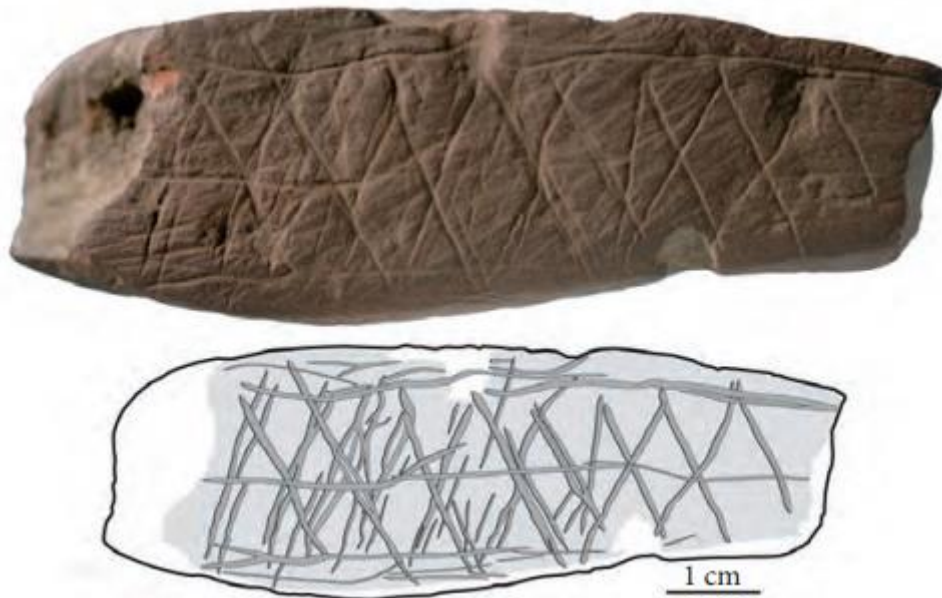


Fig. 2-1. Piece of engraved red ochre lump from the Blombos Cave in South Africa, M1 phase (Henshilwood & d’Errico 2011, p. 85).

Colouring materials are often interpreted as cosmetics, especially when found in a burial context.⁴ The finds of colouring materials in Egyptian burials in particular provide a great deal of evidence regarding Egyptian cosmetic habits and preferred colours, but care must be taken because some of those colouring materials were also used for the purpose of preservation (Lucas 1930).⁵ Egyptians paid special attention to the preparation of cosmetics, as they believed certain minerals had healing properties. When burying their loved ones, Egyptians included containers of cosmetics, due to their belief that the cosmetics would help in the process of after-life purification (Walter 2003, pp. 1-2). Among Egyptian cosmetics, the most common eye paint was made of malachite (copper ore) and galena (lead ore), while the blush on the cheeks was achieved with the use of red ochre. The remains of Egyptian cosmetics have been detected on

⁴ As closed, undisturbed units, graves provide scholar an opportunity to obtain the precise dates of burials and create timelines of settlements. Thanks to recent developments in the methodology of radiocarbon dating, samples of cerussite from cosmetics found in graves can give reliable dates of the inhumation. Radiocarbon dating of cerussite by Accelerator Mass Spectroscopy has proven to be successful during experiments on dating lead carbonates stored in the Louvre Museum in Paris (Beck et al. 2018).

⁵ The presence of colouring materials in the graves could be interpreted as testimony of ritual, or it might support certain sepulchre beliefs.

grinding stones, providing insight into preparation techniques; they have also been discovered as a ready-to-use product, either in a powder or a processed paste (Lucas 1930, p. 41, 44).

When making an overview about the most important finds of raw materials from archaeological sites, the most representative site is clearly Pompeii, Italy, destroyed in 79 AD by the eruption of the Vesuvius volcano (Coarelli, Foglia & Foglia 2005). The archaeological site of Pompeii holds remarkable evidence of both production and use of pigments for wall decorations. Scholars are greatly indebted to intact layers of Pompeii, as the artefacts and their archaeological context allow the first-ever reconstruction of the facilities for producing, refining and using the colouring materials as a pigment or a dye from Classical Antiquity. An excellent level of preservation is attested in the buildings interpreted as shops for processing and selling colours (lat. *tabernae pigmentariourum*), as well as the workshops for textile dyeing. Although there are several interesting examples of pigments, whether we talk about paint on the frescos or the finds of raw materials, one particularly important discovery was the actual painting process, which remains suspended at the time of catastrophe. These activities were testified in several houses in Pompeii, but the most representative which will be described here are the rooms with the house-shrine between the garden and the entrance of the courtyard, in the region II, insula 1, house 9 (Figs 2-2. and 2-3.). Interrupted by volcanic eruption, the painting process of the house-shrine dedicated to the domestic deity Lari was aborted, leaving half-finished paintings, artists' tools, and pigments staged in ceramic pots near the working area (Augusti 1967; Tuffreau-Libre, Brunie & Daré 2014; 2016). In contrary to Pompeii, other land excavations typically display fragmentary evidence of painting in a mostly disturbed context, requiring conjecture to suggest the function of colouring materials.



Fig. 2-2. and Fig. 2-3. Variety of the pigments in the pots related to the house-shrine for Lari preserved in Pompeii, region II, insula 1, house 9 (Tuffreau-Libre, Brunie & Daré 2016).

Up to now, colouring materials dating to the Modern Period are more commonly recovered from shipwrecks, while they are rarely found on land sites. While metal-based colouring materials could be preserved in both land and underwater environments, the inaccessibility of underwater sites has helped keep them preserved *in situ*, whereas they would probably have been reused in an accessible land environment. Most colouring materials identified in cargoes of shipwrecks from both Antiquity and the Modern period have been interpreted as either personal possessions, items intended for exchange with native people (Bruseth et al. 2017, p. 788), or materials used to repair the ship's hull (Gianfortta & Pomey 1981, p. 296).

It is not easy to differentiate shipwreck cargo intended for trading purposes from material designated for personal use. Archaeologists often interpret a purpose based on the amount present coupled with the position of the find inside the ship's hull. However, just because some of the minerals were traded in smaller amounts does not mean they belonged to an individual and not the ship's cargo. Sometimes precious materials intended to be sold were transported in amounts small enough to be smuggled in the pockets. At some archaeological sites, the colours were not found in amounts large enough to indicate their use as a trading cargo. For example, colouring materials recovered from the Planier III shipwreck in southern France could have been either merchant cargo, or colouring materials used to fix the ship's hull (Tchernia 1971, pp. 51-82).

With respect to identifying merchant cargo, it is rather complex to discuss the value of colouring materials, as it was subject to change according to political circumstances and population taste, local availability of the mineral, and technological advancements in processing and refining.⁶

Shipwreck sites with colouring materials recovered from the wreck are pinned on a map (Fig. 2-4.), with the description based on available bibliography (Appendix 1). The list is not long; according to the available published data, there are only thirteen shipwrecks which have yielded colouring materials. The data is not representative if we want to use it to draw strong conclusions about trading connections; however, it does show the variety of colouring material transported over the centuries. The ‘oldest’, the Ulu Burun ship, sunk in the fourteenth century BC, demonstrates that ships were used as transport medium for colouring materials as early as the Late Bronze Age (Bass 1986). Considering the ‘youngest’ example, the Otočac-Prižba shipwreck (Ministry of Culture of the Republic of Croatia, 2006), presumably dating to the eighteenth century, creates a timeline of more than three thousand years of maritime trade with colouring materials. It is necessary to point out a large gap from the eleventh until the sixteenth century, with a surprising absence of evidence in the fourteenth and fifteenth centuries, a period when we know that Italian cities actively traded with pigments, dyes, medicines and seasonings, encompassed with the term spices (DeLancey 2010).⁷

⁶ The field of economic history is studying the value of the merchandise.

⁷ The lack of those finds could be explained through the low number of discovered and excavated sites.



Fig. 2-4. Sunken ships with the cargo of colouring materials: 1. Ulu Burun shipwreck, Turkey, 14th c. BC; 2. Madrague de Giens, France, 75/60 – 50 BC; 3. Planier III, France, 1st c. BC; 4. Cape Glavat, Croatia, 1st AD; 5. Cape Ognina, Italy, late 2nd and early 3rd c. AD; 6. Mellieha Bay, Malta, late 2nd and early 3rd c. AD; 7. Serçe Limanı, Turkey, 11th c. AD; 8. Unknown shipwreck, Serçe Limanı, Turkey, 11th c. AD (?); 9. Gnalčić shipwreck, Croatia, 1583; 10. La Belle shipwreck, Matagorda Bay, Texas, USA, 1685 (not marked on the map); 11. T'Vliegent Hart, Vlissingen, Netherlands, 1735; 12. The Hollandia Shipwreck, Scilly islands, England, 1743; 13. Otočac-Prižba, Korčula island, Croatia, late 18th c. AD (?).

The Adriatic Sea contains three archaeological sites which are representatives of trading with colouring materials for the given period. The earliest example of a shipwreck containing a cargo of colouring materials in the Adriatic is the shipwreck near Cape Glavat on the island of Mljet, dating to the 1st century AD (Radić Rossi 2012).⁸ Excavation on the site brought to light numerous artifacts belonging to ship's equipment and the crew, and also materials probably being transported as trading goods. What makes the cargo even more interesting is the existence of mineral lead carbonate or cerussite (Fig. 2-5.), lead (II, IV) oxide or minium (Fig. 2-6.), and lead sulfide or galena.⁹ Cerussite was preserved in the shape of irregular white cubes

⁸ The rescue excavations at Cape Glavat on Mljet Island were conducted by the Croatian Republican Institute for Protection of Cultural Monuments from 1988 to 1991. Preliminary research on these artefacts revealed the provenance of trading goods from different parts of Europe and the Mediterranean. Part of the cargo consisted of mass-produced ceramic vessels arranged in rows, Dressel 21-22 and Richborough 527 amphorae, which likely originated in southern Italy; raw glass chunks believed to be cargo are most likely from the Eastern Mediterranean.

⁹ Identification was executed in the laboratory of the Croatian Restoration Institute in Zagreb (Kirigin & Malinar 1989). The identification is based on the systematic division of anions and cations, coupled with the results of

scattered on the seabed, at the position which is believed to be the hold of the ship. Minium was packed in ovoid shaped ceramic vessels with flat bottoms, which were sealed with a layer of lead (Kirigin & Malinar 1989; Radić Rossi 2012, pp. 17-24).



Fig. 2-5. and Fig. 2-6. Raw materials from the Cape Glavat shipwreck on Mljet island: cerussite, historical name lead white (left, photo: K. Batur) and lead (III, IV) oxide, historical name of minium (right, photo: D. Kalogjera).

The second site, the Gnalić shipwreck, dating to the late sixteenth century, is the focus of this dissertation. The third is the Modern Period site of the ship sunk near Otočac islet in Prižba, Korčula island, with a suggested date of the second half of the eighteenth century (Ministry of Culture of the Republic of Croatia, 2003; 2006).¹⁰ The ship carried a cargo of metal rods, coiled brass wire, barrels filled with an unknown corroded material, and stacked rectangular panes of glass which preserved the shape of their shipping crates (Radić Rossi 2005; Appendix 4). Yellow colouring material was scattered on the seabed. Preliminary analyses of the samples identified the yellow lumps as arsenic sulphide.¹¹ Based on the cargo which resembles that of the Gnalić shipwreck, and the great demand for metal in Asia Minor and the Levant in the Early Modern period, it seems likely the ship departed from Venice, probably sailing towards the East.

micro chemical analyses of anions and cations. While reviewing the report and the museum inventory in 2017, the only material mentioned in the report but not existing in the Maritime Museum in Dubrovnik is lead sulphide or galena. Galena identified by analyses could be the result of the alteration of cerussite which happened due to contact with the sea and sulphuric environment.

¹⁰ The author is grateful to Dr Domagoj Perkić from the Dubrovnik Museum for providing the reports and photographs made during the preliminary surveys of the shipwreck near islet Otočac, in Prižba, Korčula island, Croatia.

¹¹ From personal correspondence with Domagoj Perkić, the author determined that the original analyses report was lost. When the site was revisited in September 2019 during a photogrammetry workshop, sampling was executed (Appendix 4). Future analyses will determine the composition of the sample, and whether it is a yellow arsenic sulphide (orpiment), or red arsenic sulphide (realgar) which changed colour due to chemical alterations on the sea bottom.

Due to the common use of colouring materials as remedies, pharmacies and their inventories, whether preserved in their original state or described in archival documents, should be taken into consideration when studying the history of colour. Until the sixteenth century, pharmacies were the main source of raw materials which could be used as pigment and medicine.¹² Therefore, inventories of pharmacists (*spezieri*) can be recognized as a useful source for studying the availability of colouring materials in sixteenth-century Venice. Although the author of the dissertation has not done any study of the inventories of the pharmacies which could potentially yield information on colouring materials, in the text below will be given several examples of items listed on inventories of the colouring materials which match substances found at archaeological or cultural heritage sites, interpreted as a pharmaceutical supply. Considering archival sources, a great example of a merge of the function of colouring materials is given in German price lists of pharmacies (*Taxae*) from Liegnitz in Silesia, which contain the category of inventory ‘*Pigmenta et Colore*’, demonstrating that medicines, dyes, pigments and colouring materials were intertwined.¹³ A full repertoire of medical supplies, well-preserved and sealed in labeled glass containers, was attested in the ‘speziera’ or drug shop of the church Santa Maria della Scala (Figs 2-7. and 2-8.), belonging to the Spanish Order of Discalced Carmelites in Rome. The pharmacy was founded in the seventeenth century, and it was highly esteemed as the Order of Carmelites used the fused knowledge of pre-Hispanic and Islamic medicine to create remedies. When the pharmacy was closed in 1950, the repertoire of the pharmacy consisted of 231 substances, based on gems, salts, complex formulations, organic compounds, antimony, iron and mercury (de Ágredos Pascual et al. 2018; Cavallo & de Ágredos Pascual 2018).¹⁴ The pharmacy is important in studies of Early Modern medicine and science, giving us a glimpse into an actual pharmacy inventory, typically known only from historical documents. The pharmacy (*spezeria*) of the Santa Maria della Scala had a continuity of existence for three centuries, so it is assumed the remedies preserved in the labeled glass jars were made according to traditional recipes of medical treatises and pharmacopeias stored in the rooms. However, the characterization of these

¹² The change happened in Venice at the end of the fifteenth century by introducing the colour seller profession (*ven. vendecolori*), which expanded to Antwerp by the middle of the sixteenth century (*dutch verfvvercopere* or *merchand de couleurs*). See details in Matthew 2002, Vermeylen 2010.

¹³ The price lists date to 1568, 1584, 1614 and 1662, giving a possibility to analyse available materials on the transition from the sixteenth to seventeenth century.

¹⁴ The authors give a brief overview of pharmacy activity, starting in the seventeenth century, reaching a peak in the eighteenth and nineteenth centuries. It is not clear whether the pharmacy was active in the twentieth century, or if the substances date to the latest known period of activity, in the late nineteenth century.

compounds and their relation to the historical recipes requires a detailed study within the field of European pharmaceutical and medical science in the Modern era.



Fig. 2-7. and Fig. 2-8. The room intended to sell the medicine; the appearance and the organization of the room (left) and jars on the main shelf (right) (de Ágredos Pascual et al. 2018, p. 5).

While it is commonly expected to find pharmaceutical supplies in collections secured by the monastic order, the findings from Nargen 1 in Tallin Bay, Estonia, and the wreck of the *Kronan* in Sweden, prove that similar information can be found on shipwrecks as well. The first example, the Nargen 1 shipwreck, has an assumed date of wreckage in the late sixteenth century (Mäss & Russow 2015). Among the recovered cargo is a vessel identified as Siegburg stoneware, providing a *terminus post quem* and date of the shipwreck after 1580. The find that caught the attention of the researchers was a wooden box. Inside or close to the wooden box were positioned a metal skillet, jars (*albarelli*), glass bottles, a syringe, and spherical bottles probably used for distillation of antimony and mercury. Based on the contents of the box and analogies, the authors suggest the box and its associated artefacts were the property of a traveling pharmacist, instead of a ship's barber-surgeon (Mäss & Russow 2015).¹⁵ The finds from this shipwreck provide insight into elementary instruments and tools used by pharmacists at the end of the sixteenth century, previously represented and described only in historical sources. Although no raw material has been found on the shipwreck yet, it might be expected during following excavation seasons.

The war ship *Kronan* ('*The Royal Crown*'), which sunk in 1676 in the Baltic Sea, Sweden, had a full repertoire of medical drugs. Associated archival resources discovered that

¹⁵ This conclusion is based on the comparison with finds from Mary Rose (1545); while the inventory from Nargen 1 consists mostly of ceramic and glass materials, the Mary Rose medical pots are made of wood, metal and stone, which are more suitable materials for avoiding damage when travelling by ship (Mäss & Russow 2015).

among the ship's crew were a physician, medical apothecary, and barber-surgeon.¹⁶ Thorough research performed on the samples and cross-referenced to historical sources revealed at least twenty different remedies, including various seeds, herbs, elementary minerals and mixtures of mineral compounds.¹⁷ Among recovered substances are notable compounds of mixed antimony sulfide and antimony oxide, elementary sulphur, and compounds mixed with mercury (Lindeke & Ohlson 2018, p. 76; Appendix 5).

While information in Appendix 1 provides information on the variety of sites where these pigments could be expected, Appendix 2 contains a list of the artifacts that can be associated as painting tools and a list of the painted sculptures recovered from the shipwreck. The list is the consolidation of references that the author created during research, with the aim to gather as much data as possible about the state of research of the paint used on the ship.¹⁸ Reconstruction of the colour palette used in painting the stern of *Vasa*, sunk in 1628 in Stockholm, presents a pioneer work on revealing the original work on the sculptures from the underwater sites (Tångeberg 2000, p. 149; Hocker 2018, p. 96).

Finally, merging archaeological and historical data of certain archaeological artefacts with characterization analyses help us to generate a timeline of the colouring materials used across history. Due to the wide use of colouring materials as cosmetics and remedies, we should carefully study all the available archaeological analogies before giving the final interpretation. The current state of research of the pigments and colouring materials from the terrestrial sites and paintings can be complemented with the finds from the shipwreck inventories. The author's research of the Gnalić shipwreck colouring materials is, therefore, a modest contribution to the general knowledge of the production, trade and maritime transport of colouring materials in the Early Modern period.

¹⁶ In the crew of *Kronan* warship were renowned names of Swedish medicine: the Navy physician Peter Schallerus, chief apothecary Alexander Steckert, and a chief barber surgeon (Lindeke and Ohlson 2018, p. 70-71).

¹⁷ A chest with pharmaceutical supplies is also attested in excavation of English royal ship *Mary Rose*, 1545, sunk in the Solent (Lindeke and Ohlson 2018, p. 81).

¹⁸ This list is not yet complete. There is a possibility of the existence of new sources which were not available during the period of research.

3. History of the research and terminology

3.1. The history of the research in sixteenth-century Venetian colouring materials and pigments

The knowledge of pigments which were the part of the usual palette in the painter's studio is entirely based on two types of sources: Renaissance artwork and archival documents. The interest in identification of Venetian pigments on paintings started in the 1980s with the development and growth of instrumental analyses in characterization of the pigments. The analyses and identification of the pigments from the Renaissance Venetian works of art dating from 1480 to 1580 were first performed by Lorenzo Lazzarini (1983), and published in *Studi Veneziani V – Recherche di Archivio e di Laboratorio*. Lazzarini sampled paintings of representatives of the Renaissance Venetian school - A. Vivarini, V. Carpaccio, G. Bellini, G. B. Cima, Giorgione, Tiziano, Sebastiano del Piombo, L. Lotto, Palma il Vecchio, G. Pordenone, P. Veronese, M. Basaiti, Tintoretto. The layers of the paintings were studied through the stratigraphy of the samples, giving an insight into the pigments the artists used and the techniques they applied. The work of Lazzarini was supplemented by Joyce Plasters (1984) while examining selected painting attributed to Jacopo Tintoretto in the National Gallery of London.

A large leap forward was made in research methodology in which historical sources can be associated to Renaissance paintings. The existence of Venetian painter Lorenzo Lotto's Book of Expenses (*Libro di spese diverse*), written from 1540 to 1556, allowed significant progress on this topic. It not only allowed the study of a variety of materials within his studio, but it gave an opportunity to relate the terms of the materials appearing in the purchase lists of his notebook with the pigments on the works attributed to the artist. Lotto's book of expenses is an indispensable source in studying his artwork, his materials, and the techniques he applied. According to the book of expenses, the pigments which Lorenzo Lotto purchased most often were ultramarine, obtained from crushing the mineral lapis lazuli, and azurite (Bensi 1986, pp. 76-77). Although other pigments are present in the work of Lorenzo Lotto (Bensi 1986; Amadori et al. 2016), lapis lazuli and azurite appear most frequently in his Book of Expenses. Amadori et al. (2016) report artist materials attested on Lotto's paintings, such as 'lead white, verdigris, lead-tin yellow type I, litharge, realgar, orpiment, vermilion, red ochre, hematite, red-carmine type lake and madder lake, carbon black, red lead and yellow lake (saffron-based)'. It is attested that lapis lazuli and azurite were used to paint the sky and the mantle of the Virgin

Mary or the saints in his paintings, mixing them with lake pigments if it was necessary to obtain different hues. In the murals which do not represent important scenes, he used mostly indigo and smalt (Amadori et al. 2006, p. 175). The azurite and lapis lazuli appear more often in the Book of Expenses, as those were required to complete the scenes of his most remarkable works of art. Another reason for the frequent appearance of lapis lazuli and azurite, and not other pigments, might be that other pigments were available locally and the painter could have done the preparation of the pigment by himself. To purchase pigments and other artist's materials that were not at his disposal, especially with the demand on lapis lazuli and azurite, Lorenzo Lotto had to travel to Venice (Berrie & Matthew 2005).

The next phase of the improvement in the knowledge of pigments studies happened through further development in characterization techniques – optical microscopy, spectroscopy, diffraction and chromatography methods (Feller 1986; Roy 1993; FitzHugh 1997; Berrie 2007; Pollard et al. 2007; Pollard & Heron 2008; Artioli 2010). The initial problem in characterization analyses is that the scholars were restricted from taking the number of samples relevant for the research. As the sampling was done on valuable historical artwork, there was always a potential risk of damaging the painting if the size of the samples exceeded milligram or if the samples were taken in large numbers. The progress in analyses happened when characterization instruments had increased the detection capabilities, such that only micrograms of the samples were required for the analyses. The instruments that made this remarkable step forward are usually in published bibliography named with the prefix micro- (*e.g.* micro-Raman Spectroscopy, micro-FTIR). Another advantage is that most of the instruments became portable. In this way, the characterization analyses became non-invasive, as the instrument could be applied directly on the artwork or *in situ* at the archaeological site, avoiding meticulous sampling and potential risks of damage. Further, the use of synchrotron methods showed full potential by revealing impurities, and helping to define whether the pigment was natural or synthetically produced (Berrie 2012, p. 444).

Recent studies of Renaissance art demonstrate how the characterization techniques have shown their full potential in revealing historical pigments in detail, for example in the case of distinguishing two types of lead-tin yellow (type I and II)¹⁹ on Venetian and other Northern Italian paintings (Berrie 2012). A recently published manual discussing state-of-the-art characterization analyses, including case-studies of analyses on selected Italian paintings, became an important reference to field researchers (Poldi & Villa 2006).

¹⁹ According to the interpretation of B. Berrie (Seccaroni 2006, p. 65), the first is lead antimonate (Pb_2SnO_4), while the second is lead antimonate dispersed in glass ($\text{Pb}(\text{Sn}, \text{Si})\text{O}_3 \cdot \text{PbSn}_2\text{SiO}_7$).

The recent discovery of the profession of merchant colour sellers, or *vendecolori*, threw a new light on the research (Matthew 2002). The profession of colour sellers first appeared in Venice in the late fifteenth and reached its full peak during the sixteenth century. Inventories of colour seller's shops preserved in the Venetian State Archives are particularly valuable to researchers, as they provide an insight into the contents of the shops.²⁰ Therefore, studying the inventories, as well as other surviving documents, such as wills and contracts, reveals which materials were available at certain times of the sixteenth century (Appendix 7 & 9). These documents are also a valuable source for understanding the terminology for particular artistic tools and materials (pigments, lakes, binding medium).

Significant contributions were made by doing research on *vendecolori*-related documents. The main references in this topic include the work of B. Krischel (2002, 2010), L. Matthew (2002, 2011), J. DeLancey (2011), M. Hochmann (2015), and the historical research supplemented with the results of chemical analyses (Matthew & Berrie 2010; Berrie & Matthew 2011). As the remains of colouring materials are not a common find on either underwater or terrestrial archaeological sites of the Early Modern period, the current state-of-the-art of research is entirely based on the aforementioned studies.

Additionally, the sparse evidence of colouring materials in archaeological material of the Early Modern Period is the reason why this matter has not attracted the attention of large numbers of scholars from the field of the archaeology. However, archaeologists' lack of awareness about the existence of artists' materials on the sites might be the reason some colouring materials were either omitted, or incorrectly interpreted in archaeological reports.²¹

Finally, the materials and techniques used by artists in Venice became more familiar through the thorough research performed in the fields of history and art history. The research in pigments and colouring materials can go in various directions, including technological developments in production, processing, provenience and alteration studies. Possible

²⁰ Analyses of historical data can help historians to determine the role of the *vendecolori* in the society, including their identity and status, as well to understand the historical circumstances that led to the emergence of this profession. Based on the available information about colouring material amounts and shop's clients, it is even possible to conclude if a particular *vendecolore* was involved in retail, wholesale, or international trade (Matthew 2002; DeLancey 2011; Hochmann 2015; Matthew & Berrie 2010; Berrie & Matthew 2011). The profession of *vendecolori* will be discussed in chapter 7.

²¹ According to author's personal experience, some interpretations of the colouring materials from the Gnalić shipwreck in the earlier reports were misleading and published without being verified or supported by chemical analyses. One example is the presence of minium in large barrels incorrectly reported by Brusić (1996), incorrectly labelled in the storage of the Regional Museum in Biograd na Moru, and further cited by Mileusnić (2012), Berrie and Matthews (2010). The report written by Brusić (1996) mentions the large barrels filled with red material (minium) and small barrels filled with conical lead oxide. In fact, the large barrels were filled with red ochre, while the small barrels were filled with conical lead carbonate ingots. The interpretations proposed by Brusić are an obvious confusion in terminology.

discoveries of colouring materials within the archaeological context, especially on shipwreck sites, may contribute to enhanced understanding of the circulation of colouring material on both local and international scales during the Early Modern period.

3.2. Terminology discussion: colourant, pigment, dye, and colouring material

In order to assign appropriate terminology for the finds which will be presented, at the very beginning it is necessary to make a clear definition of terms which will be used in this dissertation. While in the fields of art history and conservation science these terms are standard terminology, the same terminology presents an obstacle to archaeologists. In order to ensure better understanding and avoid inconsistency, this sub-chapter will discuss nomenclature and deliver the official definitions of the terms in colour studies. Additionally, the following text will explain why the historical names of the pigments are unreliable and why they must be taken with caution. Subsequently, the terminology for each colouring material will be explained individually.

There are five main terms that will be used in this dissertation: colourant, pigment, dye, lake pigment, and colouring material. The term ‘colour’ will be used when giving very general descriptions of the finds and their visual properties. Colourant is a compound that adds colour to a substance. The category of colourant encompasses both pigments and dyes.

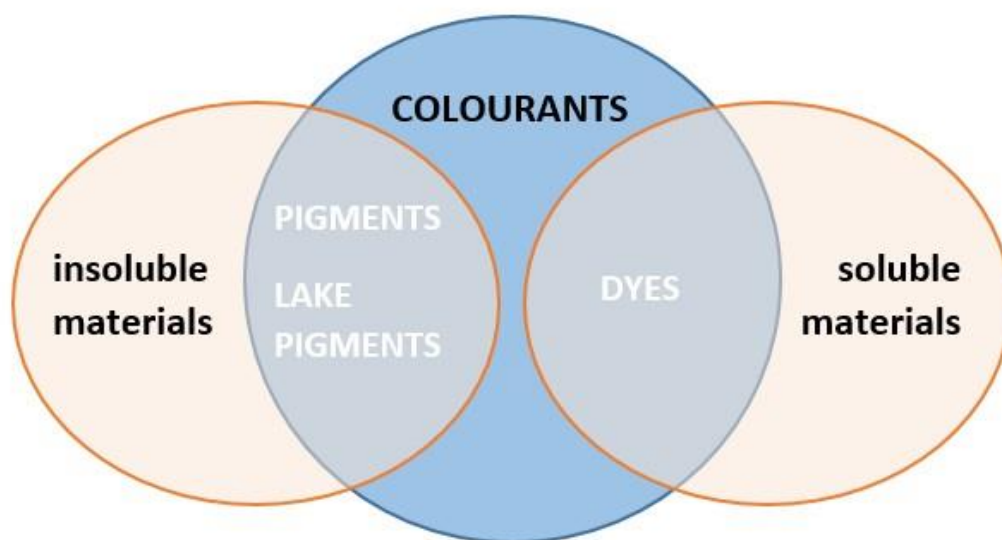


Fig. 3-1. Schematic representation of the main groupings of the terms according to the solubility of the material.

The definitions given by Gettens and Stout in *Painting Materials: A Short Encyclopaedia* in 1966 state (cited by Rapp 2009, p. 201; Artioli 2010, p. 266):

‘Pigments are finely divided insoluble materials that act as colouring agent when dispersed in a medium such as water in watercolours, oil in oil paintings, or a number of other organic media.’

‘Dyes are soluble complex organics and cannot be used on their own impart color to paint.’

The suitable definition of lake pigment was given by Kirby, Nash and Cannon in *Trade in Artists' Materials - Markets and Commerce in Europe to 1700* (2010, p. 453).

‘Lake is a translucent crimson or scarlet pigment made by precipitating a red dye onto a suitable substrate, commonly amorphous hydrated alumina, but white calcareous earths, chalk, flour and other white materials could also be used.’

Pigment is used for painting only. Before applying to the surface, it requires mixing with a binding medium, which could be natural resins, glues, animal tallow, blood, casein, eggs, urine, oil, wax, or the human saliva. The basic difference between dye and pigment is water solubility; while the pigment cannot be dissolved, the dye is soluble in the water. Dye precipitated onto dried particles produces the lake pigment. Since the lake pigment is a combination of the metal salts substrate and the organic materials precipitated on the surface, it cannot be considered as solely pigment or solely dye, but it is considered as a special category unto itself, lake pigment (Rapp 2009, p. 201; Artioli 2010, p. 266).

Colouring materials are raw materials of an inorganic (minerals, earths) or organic (plants, animals) nature which can be used as a paint, substance in production industry, cosmetics and medical supply. This nomenclature can be applied to the finds of raw materials from archaeological sites for which the contexts or historical documents do not suggest their final use.²² In the case of the materials recovered from the Gnalíć shipwreck, the term ‘colouring material’ has been used instead of ‘pigment’ or ‘colourant.’ Since the term ‘pigment’ is common in describing particles in layers on paintings or painted objects, it is appropriate to

²² The definition is suggested by author.

avoid the use of the same term for raw materials from archaeological sites. The main reason is, there is no indication for what these materials should have been employed for. Besides painting, there were other purposes that could have been given to these materials – glass production, textile dyeing, cosmetics, and medical supply. If those finds are addressed as ‘pigments,’ their use is restricted to a painting material only, thus neglecting other abovementioned potential purposes. According to published results of excavations of the sites from Prehistory, the term ‘colouring materials’ has been used to address the finds of raw materials which were probably used as painting materials (Salomon et al. 2012). Thus, the same title was used to name finds from the Gnalíć shipwreck.

As mentioned in the chapter about the historical context, it is important to point out that, when dealing with these materials, merchants or trading agents would only rarely use the term ‘pigment’, as they do not consider them as painting materials only. As expected, the documents written by painters will almost always use the term ‘pigment,’ but in the case of documents of most other artisans and merchants, it is more likely these materials will appear under the category of spices trade (DeLancey 2010, p. 78).²³

Within the terminology used in the sixteenth century, materials were not categorized as ‘pigments’ as well. In inventories of Venetian *vendecolori*, the pigments and dyes were encompassed under the term *colori*. Insurance documents issued by notaries G. A. Catti and A. Spinelli do not use the term ‘pigment’ but rather ‘colours’. Nevertheless, instead of writing very general descriptions, both notaries preferred to list each material individually.²⁴

Another matter that has to be defined prior to discussion about each find is the distinction between natural, processed, and synthesized colouring materials.²⁵ Natural colouring materials are minerals, plants, and animals which may be used in the same shape as taken from the nature, *e.g.* charcoal, or galena (lead ore) in lumps. Processed colouring materials are substances that had to be exposed to one or more refinement processes, such as roasting, different acts of purifying, grinding, or shaping into a mould (*e.g.* grinding natural lead carbonate and moulding into a conical ingot). Synthesized colouring materials have been put under an intentional process which chemically changed the composition (*e.g.* converting

²³ This idea was also delivered in the context of fourteenth century Venetian trade (DeLancey 2010, p. 78).

²⁴ A ship that left Venice for Naples in 1594 loaded three boxes of colours (Tenenti 1959, pp. 131, 358). The mention of ‘colour’ and listing cargo individually (*e.g.* cerussa, arsenico, minio etc.) as a different class of cargo is possible to explain in two ways. The first is that the arsenic may have had a different purpose other than paint. The second explanation might be that the term ‘colori’ was applied when merchants loaded packages containing various painting materials into boxes. As these materials had approximately similar value, it was not necessarily to list them individually, but rather to put the general description ‘colori’.

²⁵ These definitions are suggested by author.

goethite to hematite by heating, or creation of lead white with the so called ‘stack-process’), or by the prompt reaction of two substances (*e.g.* to cause reaction of mercury and sulphur by heating them on the fire, resulting in artificial mercury sulphide or vermilion).

The terminology of historical pigments and colouring materials is complex and requires thorough study. When there is a need to assign a proper historical term, different factors should be considered, such as period of use, geography, and processing procedure. Using the description given in historical sources should be done with caution, as the names were often given according to specific features or properties, which were in many cases the subjective descriptions of the author.

From the beginning, human senses were used to distinguish minerals. Ancient terminology could be confusing and misleading, as ancient authors were obviously assigning the title according to visual inspection. Eyesight was the most common sense to rely on. For example, Pliny states that compound named ‘ceruse’ is created by the chemical reaction of lead with vinegar fumes. Further, Pliny states that ‘ceruse’ can also be made by calcination of ‘yellow ochre’, and by quenching it in vinegar. From descriptions given by Pliny, it is plausible to think that the author gave the names according to his personal observation, and ‘ceruse’ or ‘ochre’ could have been used to address different minerals which visually resembled each other but may not have contained the same chemical composition (Rapp 2009, p. 210). Further visual-based titles used in historical sources are ‘blood like stone’ for hematite, ‘gold pigment’ for orpiment or ‘green of Greece’ for verdigris (Crosland 1962, p. 68).

One interesting example of relying on visual properties of the pigments comes from the late-fourteenth century *Il libro dell’Arte* written by Cennino Cennini. Although the author differentiates existing sorts of reds, such as sinopia, cinnabar, and hematite, he also mentions the colour *cinabrese* which is the mixture of *sinopia piú chiara* (iron oxide) and *santgiovanni* (chalk – calcium carbonate), and it has been used to paint the flesh of the figures in paintings. The pigment title is ‘cinabrese’, with the word ‘cinabre’ in the root of the title, even though the instructions do not mention the use of cinnabar when mixing the colours (Cennini 2007, pp. 52-53).

Besides visual properties, the naming of substances could also be done based on many other properties, such as smell, consistency, crystalline form, the person praised for the discovery, the geographical position where the substance began to be produced (*e. g.* Egyptian Blue) or extracted from natural deposits (ultramarine according to ital. *oltre mare* or across the sea; different names for reds, such as Spanish red, Persian red and Winford red), medicinal properties, or the method of preparation. Different names were even given to acid and alkaline

solutions, which could be distinguished by their characteristic taste (Crosland 1962, p. 68; Cornell & Schwertmann 2003, p. 512).

All human senses were taken into account when there was a need for material identification. For example, historical sources give instructions on how to differentiate between tin and lead based on examination of taste and sound (Crosland 1962, p. 68). Even in the metallurgy treatises *De la Pirotechnia* (1540), V. Biringuccio (1942, p. 67) reveals when finding iron-oxides, good quality should be verified based on the sound:

‘The sign by which you can surely tell where there is good iron is the presence of bole and another earth that is also red, soft, and fat and that does not make any crackling noise when it is squeezed by the teeth.’

As mentioned before, often the name of the pigment was given according to the specific production or preparation process. Many of the minerals which exist in nature can also be produced synthetically. Over history, especially in the Modern Period, identical pigments were even distinguished by their proper name based on production, like in the case of mercury sulphide. When extracted from mineral deposits, mercury sulphide bears the name ‘cinnabar’, while the name ‘vermilion’ is used for synthetically produced mercury sulphide (Eastaugh et al. 2008, pp. 111, 392).

Scholars fairly agree that proper interpretation of a sample depends on understanding historical recipes. This means that experiments and examinations in the laboratory are required, which replicate the process of production, refining or combining substances described in the historical sources. By dating certain manuscripts and their recipes, and interpreting archaic vocabulary, then subsequently conducting experiments, Renaissance-era knowledge about chemistry becomes familiar. Even if some translations of recipes were wrong, these mistakes can be overcome by completing technical analyses on the pigment (Van de Graaf 1962, p. 472).²⁶

Recently, order has been established from anarchy in the use of historical pigment terms, as the results of spectroscopy characterization analyses and optical microscopy have driven improvements in the methodology of associating historical terms with actual chemical identifications. All editions of *Artists’ Materials* (ed. Feller 1986; ed. Roy 1993; ed. FitzHugh 1997; ed. Berrie 2007) made significant progress in this topic by summarizing everything

²⁶ In the article ‘The interpretation of old painting recipes’, Van de Graaf (1962) gives three examples of studies, addressing the importance of using historical sources as a supplement to the technical analyses of the paintings.

known about each pigment as well as identification traits determined through the use of characterization analyses. The publication *Pigment compendium: a dictionary of historical pigments* (Eastaugh et al. 2008) finally listed all the historical pigments, their synonyms, historical sources, paintings, and artefacts from archaeological sites, along with optical microscopy picture references for each pigment.

3.3. Terminology for colouring materials from the Gnalić shipwreck site

The following sections will propose proper terms for each Gnalić site colouring material based on physical appearance and chemical composition. Characterization details, essential for assigning proper term, are given in the section 9.3, Tab. 9-1. and Appendix 21. However, if there is not enough evidence to establish a direct link between chemical / geological composition and historical term, the historical term will be omitted. This will very likely be changed in the future, should technical analyses provide additional characterization data to allow more detailed identification. The difference in terminology between synthetic and natural equivalents will be explained.

Further, historical terminology will be explained. Because of the emphasis on Renaissance-era colouring materials, this dissertation did not consult original written sources from Classical Antiquity or the Early Middle Ages. During research, primary historical sources from the sixteenth century were emphasized. A table was created for each colouring material, depicting the terms used in different types of sixteenth-century written sources. Terminology is explained in the following order:

- geological name / historical name (if applicable)
- the physical appearance of the find, and its composition
- the difference in terminology between synthetic and natural equivalents (if applicable)
- explanation of the historical term

a) **Lead carbonate (cerussite) and lead carbonate hydroxide²⁷ (hydrocerussite) / Lead White**

Numerous conical ingots (Figs 3-2. and 3-3.) recovered from the shipwreck were identified as lead carbonate (cerussite, PbCO_3), or as a combination of lead carbonate with lead carbonate hydroxide (hydrocerussite or basic lead carbonate, $2\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$).²⁸ Lead white is an umbrella term used to encompass both forms of lead carbonates and hydroxides. It is not unusual to find the combination of cerussites and hydrocerussites within the sample. Also, during the production process the lead white was sometimes adulterated by calcite, gypsum or barite (Gonzales et al. 2018, p. 10).

²⁷ Also, basic lead carbonate.

²⁸ In the bibliography published prior to 2000, it is common to find cerussite (lead carbonate) referring to natural ore, and hydrocerussite (basic lead carbonate) referring to synthetic lead carbonate. For more information, see Gettens, Kühn & Chase 1993, p. 67.



Fig. 3-2. and Fig. 3-3. Cones of lead white from the Gnalčić shipwreck (photo: K. Batur).

Modern terminology does not distinguish the synthetic or natural form of lead carbonates. However, during increased production in the Early Modern Period different terms might be used to denote synthetic and natural origin.

As the use of lead white increased at the beginning of the Early Modern period, several production centres began to appear in Europe.²⁹ First, the Venetian manufacturers had a monopoly, but in the seventeenth century it was taken over by Dutch manufacturers (Pulsifer 1888, pp. 260-261). Since the lead white produced in Venice was recognized and highly esteemed due to its quality, Venetian producers adopted the title Venetian cerussa (Matthew & Berrie 2011, p. 295). Harley (2001, p. 166) reports how the Venice ceruse (*ceruse de Venise*) is mentioned in the various English written sources dating to the end of the sixteenth and early seventeenth centuries. German documentary sources also report the procurement of Venetian lead white; e.g. it is mentioned in the Liegnitz taxa of 1568 (Burmester, Haller & Krekel 2010). Possessing Venetian lead white was probably fashionable, but it is evident that painters were familiar with the excellent properties of Venetian lead white, especially with its covering abilities and compatibility with almost all pigments.

²⁹ The best representation of the lead white variety offered on the markets can be seen in the Frankfurt trade catalogue from 1582, where three types of lead white appeared: ordinary (*bleyweiß*), Venetian (*cerussa Veneta*, *Venedisch Beyweiß*) and Antwerp / Netherlandish lead (*cerussa Antverpiana*, *Niderländisch bleyweiß*) (Berrie, Matthew 2011, p. 295).

Sixteenth-century historical sources

Term	Year	Source	Type of document
Not mentioned as cerussite, but as a lead; <hr/> <i>Plumbum nigrum lutei coloris</i> , <i>Plumbage metallica</i> refers to cerussite (lead carbonate); Cerussa refers to hydrocerussite (basic lead carbonate) ³⁰	1540 <hr/> 1556	Vannoccio Biringuccio, 1942; <hr/> Georgius Agricola, 2018	Metallurgy treatises
<i>Biacha</i> <hr/> <i>Biacha</i>	1534 <hr/> 1594	Domenico de Gardignano (Matthew 2002, p. 681) <hr/> Jacopo de' Benedetti (Krischel 2002, p. 128)	Colour seller inventory
<i>Ceruse</i> ; the document does present the differentiation between lead and cerussite	1592-1609	Tenenti, 1959	The documents issued by Venetian notaries G. A. Catti and A. Spinelli
<i>Ceruse de Venise</i>	The end of sixteenth and the beginning of seventeenth centuries	Harley 2001, p. 166	English documentary sources

Tab. 3-1. The sixteenth century terminology of the lead white

³⁰ As the author used an English translation of *De Re Metallica* published in 2018, the Latin titles and their equivalents were given in the footnotes of pages 110 and 111. The Latin titles are identified by Herbert Clark Hoover & Lou Henry Hoover, based on their analysis of the book of Gregorius Agricola *De Natura Fossilium* (1542).

b) Iron oxide-based colouring material: Red ochre - hematite ($\alpha\text{-Fe}_2\text{O}_3$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), silicon oxide or quartz (SiO_2)

The term iron-oxides is used to designate both iron-oxides, iron-hydroxides and oxide-hydroxides, a total of sixteen compounds (Cornell & Schwertmann 2003, p. 2). Among them, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is the only iron oxide which fell into massive use. Other forms of iron oxides, hydroxides and oxide hydroxides are used as a pigment, but they are compounds in the mixtures called siennas, umbers, and ochres. Red ochre is based on hematite, with the addition of minerals such as quartz, clays, gypsum, micas, feldspars, etc. (Cornell & Schwertmann 2003, p. 512; Eastaugh et al. 2008, p. 189, 206, 285).

The samples of the powder from barrels 1, 3, 4, 5, 6 and 7 attested the presence of iron-oxide type hematite $\alpha\text{-Fe}_2\text{O}_3$, alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), and silicon oxide or quartz (SiO_2). (Figs 3-4. and 3-5.). As the mixture contained hematite in a large percentage, and the minerals are not from the marine environment but from the original matrix of the sample, it is plausible to apply the term of red ochre.



Fig. 3-4. and Fig. 3-5. Iron-oxide based colouring material from the Gnalić shipwreck was preserved in powdered condition (left photo: S. Govorčín; right photo: O. Guillon).

Historical terminology of iron-oxides is rather complex, which can be observed in the inconsistent terms applied in the written sources. Throughout history, various terms were applied to denote the iron-oxide based pigments (Heldwig 2007, pp. 39-51), but those terms must be taken with caution due to the previously described problematics of assigning a red-colour term to each material based solely on visual resemblance.

Sixteenth-century historical sources

Term	Year	Source	Type of document
Bole	1540	Vannoccio Biringuccio, 1942, p. 116	Metallurgy treatises
<i>Terra ferria,</i> <i>Ferri vena,</i> <i>Galeane genus, tertium omnis metalli inanissimi,</i> <i>Schistos,</i> <i>Ferri vena jecoris colore</i> All abovementioned terms refer to iron-oxide ores, probably hematite; <i>Haematities</i> refers to mineral composed of hematite and jasper ³¹	1556	Georgius Agricola, 2018	
<i>Tera rossa</i>	1534	Domenico de Gardignano (Matthew 2002, p. 681)	Colour seller inventory
<i>Lapis ros[s]o,</i> <i>Terra ros[s]a,</i> <i>Bolo ros[s]o,</i> <i>Terra sigilada</i>	1594	Jacopo de' Benedetti (Krischel 2002, pp. 102-103)	
Mentions 'terra rossa and crimson' only. Crimson probably refers to red lake pigment.	1607	Tenenti 1959, p. 496	The documents issued by Venetian notaries G. A. Catti and A. Spinelli

Tab. 3-2. The sixteenth century terminology of the iron-oxide based colouring materials

Biringuccio uses the term bole, explaining its iron origin and similarity to so called *terra sigillata* or iron-rich sealed earth used as a painting material (Biringuccio 1942, p. 63).³² Italian sixteenth and seventeenth century treatises used the term *gialla abbruciata* or burnt yellow, probably referring to iron oxide made in a synthetic way, *i.e.* by burning the yellow ochre based on goethite, FeO(OH), to obtain red (Heldwig 2007, p. 46). Lazzarini uses the name *rosso veneziano*, as a term for clay rich in hematite, which can be found in the locality Badia di

³¹ Same as note 30.

³² According to Eastaugh et al. 2008, 'the bole is either a naturally occurring or iron-rich material (such as red ochre; q.v.) particularly suited to applications such as substrates for gilding where a high surface polish is required'.

Calavena in the region of Verona (Lazzarini 1987, p. 118). Hochman (2015, p. 177) reports the name *terra rossa di ponente* is mentioned in documents dating to 1572, when the Spanish royal family ordered pigments from Venice.

Additionally, *lapis rosso*, *terra rossa*, *bolo rosso*, and *terra sigilada* mentioned by Jacopo de'Benedetti demonstrate the complexity of terminology of the iron-oxide based pigments available in retail shops in Venice (Krischel 2002, pp. 102-103). On the other hand, iron-oxide based colouring materials are almost absent in the documents issued by notaries in the period of 1592-1607 (Tenenti 1959, p. 496).

c) Mercury (II) sulphide / α -HgS

Mercury (II) sulphide (α -HgS), a red mineral of intense crimson colour and bladed crystal structure, was attested in two types at the Gnalić shipwreck site, in this dissertation designated types A and B (Figs 3-6. and 3-7.). Type A refers to bell-shaped mercury (II) sulphide, while the type B title is given to finds of mercury (II) sulphide lumps (Batur & Radić Rossi 2019, pp. 112-114). Due to the exhibition conditions in the Regional Museum of Biograd na Moru, the bell-shaped type – A variants developed a grey alteration layer.



Fig. 3-6. and Fig. 3-7. Mercury (II) Sulphide from the Gnalić shipwreck: Type A – bell shaped and type B – lump shaped (left photo: N. Ćuk; right photo: S. Govorčin).

Mercury (II) sulphide (α -HgS) can be distinguished in three types: the natural mineral called cinnabar, and its two synthetic derivatives named vermilion. Vermilion can be produced synthetically, by two different production processes called wet and dry (Gettens, Feller & Chase

1993, p. 159; Eastaugh et al. 2008, p. 735).³³ While the aim of the dissertation was to identify colouring material, the exact nature and origin of the mercury (II) sulphide recovered from the site was not determined by instrumental analyses. Therefore, this text will not use the nomenclature vermilion or cinnabar, but simply mercury sulphide.

After Classical Antiquity, mercury sulphide was addressed with the terms *vermiculus*, *cinnabaris* and *cenobrium*³⁴ were applied to denote either natural or processed pigment. The word *vermiculus* contains the root word *vermes*, which originally described kermes, an insect collected to create a red dye. On the other hand, the word cinnabar is of Indian origin and it has been used to describe red dyes and resin (Gettens, Feller & Chase 1993, p. 159).

Sixteenth-century historical sources

Term	Year	Source	Type of document
n/a	1540	Vannoccio Biringuccio, 1942	Metallurgy treatises
<i>Minium nativum</i> ³⁵	1556	Georgius Agricola, 2018	
<i>Cinabro</i>	1534	Domenico de Gardignano (Matthew 2002, p. 681)	Colour seller inventory
<i>Cenaprio</i> (from Spain)	1556	Mattheo dai colori (Matthew & Berrie 2010, p. 246)	
<i>Cenaprio</i>	1594	Jacopo de' Benedetti (Krischel 2002, pp. 102-103)	

Tab. 3-3. The sixteenth century terminology of the mercury (II) sulphide

Only from the seventeenth century did the distinction become clear that cinnabar is native mercury (II) sulphide mineral and vermilion is synthetically produced mercury (II) sulphide (Harley 1982, p. 125, Eastaugh et al 2008, p. 393). Venice was well-known for the production of vermilion. Nevertheless, Venice could not satisfy the demands of the market, so it probably began to import mercury (II) sulphide from Spain. This explains the existence of Spanish cinnabar in the inventory of Mattheo dai colori from 1556 (Matthew & Berrie 2010, p.

³³ The difference between the particles of wet and dry process observed by optical microscopy is explained in Gettens, Feller & Chase (1993).

³⁴ Used by Theophilus (12 c. AD).

³⁵ Same as note 30.

246). It is important to note that, when Agricola composed his treatises, he referred to mercury (II) sulphide as *minium nativum*, which is probably a reminder of the title used by the Classical authors.

d) Lead (II, IV) Oxide / Lead Tetroxide / Red Lead / Minium

Several irregular lumps of mineral, containing red/orange core and black/grey outer layer, have been identified as lead (II, IV) oxide (Pb_3O_4) (Fig. 3-8.). The absence of regular shape makes it difficult to distinguish the lumps from the ballast stones.



Fig. 3-8. A lump of minium, broken into three parts, from the Gnalić Shipwreck (photo: K. Batur).

Regarding historical terminology, written sources are often misleading as many of them use the terms minium, cinnabar or red ochre interchangeably. In the Middle Ages, the term minium became widely accepted (West FitzHugh 1986, p. 109; Eastaugh et al. 2008, pp. 235, 270). Still, a small percentage of the sources are using the word minium to describe mercury (II) sulphide, as can be seen in the Tab. 2-3. (Agricola 2018, p. 110).

There are two forms of lead (II, IV) oxide described in the sixteenth century sources. While the inventory of Jacopo de Benedetti (1594) mentions the existence of two types of minium – the ‘minium of lead (ven. *piombo*)’, and the ‘minium of lead white (ven. *biacha*)’, insurance documents issued by notaries in 1605 and 1607 list ‘minium’ and ‘ordinary’ minium. This difference in terminology probably refers to different production processes used to obtain minium. The first process included heating the litharge (α -PbO), which probably refers to Benedetti’s ‘minium of lead’. The second process was based on heating lead carbonates, and it

could be related to Benedetti's 'minium of lead white'. Which of these two types of minium is considered ordinary, as mentioned in notaries' documents, remains unknown (West FitzHugh 1986, p. 122; Krischel 2002, p. 105; Tenenti 1959, p. 445, 497; Hochmann 2015, p. 176).

Sixteenth-century historical sources

Term	Year	Source	Type of document
<i>Ochre</i> (explained as 'caused by fumosity of lead ore')	1540	Vannoccio Biringuccio, 1942, p. 116	Metallurgy treatises
<i>Minium secundarium</i> ³⁶	1556	Georgius Agricola, 2018	
<i>Minio</i>	1534	Domenico de Gardignano (Matthew 2002, p. 681)	Colour seller inventory
<i>Minio del piombo</i> <i>Minio de biacha</i>	1594	Jacopo de' Benedetti (Krischel 2002, p. 105)	
Distinguishing minium and ordinary minium	1592 - 1607	Tenenti 1959, pp. 445, 497	The documents issued by Venetian notaries G. A. Catti and A. Spinelli

Tab. 3-4. The sixteenth century terminology of the minium

³⁶ Same as note 30.

e) Arsenic sulphide based colouring material (realgar)

Intensely-coloured yellow and orange powders preserved on the wooden surfaces and in the sediment at the Gnalić site have been identified as remains of arsenic sulphide realgar (Figs 3-9. and 3-10.). Arsenic sulphide is a mineral found in nature as an orange-red arsenic sulphide – realgar (β -AsS) and pararealgar (α -AsS) – and as a yellow arsenic sulphide – orpiment (As_2S_3). It is not unusual to recognize synthetic analogues or alteration products together with the above mentioned naturally occurring types. As these two similar minerals are often discovered jointly in nature, it is common to find their coupled use in art as well (Eastaugh et al. 2008, pp. 29-30).

The characterization analyses revealed the presence of arsenic-based colouring material realgar in the cargo of the sunken ship. However, alterations and environment products are present in the samples, so it is not possible to distinguish whether the recovered material was originally orpiment, realgar or the mixture of both. With respect to the limitation of the analyses, in the rest of the dissertation the term arsenic sulphides will be used instead of orpiment and realgar.

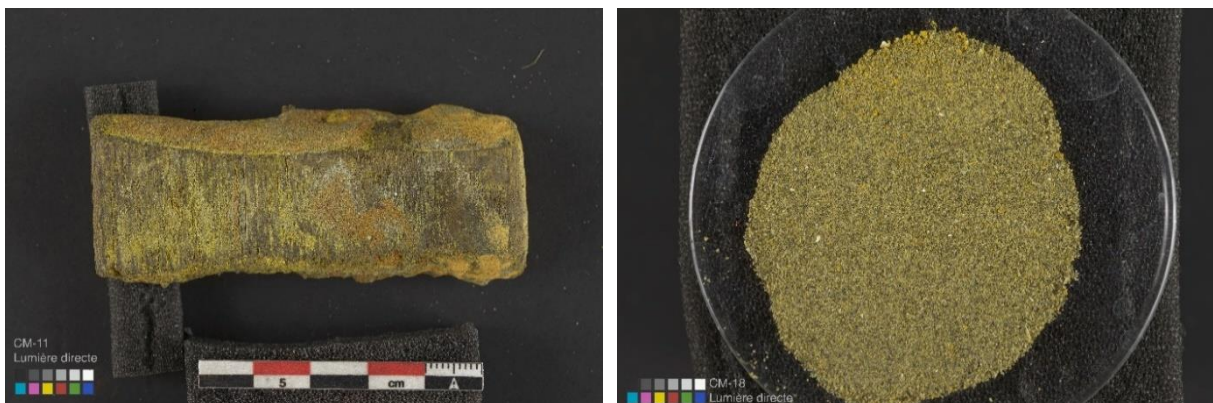


Fig. 3-9. and Fig. 3-10. Arsenic sulphides are preserved as traces on the wooden ship's hull and artifacts, or in the sediment (photos: O. Guillon).

Over history, arsenic sulphides adopted different names. In Arabic alchemy, the minerals attested as being coupled in nature were commonly titled the 'two kings'. The root of the word realgar derives from the Arabic *rahj-al-ghar* which bears the meaning 'the powder of the mine'. (West FitzHugh 1997, pp. 47-54; Harley 2001, p. 94; Eastaugh 2008, p. 325).

Sixteenth-century historical sources

Term	Year	Source	Type of document
Differentiates orpiment, crystalline arsenic and realgar	1540	Vannoccio Biringuccio, 1942, pp. 106-107.	Metallurgy treatises
<i>Auripigmentum</i> refers to orpiment, <i>Sandaraca</i> refers to realgar ³⁷	1556	Georgius Agricola, 2018	
<i>Rexegal oropimento</i>	1534	Domenico de Gardignano (Matthew 2002, p. 681)	Colour seller inventory
<i>Oropimento comum</i> [sic]m[asena]do; <i>Oropimento intt cernido</i> ; <i>Oropimento c[hiaro]</i> ; <i>Oropimento mezan</i>	1594	Jacopo de' Benedetti (Krischel 2002, p. 128)	
Differentiates arsenic and orpiment	1603-1606	Tenenti 1959, p. 358, 448, 463.	The documents issued by Venetian notaries G. A. Catti and A. Spinelli

Tab. 3-5. The sixteenth century terminology of the arsenic-based colouring materials

Vannoccio Biringuccio states there is a difference between orpiment and crystalline arsenic. Orpiment is white or yellow, while crystalline arsenic has a golden colour due to the presence of sulphur in its composition. He also differentiates realgar, which is made by sublimation after heating mixed crystalline arsenic and orpiment (Biringuccio 1942, p. 105). The inventory of Jacopo de' Benedetto provides in total four types of arsenic sulphides (Hochmann 2015, p. 187). In the cargo of ships mentioned in the insurance documents issued by notaries G. A. Catti and A. Spinelli, arsenic-based cargo appears only after 1605, in two variations – arsenic and orpiment (Tenenti 1959, p. 358, 448, 463).

³⁷ Same as note 30.

f) Antimony (III) sulphide / stibnite

Antimony (III) sulphide is a black to grey mineral with bladed surface, having the chemical composition Sb_2S_3 (Fig. 3-11.). It is also known under the names antimonite, antimony glance, and grey antimony. However, the historical colouring material was always known as antimony (III) sulphide, but the ‘sulphide’ word was omitted in the terminology (Agricola 2018, p. 110). The etymology of the title is derived from the Greek word for antimony, *stimmi* or *stibi*, and in Latin, *stibium*. The Greek word *antheon*, meaning flower, is also related to the mineral, describing the disposition of crust of the crystals on the inner surface of the crystals (Eastaugh et al 2008, p. 22, 359).

During the sixteenth century, the term stibnite became accepted in common use (Eastaugh et al 2008, p. 22, 359). The words antimony and stibnite are used interchangeably, and they both refer to antimony (III) sulphide.



Fig. 3-11. Antimony (III) sulphide (photo: K. Batur).

Sixteenth-century historical sources

Term	Year	Source	Type of document
Antimony	1540	Vannoccio Biringuccio, 1942, p. 92	Metallurgy treatises
<i>stibi, stibium</i> ³⁸	1556	Georgius Agricola, 2018	
Antimony (<i>Antimonio</i>)	1594	Jacopo de' Benedetti (Krischel 2002, p. 128)	Colour seller inventory

Tab. 3-6. The sixteenth-century terminology of the antimony (III) sulphide

g) Mercury (Hg)

Mercury is a heavy, cold, silvery metal which remains in a liquid state when stored at room temperature. At the Gnalíć shipwreck site, elemental mercury has been found in pools, on the wooden hull, on artefacts and beneath the sediment. It was also a component of the reflective surface on glass mirrors, by creating an amalgam with the addition of tin (Figs 3-12. and 3-13.).

Historically, two terms were used - quicksilver (lat. *argento vivo*) and mercury (lat. *mercurio*). The term quicksilver was adopted due to the silver colour coupled with the fast movement of the substance provided by its weight and liquid condition. The term mercury was given according to the archaic alchemist tradition of naming the metals according to planets (Pulsifer 1888, p. 11). Its fast movement ability could be also related to the Roman god Mercury, the winged and speedy messenger god (Biringuccio 1942, pp. 79-85).

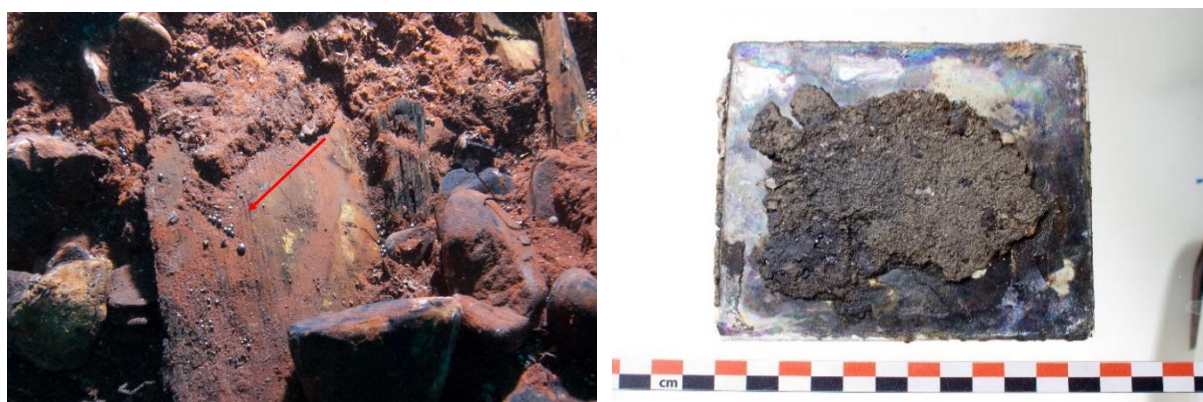


Fig. 3-12. and Fig. 3-13. Mercury drops at the site and as reflecting surface on the mirrors (photos: S. Govorčin).

³⁸ Same as note 30.

Sixteenth-century historical sources

Term	Year	Source	Type of document
Both English translations mentioning quicksilver, without mentioning its Latin equivalent	1540 _____ 1556	Vannoccio Biringuccio, 1942, p. 92 _____ Georgius Agricola, 2018	Metallurgy treatises
Mercury _____ Mercury	_____ 1594	Domenico de Gardignano (Matthew 2002, p. 681) _____ Jacopo de' Benedetti (Krischel 2002, p. 128)	Colour seller inventory
<i>Argentum vivo</i>	1597-1609	Tenenti 1959, p. 197, 292, 358, 442, 594	The documents issued by Venetian notaries G. A. Catti and A. Spinelli

Tab. 3-7. The sixteenth-century terminology of the mercury

h) Red lake pigment – cochineal ($C_{22}H_{20}O_{13}$), madder ($C_{14}H_8O_4$), redwood / brazilin ($C_{16}H_{14}O_5$)



Fig. 3-14. Red lake pigment from the Gnalíć shipwreck (photo: K. Batur).

The red lake pigment on the Gnalíć shipwreck was found shaped in balls (Fig. 3-14.). The samples were made on a substrate of alunite with precipitations of three different red dyes, cochineal ($C_{22}H_{20}O_{13}$), madder ($C_{14}H_8O_4$), and redwood / brazilin ($C_{16}H_{14}O_5$). Since the samples are composed of three types of red lake, the definition will be given for each individually, while the table will address the historical titles appearing in the documents. There are different types of red lake pigments, depending on the species of plants or insects used for their production. During the Middle Ages, red lake pigment was called *grana (ital.)*, because the dried insects used for the dye and pigment production resembled grains. While all of the other colouring materials carried on the *Gagliana grossa* were from inorganic sources, the red lake pigments were derived from organic materials.

Cochineal, sometimes referred to as *grana*, is a crimson coloured pigment, used for dyeing clothes, and if made in the form of red lake pigment it was used for painting. The first mention of cochineal can probably be related to the Greek word *kokkos* and the Latin word *coccinum*. Later, in the Modern period, the terms *carmesinus* and *carmine/crimson* were

adopted (Eastaugh et al. 2008, p. 124). Different names were assigned to cochineal lake, depending on the quality or the region of origin (e.g. Polish cochineal or *chremisi minute*, Armenian cochineal or *chremisi grosso*), or depending on the city where the pigment was produced - of Venice, of Florence, of Antwerp. After the 1520's, a new so-called New World cochineal was introduced in Europe, made from an insect (*Dactylopius coccus*) imported by the Spanish (Matthew 2011, p. 293; Kirby, Nash & Cannon 2010, p. 449; Andersen 2015, p. 342; Kirby 2015, p. 174).

Madder is a commonly used red colour made from the root of the madder plant, *Rubia tinctorum*. The colour variation ranges from orange to purple and brown, mostly depending on the type of substrate. It is used in wool dyeing and lake pigment production (Eastaugh et al. 2008, p. 250; Kirby, Nash & Cannon 2010, pp. 454-455).

Brazilwood (ital. *verzino*) is a bright-red colour, used for dyeing clothes, for lake pigment making, and as an ink. There are two sources for this colouring material; until 1500, it was made from sappanwood (*Caesalpinia sappan L.*) originating from central and southern India, Malaysia, and Sri Lanka. Along with the import of the New World cochineal, the Portuguese and Spanish started to import brazilwood or Pernambuco wood (*Caesalpinia echinata*) to Europe (Kirby, Nash & Cannon 2010, p. 449).

It can be seen that the terminology (Tab. 3-9) for sixteenth-century lake pigments is complex, due to the variety of insects and plants of different origins. Introduction of the New World cochineal influenced the Venetian dyeing industry. As the industry had a large production scale, the dyers were probably experimenting with different recipes. Since red lake is a by-product of the textile industry, it is possible to imagine that the wide choice of textile products was reflected in the creation of different sorts of lake pigments. Thus, the existence of various terms is understandable as a consequence of incoming materials of various origin and different recipes employed.

Sixteenth-century historical sources

Term	Year	Source	Type of document
<i>lacca</i> , <i>lacca fine</i> , <i>lacca di cimatura</i> , <i>lacca di grana lacha</i> for the lake pigments; <i>cremesin</i> , <i>cremese</i> , <i>lacca fine di chermisi</i> for different sorts of cochineal appearing from 1570	through sixteenth century	Kirby 2015, p. 177	Painters records
<i>Cremexe</i> (crimson of Old World cochineal) <hr/> <i>Lacha di grana</i> ; <i>Lacha de crimese</i> ; <i>Lacha</i> ; <i>Lacha de verzin</i>	1534 <hr/> 1594	Domenico de Gardignano (Matthew 2002, p. 681) <hr/> Jacopo de' Benedetti (Krischel 2002, pp. 93–158)	Colour seller inventory
Crimson, grana, wood of verzin, lake vezin, verzin intero.	1597-1600	Tenenti 1959, p. 1988, 220, 224, 239, 241, 243, 284, 348, 372, 429, 461, 496, 558	The documents issued by Venetian notaries G. A. Catti and A. Spinelli

Tab. 3-8. The sixteenth-century terminology for the red lake pigments

By giving an overview of the sixteenth-century colouring materials terminology, the author wanted to suggest possible titles for the finds from the *Gagliana grossa* (Tab. 2-10). Some colouring materials cannot be precisely identified without more specific analyses. For example, arsenic-based pigments (arsenic sulphides) have been chemically altered by their immersion in sea water, so it is not possible to verify if they were originally orpiment and/or realgar. The variety of the terms appearing in historical sources – metallurgy treatises, inventories, insurance documents – demonstrates that even contemporary manufacturers, artists, and traders struggled to define unique names used for the colouring materials in the different level of trade. In an ideal situation, in order to assign proper names, the identified colouring materials from the Gnalić shipwreck should be compared to the titles of the colouring materials as designated on cargo lists of the *Gagliana grossa*. Although over two hundred documents have been located which provide information about this shipwreck, unfortunately, in the case of Gnalić shipwreck no bill of lading (*ven. carichi*) providing information on cargo

loaded onto the ship has been found. Should one be discovered in the future, it would be interesting to see how the colouring materials were titled and categorized.³⁹

Chemical name	Suggested historical title	Chemical formula	Possible variation	Nomenclature in this dissertation
Lead white	<i>cerussa</i>	PbCO ₃ 2Pb(CO ₃) ₂ · Pb(OH) ₂	- lead carbonate (cerussite) - basic lead carbonate (hydrocerussite)	Lead white
Red ochre: + hematite + alunite + quartz	<i>terra rossa</i>	α-Fe ₂ O ₃ KAl ₃ (SO ₄) ₂ (OH) ₆ SiO ₂	/	Red ochre
Mercury (II) sulphide	<i>cinabro</i>	α-HgS	Cinnabar – natural mercury (II) sulphide; Vermilion – synthetic mercury (II) sulphide	Mercury sulphide
Lead (II, IV) Oxide Lead Tetroxide Red Lead Minium	<i>minio</i>	Pb ₃ O ₄	/	Minium
Arsenic sulphide - realgar	<i>oropimento rosso</i>	β-AsS α-AsS As ₂ S ₃	- realgar - pararealgar - orpiment	Arsenic sulphide / realgar
Antimony (III) sulphide Stibnite	<i>antimonio</i>	Sb ₂ S ₃	/	Stibnite
Mercury	<i>mercurio</i>	Hg	/	Mercury
Red lake pigment: + alunite + cochineal + madder + brazilin	<i>lacha</i>	KAl ₃ (SO ₄) ₂ (OH) ₆ C ₂₂ H ₂₀ O ₁₃ C ₁₄ H ₈ O ₄ C ₁₆ H ₁₄ O ₅	/	Red lake pigment

Tab. 3-9. Representation of all terms used in the dissertation, coupled with the chemical equivalents

³⁹ Based on personal correspondence with Mauro Bondioli (December 2019) and an article published by Louisa Matthew (2011, p. 302), these documents either do not exist, or have not yet been discovered.

4. Methodology

Research methodology is based on merging the archaeological data, the results of characterization analyses and the results of the information withdrawn from selected primary and secondary historical sources. The methodology is schematically represented in Figure 4-1. and explained in detail in following sections.

In general, the research was separated into four phases of collecting data:

- underwater recording and sampling;
- photo documentation and visual observations;
- characterization analyses;
- review of the secondary historical sources.

The identification of the material would be impossible without application of the characterization analyses. Without understanding the chemical composition, it would not be clear which materials constituted the cargo. This mean the links from archaeological artefacts to the historical sources would be lost.

The characterization analyses are conducted with the aim to define:

- chemical composition (X-Ray Fluorescence: XRF and Scanning Electron Microscopy – Energy Dispersive X-Rays: SEM-EDX)
- crystallographic phases (X-Ray Diffraction: XRD)
- molecular bonds (Raman Spectroscopy: RS and Fourier-Transform Infrared Spectroscopy: FTIR)
- organic components (Ultrahigh Pressure Liquid Chromatography: UHPLC)

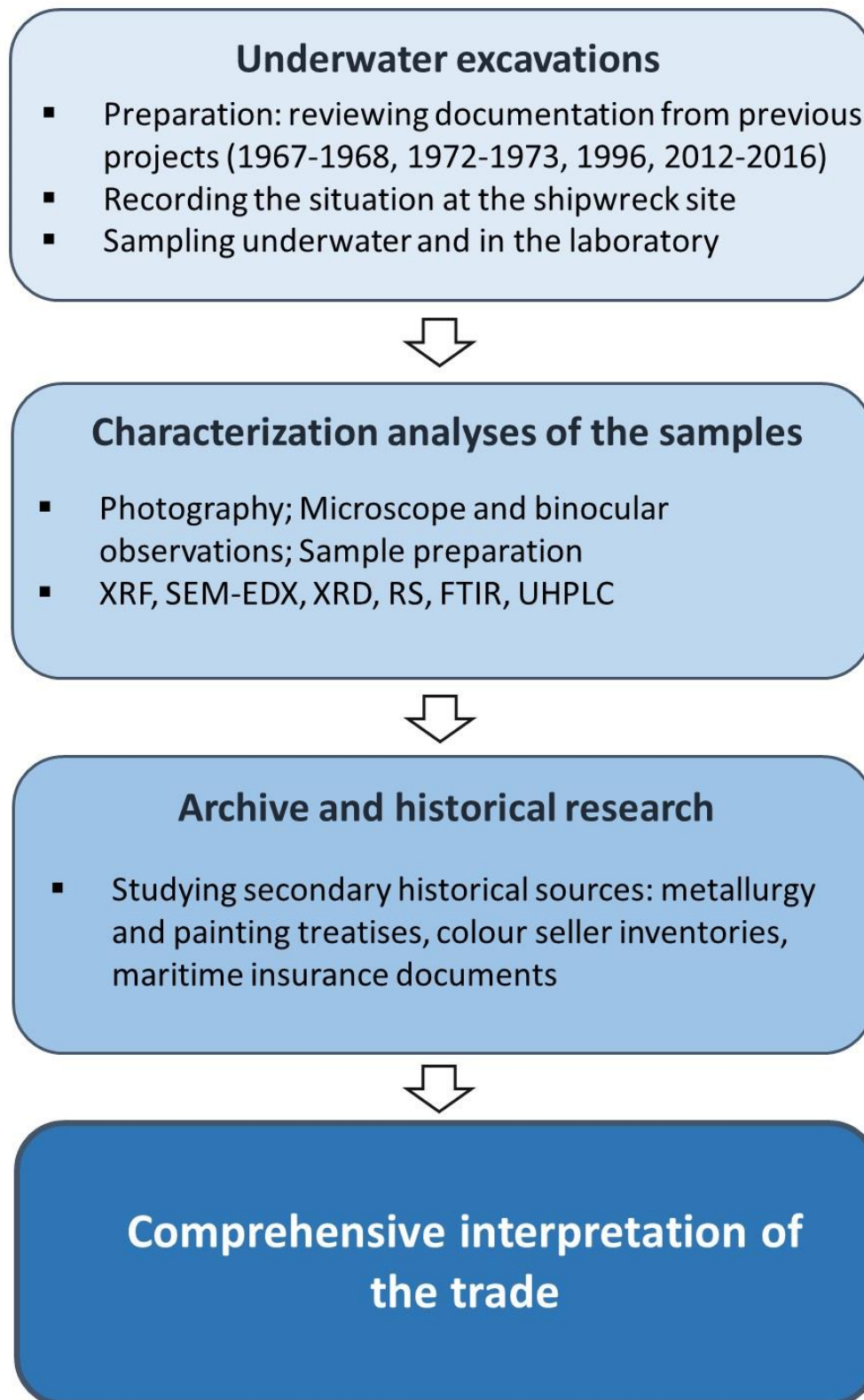


Fig. 4-1. Schematic representation of the methodology of the dissertation. The research was done following steps described in each section.

4.1. Underwater recording and sampling

In early 2017, prior to that year's Gnalić excavation season, this project began by taking notes of the current state of colouring material research based on the article published by Ivo Kelez (1970), as well as reviewing reports from the excavation campaigns from 1967 to 1973 and in 1996, stored in the Conservation Department⁴⁰ in Zadar, Ministry of Culture of the Republic of Croatia. The research also included the documentation made within the project *Gnalić Shipwreck - The Mirror of the Renaissance World*, from 2012 to 2016. Subsequently, examinations were conducted on the stored colouring materials from the Regional Museum of Biograd na Moru and the laboratory of the Gnalić excavations, at the time situated in Tkon, Pašman island, Croatia⁴¹.

After becoming familiar with the published bibliography and with the situation at the site, the author made a provisory list of the samples which should be collected during the 2017 Gnalić season. Multiple dives were performed at the site with the aim of recording colouring materials in barrels and taking sand samples that could potentially contain colouring materials. Further, observation notes were taken, including the position of the colouring materials within the ship's hull, amounts present, packaging methods, and remarks about the surrounding environment (Fig. 4-2.). As artists' artefacts were never attested during archaeological excavations in such wide varieties and extensive amounts, the author faced multiple challenges in how to sample, store, treat, and study the colouring materials.

⁴⁰ During the spring of 2016, author digitalized documents in the archive of Gnalić project stored in Conservation Department in Zadar.

⁴¹ Since June 2019, the laboratory of the Gnalić project is situated in Neviđane, Pašman island, Croatia.



Fig. 4-2. Observations about the colouring materials traces within the ship's hull (photo: K. Yamafune).

The sampling was done during the underwater excavations in the summer of 2017. Glass jars, boiled in water and labelled, were taken to the site. The samples were then collected on the positions according to the plan (Figs 4-3. and 4-4.).

As is the case in other research, profound planning is required to obtain the desired results and at the same time to be time- and cost-efficient. This especially applies if the sampling is done at 26 to 30 meters depth, as the diver is occupied with safety regulations, lack of light, lower temperatures and sometimes low visibility. The diver has to have a plan for the order in which the sampling should be done to maximize the use of the limited 30 minutes of bottom time. All sampling tools must be ready, with glass storage containers cleaned, labelled, and safely stabilized in the basket. It is strongly advised to take samples in glass jars, not only to avoid the contamination of the sample with plastic, but also because plastic containers strive to float up when submerged under water. It is especially important to ensure a good support to stabilize the glass jars in baskets, because 30 minutes of work at the depth of 26 to 30 meters requires 15 to 20 minutes of ascending.⁴² This means a potential disturbance of the glass jars while the diver is moving through safety decompression stops.

⁴² The long ascending is done for a safety reason, to prevent the diver's decompression disease, known as the bends.

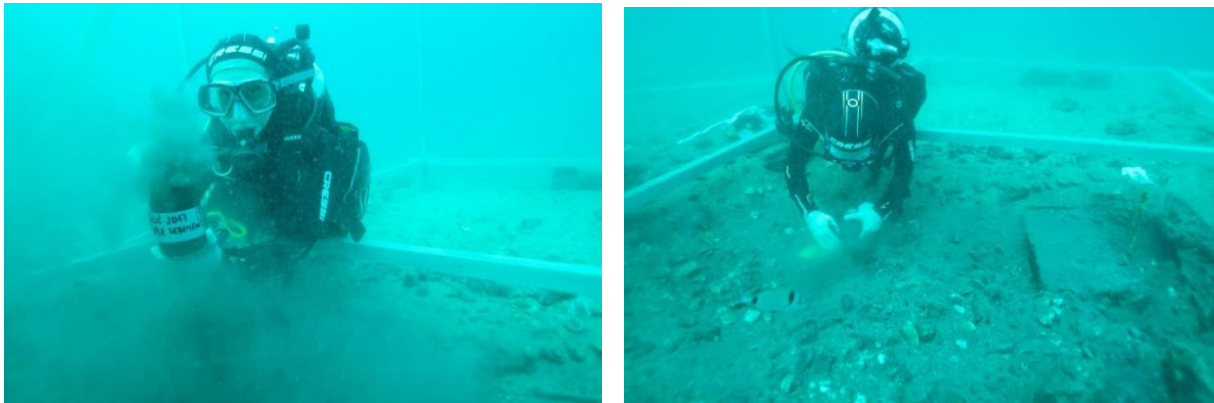


Fig. 4-3. and Fig. 4-4. Sampling sediment during the 2017 excavation season (photo: M. Martinčák).

The sampling started at the most perceptible colouring materials position on the site, the hold of the ship in the aft midship area (Fig. 4-5.). This area, in documentation marked as the ‘barrel area’ encompasses a row of six barrels filled with red powder, as well as one horizontally positioned empty barrel. North of the barrels was an accumulation of ballast stones, while south of the barrels were numerous casks filled with small white cones, determined to be lead white. A large number of barrels are partially preserved, leaving complete only the parts where metal-based material content such as lead or iron prevented the barrel from disintegrating. Exceptions are casks 30, 31, and 51 stuck below barrels 4, 5, and 6; casks 36, 38, and 45 with missing head only, and entirely preserved casks 35, 37, and 52. While excavating this area, archaeologists also recorded the appearance of yellow colour in the sand, in the same layer as the lead white cones and lumps of red colour that fell out of the barrels and casks.

In 2017, barrel 1 was recovered on board and sampled from the staves, while the barrels from 3 to 7 were sampled underwater. Barrel 2 was not sampled as it was found empty, so it is not clear whether the red traces reflect its original contents or contamination from other barrels. Two more barrels filled with red powder existed north of barrel 1, named barrel 12 and 13, but those were not sampled as they were removed in the 2014 excavation campaign. The lead white cones were not sampled underwater, but recovered in groups according to their position within the trench or casks. Those artefacts were placed in nets, retrieved, and safely stored in the laboratory of the Gnalić Project.



Fig. 4-5. The barrel area (orthophoto: R. Torres, K. Yamafune & S. Govorčin).

The largest amount of yellow pigment was detected in the hold of the aft midship area, over and around the remains of the ship's pump (Batur & Radić Rossi 2020). The first layers of the fine sand were mixed with yellow particles, but removing the layers of sand uncovered more intensive yellow colour. Besides sherds of broken window pane cargo, almost no artefacts were found in this area. At the angle of the ship's pump well, on stringer T394 (which also had a role of reinforcement of the pump well from the southern side), was a solid accumulation of pebbles, rounded rough pottery sherds, and yellow colour (Fig. 4-6.). Since this mound was evidently not disturbed by divers during previous excavation campaigns, several samples were taken.



Fig. 4-6. Yellow pigment in the layers of the midship area, below the ship's pump (photo: K. Yamafune).

Upon reaching the surface of the wooden frames and planks, pools of elementary mercury were spotted on the bottom. Beginning with the excavation in 2012, liquid mercury was observed in the upper layers of the site. Excavating deeper revealed whole pools of mercury, which is not surprising as the mercury penetrated deeper into the sediment due to its heaviness. After reaching the mercury layer, team members were directed to stop the fine cleaning, collect the mercury with syringes and place it in glass jars. In this way, the mercury was extracted from the layers, removing a potential hazard from the biological environment. Mercury was not sampled as no characterization or identification was needed. Additionally, the provisional laboratory of the Gnalić project had only modest storage conditions, so the mercury could not be stored there to remove the potential risk of contaminating laboratory space with a hazardous metal.

Additional samples were taken from the samples and artefacts already recovered in previous excavation campaigns and stored in the laboratory. In the case of such sampling, the database entry described the sample location, the condition in which the sample was stored, and if it was being soaked in sea, tap or deionized water. In total, 52 samples of any recovered artefacts that could possibly be identified as colouring materials or artists' tools were chosen

for identification. These samples were labelled GN-2017-CM-number, with ‘GN’ as the abbreviation for the ‘Gnalić’ site, 2017 as the year of the sampling, ‘CM’ as ‘colouring material,’ and then a progressive number. With the aim of having comparative material from the environment, five samples of sediment were also collected on the site, particularly from places where colouring materials were covered with sediment. Those samples were labelled as GN-2017-SS-number, with SS indicating ‘sediment sample’.

Most of the sampling was done in the summer of 2017, while additional sampling of the lead white cones was performed in 2018, since the work on lead isotope analyses and radiocarbon dating of lead white required a new set of samples. The selected cones belonged to the group recovered together with the barrels during the excavation campaigns of 2013 and 2014 (Appendix 20). As this is a group of samples used for analyses that were not originally made for the purpose of dissertation research, they were labelled GN-2018-LW-number, indicating the new year of sampling, and that it was performed on ‘lead white’ to do analyses going beyond the scope of identification and characterization, which is the aim of this dissertation.⁴³

Due to the limited time of instrument availability and the large amount of time required to characterize and identify each sample, it was decided to select relevant samples to perform specific analyses (Fig. 4-7.). Samples were considered relevant if their context was thoroughly recorded, with photos from the site, descriptions, and information about storage conditions. The priority was given to samples collected *in situ*. In total, 16 samples were selected for analyses (Tab. 9-1. and Appendix 21). Selection was made in the laboratory, while a great care was taken to have a representative sample of each cargo type, as well as to consider where an alteration layer could be defined. Sampling was destructive, as preparation required cutting the sample, embedding it in epoxy resin (GN-2017-CM15, -CM39 and -CM42), or just scraping off the surface of the material to reach the core.

⁴³ The lead isotope analyses were performed by Gareth Davis and Paolo d’Imporzano from Vrije University in Amsterdam, Netherlands, whereas radiocarbon dating with isotopes ¹³C and ¹⁴C was tested by Lucile Beck and Cyrielle Messager from CEA - Atomic Energy and Alternative Energies Commission, in Gif-sur-Yvette, Paris, France. The samples are presented in Appendix 20, but the results will be delivered in papers published by abovementioned scholars. On the same samples, the analyses of the quality of lead white were performed by using SEM-EDX, in the Ateliergebouw as a part of training with Maartje Stols-Witlox at the Department of Conservation and Restoration, University of Amsterdam.



Fig. 4-7. Selection of the samples for analysis in CICRP (photo: K. Batur).

4.2. Photo documentation and visual observations

4.2.1. Photography of the sample condition

After choosing the most appropriate samples for characterisation of the colouring materials, the samples' current state was documented (Fig. 4-8.). First, photographs were taken of the samples in their packages, whether glass jars or plastic zip-bags. The photos were taken with direct light (Fig. 4-9.; *lumière directe*) and with raking light (Figs 4-10. and 4-11.; *lumière rasante* or *lumière semi-rasante*).⁴⁴

⁴⁴ The photos were taken with a Nikon D810 camera attached to a tripod; focal length 60 mm, ISO-200, exposure time 1/125 sec, F-stop f/11 in the case of direct light, and focal length 60 mm, ISO-200, exposure time 1/125 sec, F-stop f/9 in the case of grazing angle of the light.



Fig. 4-8. Photo documentation of the samples (photo: L. Boulogne).



Fig. 4-9., Fig. 4-10. and Fig. 4-11. Photos taken with direct light and with raking light (photo: K. Batur).

4.2.2. Multi-image photogrammetry

Multi-image photogrammetry is a recording technique which uses software to identify the matching features on the images, thus creating a three-dimensional model through computer processing (McCharty & Benjamin 2014, p. 96). Sampling of some materials necessitated the use of destructive methods, so the multi-image photogrammetry recording was done to preserve the visual data about a particular sample, in this case lead white ingots.⁴⁵

In order to create overlapping photos with precision, photographs were made on a rotating wheel, with marks at every 15 degrees. Two cameras were set on tripods, with the following settings:

- Nikon D810: set on the tripod at the level of the sample (0° angle). Settings: focal length 60 mm, ISO-100, exposure time 1/125 sec, F-stop f/11.
- Nikon D810: set on the tripod at an approximately 60° angle, turned towards the sample. Settings: focal length 35 mm, ISO-100, exposure time 1/125 sec, F-stop f/11.

Each camera made 24 photographs of the sample in an upright position, after which the sample was turned upside-down in order to create the same sets of photographs for the bottom part. The photographs were processed in *Agisoft Photoscan*⁴⁶, in which two models of the samples were created. After aligning photos, building the dense cloud and mesh in each of the two processed chunks, scales were added to create precise measurements of the model. The next step involved erasing the base on which the sample rested, masking the photos, and finally merging two masked chunks into one complete 3D model (Fig. 4-12.). The texture was built upon completion of the process.⁴⁷ The workflow is described in Radić Rossi et al. (2019, pp. 58-61).

The advantage of multi-image photogrammetry model is that it is user-friendly, and after the model is created, it can be used to export accurate orthophotos from different views, including section profiles. In the author's opinion, the specific shape and size of the lead white

⁴⁵ The samples of sections were embedded in epoxy resin and dried (GN-2017-CM15, GN-2017-CM39 and GN-2017-CM42).

⁴⁶ In the beginning of 2019, the software *Agisoft Photoscan* updated to the version *Agisoft Metashape*.

⁴⁷ Although tests were done with different focal lengths and ISO-settings, this was by far the best solution when creating 3D models. Nevertheless, the texture was not completely satisfying, and in order to improve it, it will be necessary to take more photographs of the samples.

ingot's mould could possibly designate a difference in quality of the lead white, as during the sixteenth century lead white could contain different ratios of cerussite and hydrocerussite, or be adulterated with chalk. Having three-dimensional models of the ingots would allow comparison of shapes after the characterization analyses are done. In this way, the author could compare the section of the ingots and their composition to evaluate the abovementioned hypothesis. The results of multi-image photogrammetry recording are presented in Appendix 15 & 16, including five lead white ingots and one minium lump. In the future, complete analyses of composition and shape of cones of different sizes and weights, will suggest whether the shape of the cone mould has any designation of the composition.

Another advantage of multi-image photogrammetry is that it is much safer to record lead white from a distance; drawing by hand would include the risk of potentially inhaling perilous lead powder.

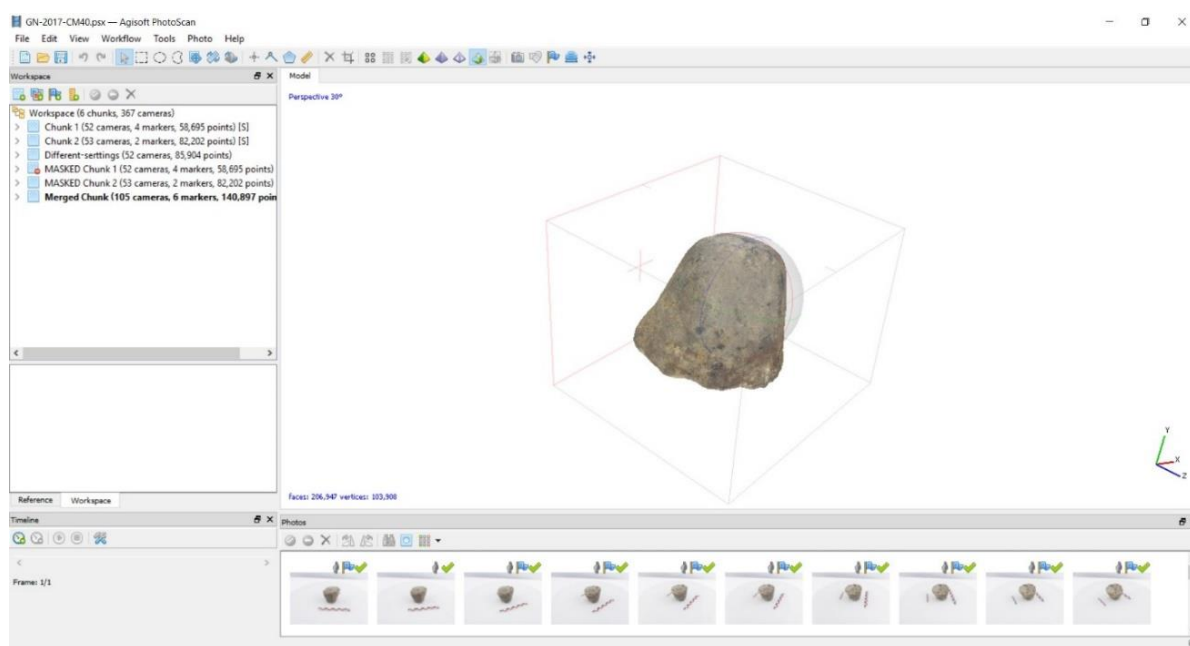


Fig. 4-12. Photogrammetry of lead white ingot processed in *Agisoft Photoscan* (photo: K. Batur).

4.2.3. Binocular and microscope observations

Samples in both solid and powder forms were observed under an Olympus SZX7 stereo microscope and an Olympus BX60 microscope. Photos were taken using Olympus Stream Image Analysis Software.

Observations of each sample's morphology were made using both the microscope and the stereo microscope. The composition of each sample was recorded as either homogeneous or heterogeneous, including the size, shape, and colour of the particles.⁴⁸

4.2.4. Multispectral imaging: Photography under different wavelengths (visible light - VIS, ultraviolet induced visible luminescence - UVL, infrared – IR, infrared false colour - IRfc)

The term 'spectral imaging' refers to digital images taken under light of different wavelength (visible, ultraviolet, infrared), potentially revealing anomalies in landscapes or on the surface of objects. It was developed 50 years ago, and its main use was in astrophysics, remote sensing and military applications. In the late nineties, it began to be used in recording the state of preservation and conservation of material. Today, it has found a wide use in documenting pigments on paintings, with the aim to differentiate surface materials, to understand whether some areas of a painting had previously been exposed to treatment, or to monitor the degradation in the layers of a painting. This is a very useful method which allows for the study of spectral and spatial information on a painting, without applying any destructive techniques (Fischer 2006, p. 3). A recent publication discusses various terms used to name this technique but also presents its wide application in conservation science (Piccolo, Stols-Witlox & Fuster-López 2019).

While recording Gnalić site colouring materials, multispectral imaging was used to observe if there were visible layers on a lump, or if powders were composed of multiple materials. The differences in structure of the materials revealed by photo shooting under visible, ultraviolet, and infrared light, as well as merging these images in false colour imaging technique, helped to select the appropriate sampling spots (Figs 4-13., 4-14., 4-15. and 4-16.). The methodology of the work described below is usually applied on recording paintings in Centre Interdisciplinaire de Conservation et de Restauration du Patrimoine (CICRP) in Marseille. The methodology of the work applied on example of recording the fifteenth century

⁴⁸ For the reference to description of particle shape, author referred to Eastaugh et al. 2008, p. 959.

wall painting in chapel of Our Lady of the Fountains in La Brigue, France, is the same applied in this dissertation (Boularand et al. 2019).⁴⁹

The sample GN-2017-CM35 clearly shows a core of pigment surrounded by an alteration layer. Differences in colour of the red core also show that the core changed composition near the surface due to the reaction with air in the storage room. With respect to this oxidation layer, before taking a sample, three to five millimetres of the surface layer of the material was removed.

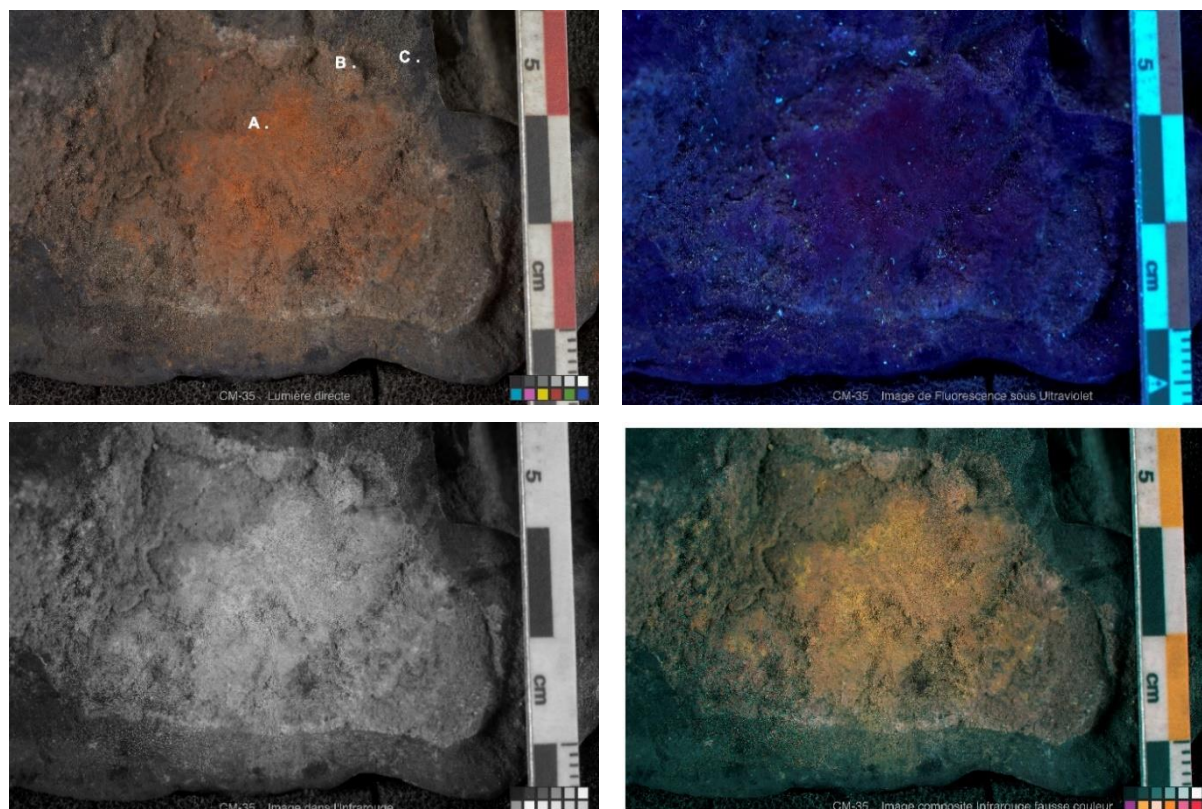


Fig. 4-13., Fig. 4-14., Fig. 4-15. and Fig. 4-16. Lump of red lead, sample GN-2017-CM35. Spectral imaging applied during preliminary documentation of the samples in following order, from up to down and from left to right: visible, ultraviolet, infrared, and infrared false colour imaging technique. Letters A, B, and C on Figure 4-13. represent sampling spots (photo: O. Gullion).

The following imaging acquisition settings were applied:

Documentation with visible light – VIS (Fig. 4-13.) is the imaging technique widely used to capture the details under visible radiation⁵⁰ and produce high-resolution images.

The photos were taken with a Nikon D800E camera. Settings: focal length 60 mm, ISO-200, exposure time 1/125 sec, F-stop f/9.

⁴⁹ The author is grateful to have a chance to be supervised by photographer O. Guillion during the work on recording with multispectral imaging. All the descriptions of techniques and acquisition author used are based on the instruction of O. Guillion and recently published work (Boularand et al. 2019).

⁵⁰ Region from 4×10^{-7} to 7.5×10^{-7} m of wavelength in the electromagnetic spectrum (Artioli 2010, p. 19).

Documentation with ultraviolet induced visible luminescence – UVL (Fig. 4-14.) is the imaging technique based on the principle of sending UV radiation⁵¹ to the surface of the object. The radiation emitted from the surface of the object is collected, while using a filter (Kodak Optical Filter, 2E, 75x75 mm filter) to prevent UV light from directly reaching the camera sensor. The photos were taken with a Nikon D800E camera. Settings: focal length 60 mm, ISO-200, exposure time 30 sec, F-stop f/9.

Documentation with infrared light – IR (Fig. 4-15.) is the imaging technique based on the principle of irradiating the object with infrared light⁵², and capturing the information while using a filter (Kodak Gelatin filter 87C, 75x75 mm) which prevents infrared light from directly reaching the camera sensor.

The photos were taken with a Nikon D800E camera. Settings: focal length 60 mm, ISO-200, exposure time 1/125 sec, F-stop f/11.

Documentation with infrared false colour imaging technique – IRfc (Fig. 4-16.) is a digital rendering imaging technique which is based on changing the effects of image with visible light (RGB⁵³ layers) with the IR image, creating a rather composite image. With the help of the software, RGB layers of an image taken with visible light are replaced with an image taken with IR light. The red is replaced with the IR light, the green is replaced with red, and the blue is replaced with green colour.⁵⁴ The use of IRfc highlights the differences in the core and the alteration layer of the object in the case of recording colouring materials from the Gnalić shipwreck, but it is also used for material identification and determination of layers on paintings.

⁵¹ Region from 10^{-9} to 4×10^{-7} m of wavelength in the electromagnetic spectrum (Artioli 2010, p. 19).

⁵² Region from 2.5×10^{-6} to 2.5×10^{-5} m of wavelength in the electromagnetic spectrum (Artioli 2010, p. 19).

⁵³ Red, green and blue colour layers which constitute images.

⁵⁴ Information obtained from: <http://www.arcanes.eu/fr/atelier/infrarouge-fausses-couleurs/> [Accessed: June 2020]

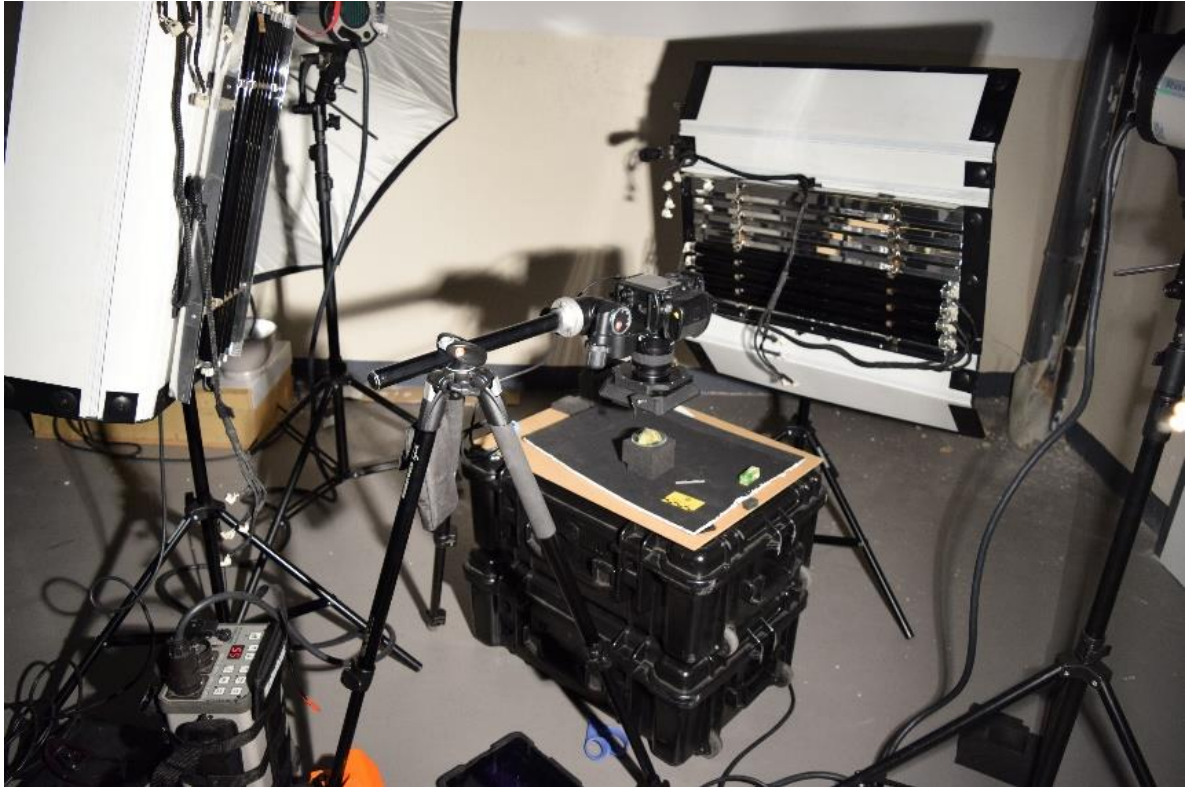


Fig. 4-17. Equipment used for multispectral imaging (photo: K. Batur).

4.3. Characterization analyses

Scholars continue to innovate and apply newly developed scientific techniques (in further text: characterization analyses) in archaeology. Some of these attempts were not successful due to the lack of mutual understanding between scientists and archaeologists (Artioli 2010; Pollard & Bray 2007). It is important to point out that before employing characterization analyses in research of a cultural heritage object, it is essential to be familiar with the nature of the material and the history of the object to be able to impose the right questions. The samples being analysed were discovered in an archaeological context as a result of human activities. The artifacts contain much more information than simply chemical composition; their contexts alone have value for studying past societies, so the role of archaeology should not be underestimated (Artioli 2010, p. 108-111).

Further knowledge about capabilities and limitations of each characterization instrument enables one to enhance methodology with the application of appropriate techniques. Archaeologists should strive to interact with physicists, chemists, geologists, or conservation scientists, simply because each scientific technique has its applications and limitations. Additionally, it takes time and experience to master instrument analyses. Pollard and Bray (2007) pictured the collaboration as a 'bicycle made for two'. Contributions from each side are

equally important: an archaeologist who is familiar with relevant historical questions and knows the context of the object, then poses direct questions, working with a scientist who has knowledge of the proper analytical method crucial to test the hypothesis. Only by merging both fields can data lead to valid interpretation, and – most importantly – deliver the results for historically important questions.

The aim of the characterizations within this dissertation is to identify the Gnalić wreck colouring materials. These characterizations are particularly important for two independent reasons:

- All knowledge of the trade of colouring materials comes from historical sources. Therefore, these colours are known only by their historical names, but their exact chemical compositions are not clear. What little data exists comes from the analyses of Renaissance paintings. Analyses executed on Gnalić colouring materials yield exact data about the colouring materials in their raw condition, before they were prepared to be applied on canvas, used in dyeing or glass industry, or as cosmetics or medical supply.
- The analyses will provide results precisely dated to late October or early November of 1583, when the ship sunk. The database will be the foundation containing the results of analyses which will serve in the future for building a reference collection for comparative studies.

With the aim to conduct these identifications, it was necessary to obtain data about the chemical composition, crystallographic structure, and molecular bonds. This data was compared to the databases and published bibliography, with the goal of finding a match in the identification. The characterization methods explained in the further text are employed in archaeological and conservation science from other scientific disciplines. The bases for the characterization are methods used by scientists, such as geologists, physicists and chemists.

After selecting the samples which are representative of the *Gagliana grossa*'s colouring materials cargo, the appropriate instrumental analyses were combined to identify the sample. This section describes the principles of each characterization method used for material identification. Due to limited instrument availability coupled with the specific research questions, not all methods were applied to each sample. Tab. 9-1. includes information about all the samples analysed, while Appendix 21 present individual sheets with information regarding archaeological context and storage conditions as well as the results of characterization analyses for each colouring material. The data in these appendices form the bases for interpretation (chapter 9).

4.3.1. X-Ray Fluorescence (XRF)



Fig. 4-18. XRF instrument in CICRP (photo: Olympus, portable XRF, 2013).

X-Ray Fluorescence (XRF) is widely used for the identification of chemical elements in archaeological artefacts (Fig. 4-18.). The method is based on the emission of primary X-rays from an X-ray source, usually an X-ray tube, which excites electrons from their shell, creating vacancies. The atom becomes unstable and, in order to return to its stable condition, the vacancies need to be filled. Electrons positioned in the lower shell pass into the next orbital to make the atom stable again, and while doing this they release energy, *i.e.* secondary X-rays. The amount of energy released corresponds to the chemical elements present in the sample (Pollard et al. 2007, p. 101).

Sample preparation: No preparation needed.

Instrument	Laboratory	Samples analysed
A DELTA DP-6000 Alloys and Metals Handheld XRF Analyzer (Olympus Corporation)	CICRP	GN-2017 - CM05 - CM06 - CM15 - CM16 - CM18 - CM33 - CM35 - CM36 - CM39 - CM42 - CM52

Tab. 4-1. List of the instruments and specifications used for XRF analyses

4.3.2. Scanning Electron Microscopy – Energy Dispersive X-Rays (SEM-EDX)

Scanning Electron Microscopy – Energy Dispersive X-Rays (SEM-EDX) is based on high resolution microscopy combined with the energy of X-rays as measured at the moment when electrons emitted from the microscope are reflected by the sample (Fig. 4-19.). This method relies on the same fundamentals as X-ray fluorescence. The only difference is in the source of primary energy, which is in this case is emitted electrons rather than X-rays. This type of analysis is very useful when examining small areas, particularly in verifying the homogeneity of a sample (Pollard et al. 2007, p. 109).

Sample preparation: In both cases, samples were grinded with pestle until the grains were fine. Miligrams of samples were placed on carbon tape and stands, and then in the instrument.

Instrument	Laboratory	Settings	Samples analysed
SEM Philips xl 30, EDX Detector Apollo 10 SDD	CICRP (performed in the laboratory of Aix-Marseille University)		GN-2017 - CM11 - CM15 - CM16 - CM18 - CM33 - CM35 - CM39 - CM42 - CM52
SEM JEOL5910LV, EDX Detector Thermo Scientific SDD	Ateliergebouw (RCE)	Acquisition time: 30 seconds	GN-2017 - CM02 - CM04 - CM05 - CM06 - CM14 - CM31

Tab. 4-2. List of the instruments and specifications used for SEM-EDX analyses

4.3.3. X-Ray Diffraction (XRD)

An X-Ray Diffraction (XRD) instrument (Fig. 4-20.) uses X-rays of known wavelength to determine distances between molecules within crystalline structures, which helps to identify the chemical compounds within a sample. When emitted, some X-rays penetrate the surface of the sample, while some are reflected. The reflections are shown in a diffraction pattern, which is then compared to existing databases within analytic software. In general, the software could easily recognize samples which were transported in a solid form (for example, GN-2017-CM33 was easily identified as a mercury sulphide). However, if the sample was in powder form, it likely mixed with surrounding sediment or was otherwise partially altered in the underwater environment. As expected, some of the samples contained several overlapping mineral phases, which caused difficulties with the spectrum (Pollard et al. 2007, pp. 113-115). The XRD diffraction patterns were processed and analysed using EVA software and Match! Software.

Sample preparation: In both cases, samples were grinded manually with the pestle until the grains were fine. Afterwards, the fine powder was placed into sample holder.

Instrument	Laboratory	Settings	Samples analysed
Bruker Focus D8 Advance	CICRP	0.20 tube: 6 Rotation: spinner on, 15 rpm (rotations per minute); Range angle: 5 to 60° 2 θ ; Step size: 0.02° 2 θ Time by step: 8 seconds; Tube: Co; K α_1 = 1.78897 Å (K α_2 = 1.79285 Å); Energy: 35 kV, 40 Ma. Incident beam: primary soller slit = 2.5°; divergence slit = 0.6 mm; Secondary soller slit = 2.5°; detector slit = 3.27 mm; Anti-scatter slit = 2.39 mm.	GN-2017 - CM05 - CM06 - CM16 - CM33 - CM39
Rigaku MiniFlex II desktop Xray diffractometer	Ateliergebouw	Cu K α radiation (λ = 1.541 80Å) at ° 30 kV and 15mA. The equipment was fitted	GN-2017 - CM36 GN-2018 - LW02 - LW03

		with a Ni K β suppression filter. Diffractograms were recorded in a $2\theta = 1-40^\circ$ range (2.5 $^\circ$ /min scan rate and 0.025 $^\circ$ step size)	
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Tab. 4-3. List of the instruments and specifications used for XRD analyses

4.3.4. Raman Spectroscopy (RS)

Raman spectroscopy analysis was invented by the physicist Chandrasekhara Raman in 1928, but it took almost a half-century before it began to be widely used. When passing through a medium, only part of the emitted beam is scattered in all directions. Raman spectroscopy is intended to distinguish between types of materials, as Raman discovered that once a sample is excited, different materials lead to measurable differences between incident and scattered radiation (Fig. 4-22.). This is one of the most useful techniques for identifying the compositions of archaeological artefacts and works of art. A significant advantage is the ability to characterize particles of very small size, but its non-destructive character is of even greater importance (Pollard & Haron 2008, p. 68).

Sample preparation: In CICRP, samples were embedded in epoxy resin. In Ateliergebouw, aluminium foil was taped on the glass slate. Several milligrams of powder were placed on the glass, before putting glass in the instrument.

Instrument	Laboratory	Settings	Samples analysed
Renishaw Spotlight 400, Invia Raman System Spectroscope. Software Wire 4.2, build 5037; Master: Renishaw.	CICRP	Red laser (633/780 nm)	GN-2017 - CM15 - CM39 - CM42
Perkin Elmer, Raman Micro300	Ateliergebouw (RCE)	Near-infrared laser (785 nm)	GN-2017 - CM02 - CM04 - CM05 - CM06 - CM14 - CM31

			GN-2017 - CM18
Renishaw inVia Reflex confocal -Raman spectrometer with a Peltier-cooled CCD detector and WIRE software	Ateliergebouw (Rijksmuseum)	Green Nd:Yag laser operating at 532nm, 1800 lines mm ⁻¹	GN-2017 - CM08 - CM11c

Tab. 4-4. List of the instruments and specifications used for RS analyses

4.3.5. Fourier-Transform Infrared Spectroscopy (FTIR)

This method is based on the infrared radiation emitted in the transition between vibrational and rotational energetic states in molecules (Fig. 4-21.). Infrared radiation is absorbed and emitted in rotation, indicating the molecular bonds and, by extension, the molecules, present in the sample. The spectrum produced indicates molecular bonds, which are of particular importance in identifying organic materials.

In the electromagnetic spectrum, infrared radiation occupies wavelengths from 400 to 750 μm . FTIR is the most commonly used technique in archaeology and art history and, together with the complementary technique of Raman Spectroscopy, has been previously used to identify archaeological material (Pollard & Heron 2008, pp. 66-67, Pollard et al. 2007, p. 70).

Sample preparation: Prior analyses, samples were grinded with pestle to fine grains.

Instrument	Laboratory	Settings	Samples analysed
Microspectrometry FTIR Imaging System, Perkin Elmer	CICRP	Transmission mode in compression diamant cell; domain of accession: 4000 - 650 cm^{-1} , resolution: 2 cm^{-1}	GN-2017 - CM16 - CM39
Perkin Elmer Spectrum 100 FTIR spectrometer	Ateliergebouw (RCE)	Specac Golden Gate Single Reflection Diamond Attenuated total reflectance mode; domain of accession: 4000 - 650 cm^{-1} resolution: 2 cm^{-1}	GN-2017 - CM02 - CM04 - CM05 - CM06 - CM14 - CM31

Tab. 4-5. List of the instruments and specifications used for FTIR analyses

4.3.6. Ultrahigh Pressure Liquid Chromatography (UHPLC)

When finding an organic material of unknown composition at an archaeological site, it is usually composed of a complex mixture of original molecules, contaminated by degradation products which are the consequence of either artifact handling or storage conditions. The proper analytical techniques used for precisely separating organic residues into molecules are based on chromatography. Chromatography separates the molecules based on the physical behaviour, such as weight, functional group types, and molecular shape. The basis for the separation lies within the interaction of mobile and stationary phases within the chromatographic system. In the case of UHPLC, liquid is used for both the mobile and the stationary phase. Another difference from gas chromatography is in the fact that the samples do not have to be volatile, as it is necessary only to dissolve them in solvents (Pollard et al 2007, pp. 137-147).

In this dissertation, the UHPLC was performed with the aim of examining organic colouring materials, and to be more specific, lake pigments (Figs 4-23. & 4-24.). The analyses were conducted only on the samples on which the results of XRF, SEM-EDX, XRD, or FTIR suggested the existence of organic matter.

The methodology of the UHPLC was based on previously published work (Serrano, van Bommel & Hallett 2013).⁵⁵ The UHPLC was coupled with Photo Diode Array detection (UHPLC-PDA), while the samples were identified by the comparison of the UV-VIS spectra and retention time with the reference materials.⁵⁶ Even when the spectra of an analysed sample is compared to the database, sometimes it is not possible to identify materials. The reasons could be the absence of a reference sample or a low amount of the provided sample.

Sample preparation: As already mentioned, the difference in UHPLC and other chromatography and spectrometry techniques is in the use of solvents for the sample preparations.⁵⁷ Firstly, the samples were treated using oxalic acid and hydrochloric acid to

⁵⁵ The UHPLC was tested with seven different sizes of UHPLC columns and stationary phase compositions by applying several mobile phases, flow rates, temperatures, and runtimes. The methodology is described in Serrano, van Bommel & Hallett 2013, and it allows to precisely distinguish the chromatographic spectrum profiles to understand the source and the provenience of the dye.

⁵⁶ The Cultural Heritage Agency of Netherlands owns the database (in the text HPLC-library) on lake pigments and dyes created by Ana Serrano, Maarten van Bommel and Jessica Hallett. The reference collection contains a total of 59 reference materials, including anthraquinoids, flavonoids, indigoids, carotenoids and tannins, based on the physiochemical properties reported from plants and animal dye sources (Serrano, van Bommel & Hallett 2013). The identification could not have been completed without involving the expertise of Maarten van Bommel.

⁵⁷ Sample preparation and the instrument specification are provided by the report of Maarten van Bommel, which I received on 26 June 2019.

extract the organic compounds in the solution. Oxalic acid was used as a mild treatment, but if a stronger solution was required, the hydrochloric acid was used.

The sample was placed in a 250 µl vial, then 100 µl of extraction agent was added: either based on oxalic acid (mixture of water / methanol / acetone / 0.5 M oxalic acid in ratio of 40/30/30/1) or based on hydrochloric acid (mixture of water / methanol / hydrochloric acid, 1/1/2). Afterwards, the vial was heated for 10 minutes in a 100°C water bath to extract and dissolve organic colourants. The sample was then decanted, evaporated to dryness, and dissolved in 50 µl dimethyl sulfoxide (DMSO). The samples were centrifuged for 10 minutes at 2000 rpm to remove precipitates. If necessary, the solvent was transferred to another vial and the centrifuging process was repeated for 10 minutes at 2000 rpm. Only 5 µl of sample is required to inject to be analysed by UHPLC-PDA.

The samples were analysed using BEH-Shield column, based on gradient of water, methanol and formic acid. Settings of the instrument in Ateliergebouw:

UHPLC-conditions:

System: Waters Chromatography Acquity H-Class UPLC system in UHPLC mode.

Column: BEH-Shield C₁₈ column, 1.7 µm (150 x 2 mm) with 0.2 µm filter. Column oven at 40 °C

Effluent: Buffer A: 10% methanol in water, buffer B: pure methanol, buffer D: 1 % formic acid in water, flow rate 0,2 ml/min.

Time	%A	%B	%C	%D
0	80	10	0.0	10
1.33	80	10	0.0	10
2.33	74	16	0.0	10
5.33	55	35	0.0	10
9	55	35	0.0	10
14	30	60	0.0	10
25	5.0	85	0.0	10
26	0.0	100	0.0	0
30	0.0	100	0.0	0
32	80	10	0.0	10
40	80	10	0.0	10

PDA-Detection: Waters Acquity PDA, 200 to 800 nm, resolution 1.2 nm, 2 scan/s equipped with an 0.5 µm cell.



Fig. 4-20. SEM Philips xl 30, EDX Detector Apollo 10 SDD (photo: K. Batur).

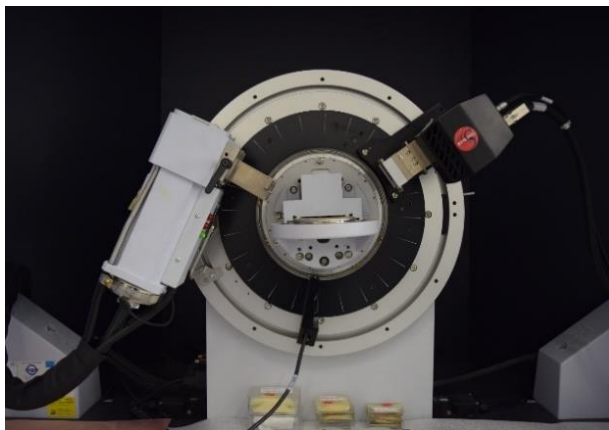


Fig. 4-19. XRD Instrument - Bruker Focus D8 Advance (photo: K. Batur).

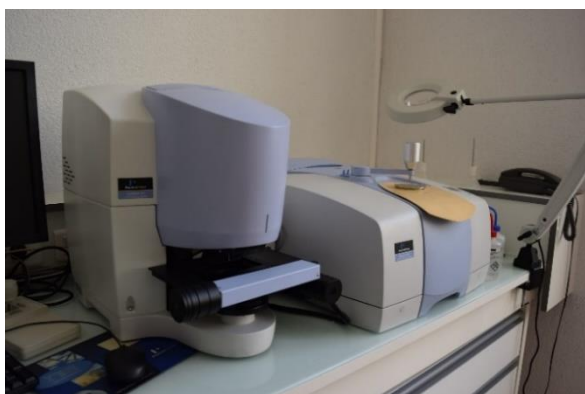


Fig. 4-21. FTIR instrument: Imaging System, Perkin Elmer (photo: K. Batur).



Fig. 4-22. RS instrument: Renishaw Spotlight 400, Invia Raman Spectroscopy (photo: K. Batur).

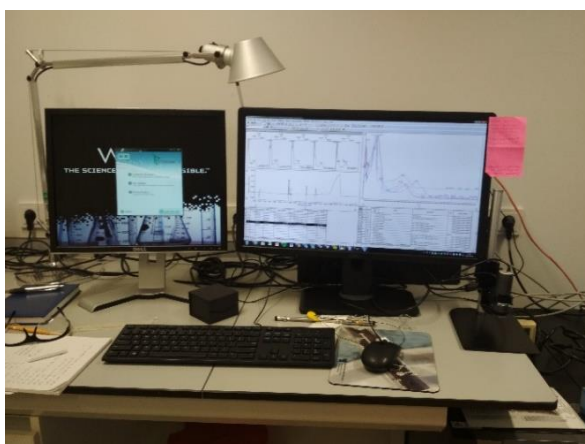


Fig. 4-23. and Fig. 4-24. M. van Bommel performing UHPLC analyses on the samples of Gnalčić lake pigment in Ateliergebouw, Amsterdam. Instrument: Waters Chromatography Acquity H-Class (photo: K. Batur).

4.3.7. Data processing

The database containing the descriptive information and photography documentation of each sample was created in *Filemaker Database*. After the analyses were executed, the data was saved in raw or PDF/word format:

XRF: exported in PDF;

SEM-EDX: spec, and exported to png, txt and docx;

XRD: raw and processed with *Diffraction Eva* and *Match!*. *Eva* software uses CDD PDF2/PDF4+/PDF4 Minerals/PDF4, while *Match!* software uses COD-Inorg REV248644 (last update on 3 March 2020). For comparative data, the RRUFF Database was used.

RS and FTIR: asci, csv and exported to jpg via software *SpectraGryph* 1.2. The data for comparison was consulted in published bibliography, and in the online sources RRUFF Database and IRUG Spectral Database.

UHPLC: Raw data was compared to database of organic materials owned by RCE.

CrystalSleuth software was often used to remove the background of spectra and read the peaks. All exported data is provided in Appendix 21 at the end of dissertation.

4.4. Review of the secondary historical sources

By completing identifications of the colouring materials, the main link was created that allowed comparisons to be made with the secondary historical sources. For the purpose of the research, the author selected the sources which would help to reconstruct the view on colouring material production, trade, and maritime transport. The selected written sources fall into five main categories:

- Metallurgy treatises (Vannoccio Biringuccio, 1540⁵⁸; Georgius Agricola, 1556⁵⁹);
- Published articles and books which are based on research of the documents about Venetian colour sellers, *vendecolori*;
- Maritime insurance documents: The book *Naufrages, corsaires et assurances maritimes à Venise* (Tenenti 1959);

In all the abovementioned sources colouring materials were mentioned in different categories of level of trade or use, thus providing various sorts of information. During research, the author relied on translations and interpretations of the primary sources written by historians and art historians, as their expertise and comments on the topic made the work highly reliable.

Within the secondary historical sources, a special attention is given to *Naufrages, corsaires et assurances maritimes à Venise, 1592-1609*, published by historian Alberto Tenenti in 1959. In a comprehensive manner, this publication lists the shipwrecks, breakdowns and pirate attacks from the period of 1592 to 1609, based on the insurance documents issued by Venetian notaries Giovan Andrea Catti and Andrea Spinelli. By obtaining insurance, the owners of the goods and the merchant ships protected themselves against losses. Considering the perilous situations that could be encountered on the maritime trading routes (explained also in Appendix 6), the loss of merchandise was common. If an accident happened, the owner of the goods would sign a transfer of claim with the aim to charge the merchandise loss. The insurance records of Catti and Spinelli provide insight into specific cargo carried, including colouring materials.

Since the comprehensive cargo lists and port books for the end of the sixteenth century are not preserved (Matthew 2011), the lists of the insured cargoes lost in accidents represent the only available data on which a study about late-sixteenth century shipping can rely. The pattern obtained from the data about cargo, destination, merchants and the ship types, provide

⁵⁸ Translation by Cyril Stanley Smith & Martha Teach Gnudi, published in 1942.

⁵⁹ Translation by Herbert Clark Hoover and Lou Henry Hoover, published in 2018.

a unique overview of the trading connections and material exchanges between Venice, Western Europe and the Eastern Mediterranean at the dawn of the sixteenth century. Although the data delivered by documents issued by Catti and Spinelli can be studied from different points of view, these documents cannot be taken as a representative picture of the late Renaissance state-of-the-art in maritime transport. Besides Catti and Spinelli, there were numerous other notaries in Venice actively working at the end of the sixteenth century. The data about insured cargo published by Tenenti was used only to demonstrate the presence of colouring materials in the cargo of shipwrecks.

Although it is not related to any circulation of the colouring materials at the international level, the translations of Renaissance treatises on painting materials originating from Northern Italy was used to supplement the information obtained from abovementioned sources (Merrieffield 1967). Treatises dating from the twelfth to seventeenth centuries were translated by Mary Philadelphia Merrifield and encompassed in the publication *Original Treatises* in 1849. By already having experience with translating painting treatises to enrich the understanding of the technology of painting, like *Treatise on painting* by Cennino Cennini (1844) and *The Art of Fresco Painting as Practiced by the Old Italian and Spanish Masters* (1846), Merrifield's work on *Original Treatises* is recognized as a one of pioneering contribution in translating and understanding the painting treatises. Merrifield's work on treatise translation adds value, as she travelled to Venice to consult with contemporary painters and recorded surviving oral information on the preparations of the pigments. Although important, this source was used to supplement other historical sources, as it was created over a century and a half ago. It must be taken with caution, as further scientific and historical research has developed the studies of the artist's materials.

4.5. Research limitations

At the end of this chapter, it is important to address the limitations of the research.

- One of the main issues in the characterization methodology is dealing with alterations caused by the surrounding environment. Since the colouring materials ended up on the seabed, many surface changes may have occurred. These changes are initiated by either environmental conditions, for example, alkaline conditions of the underwater environment, or reactions caused by the presence of incompatible metals. Alterations of the material could even be created after recovery due to inappropriate storage

conditions. Some of the colouring materials have either alteration layers (those found in the shape of the lump) or the presence of multiple crystallographic phases (those found as powders). Although studying alteration is beyond the scope of this work, it is important to understand which layers of material belong to the original material, and which result from subsequent reactions. The matter of colour alteration was recorded as a common problem during the examinations of the colours from the Vasa shipwreck (Tångeberg 2000, p. 149; Hocker 2018, p. 96).

- Colouring materials are often found at land excavations. In contrast, during underwater surveys and excavations those type of finds are not easily discoverable. The main obstacle is the depth, since the lack of light influences the poor visibility of the colour. As a result, it is sometimes easier to detect colouring materials packed in wooden barrels or ceramic containers on the sea floor. However, the most valuable materials were traded in relatively low amounts, placed in small-scale packages or sometimes wrapped in paper or textile. Since paper and textile have a tendency to disintegrate quickly unless stored in a well-sealed anaerobic condition, the most valuable materials can end up without a container, covered and mixed with mud and sand. Consequently, it is recommended to sieve the sand from an archaeological excavation.
- Another issue is the disintegration of organic-based colouring materials in the underwater environment. The red lake pigment survived only because of its component of alunite, which is the base for the precipitation of lake pigments.
- If we consider that the Gnalić wreck is positioned at a depth of 26 to 30 meters, due to the lack of penetrating sunlight most of the colours visible to excavating divers are blue and green. Thus, there is a possibility some blue and green colouring material were not seen in previous excavations due to poor visibility or a lack of contrast.

Finally, it is worth noting that half of the shipwreck is still covered with a 0.8-1 m thick sediment, and we may still expect to find other types of colouring materials in future excavation seasons. Among colouring materials, the as-yet unrecovered part of the cargo could contain other substances that commonly appear on the lists of insured goods from the documents issued by notaries Catti and Spinelli, or in some of the *vendecolori* inventories (Tenenti 1959; Krischel 2010). These include wax, resins, turpentine, and other substances that could be identified as

artists' materials (Appendix 8). Analyses of the artefacts recovered at Gnalić allows us to correctly identify colouring materials and then to assign appropriate historical names to the materials, which will help us to trace the materials in the published results of the archival studies, or the results of analyses in Venetian paintings.

5. *Gagliana grossa* – Venetian merchant ship in the light of historical sources

5.1. Location of the Gnalić shipwreck

Gnalić is the name of a rocky islet positioned at the southern entrance to the Pašman Channel, with a surface area of 4 700 m². It is surrounded by the islands of Pašman, Žižanj, Gangaro and Vrgada (Fig. 5-1.). In cartographic representations from 1824, it is named *Sco(glio) Kamicich*, while elderly generations of nearby villages refer to the islet as Kamenčić Gornji, from the diminutive of ‘stone’ (cro. *kamenčić*), modified by the adjective ‘upper’ (cro. *gornji*). Evidently, the etymology of the contemporary title Gnalić refers to cape Punta Gnala, which overlooks the islet from the nearby island of Pašman. This title was mostly used by fishermen sailing from the island of Murter to the south; when entering the Pašman Channel they commonly used cape Punta Gnala as a navigation reference point (Jurđana 2013, p. 16; Radić Rossi & Nicolardi 2019, pp. 9 - 11).

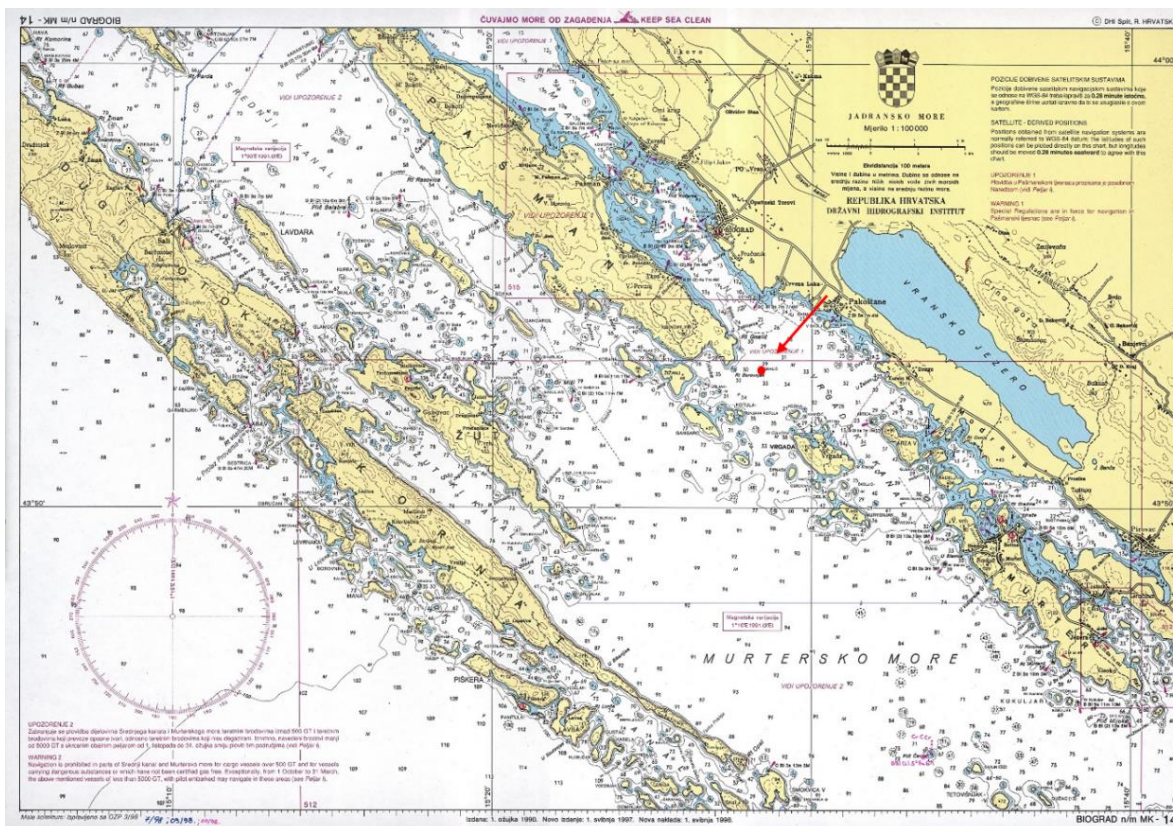


Fig. 5-1. Map of Zadar and Šibenik Archipelago. Red dot and arrow are marking the position of the shipwreck (Hrvatski hidrografski institut, Biograd n/m MK 14).

The Pašman Channel was an important segment of the route used from Antiquity to the Modern era by seamen sailing the Eastern Adriatic. Frequent sailing through the channel was encouraged by the nearby cities of Zadar (ven. *Zara*) and Biograd na Moru (ven. *Zara Vecchia*), where ships often made stops to renew their supply of fresh water. Contemporary pilot books (Hrvatski hidrografski institut 2012, pp. 174-176) warn sailors to carefully sail through the Pašman Channel, as there are many natural obstacles in the southern part of the channel, including numerous rocky islets and rocks (Babac, Muntan, Mali Dužac, Veli Dužac, Čavatul, Frmić, Planac, Sv. Katarina). Around the abovementioned islets, a special warning is given for the islets just off the coast of the city of Pašman (Muntan, Mali Dužac, Veli Dužac and Čavatul), as an unexperienced seaman could be surprised by the shallow water in this area. The channel is also frequently exposed to the strong gusts of local winds (cro. *jugo* and *bura*) blowing from the south and north-east (Hrvatski hidrografski institut 2012, pp. 174-176). Additionally, navigation in this area was considered perilous due to the presence of strong currents. Thus, navigation was consequently forbidden by the Venetian Senate in the winter period, as explained in appendix 6 section ‘Navigational restrictions and dangers at the sea’. Although archival documents do not state the cause of the wreck of the *Gagliana grossa*, it would not be surprising if poor late-autumn weather played a role in the loss. The location of Gnalić in the south-western part of the Pašman channel is particularly dangerous for seafaring. Compared to the Zadar Channel, this area is less protected from winds and waves coming from the south. The shipwreck is located around 100 meters from the Gnalić islet to the south, at a depth of 26 to 30 meters.

5.2. The discovery and excavations of the shipwreck

Although the location of the shipwreck was known to local sponge divers and foreign tourists before it was publicized, the shipwreck was officially discovered in September 1967.⁶⁰ Interest in the shipwreck was awakened when rumors about its existence reached Zadar. Miljenko Barić, the captain of touristic boat Borik from Crvena luka, revealed several artifacts to a group of art historians from Zadar. Realizing that a shipwreck site with preserved artifacts was of significant importance, the experts immediately organized an expedition to the site of the discovery during the following days. Divers were quickly assembled to assess the wreck, directed by Ivo Pericoli, Art Historian from Faculty of Philosophy in Zadar, and Valentin

⁶⁰ The history of the discovery and the first excavation campaign as presented here are based on: Radulić 1970; Radić Rossi et al. 2013; Radić Rossi, Nicolardi & Batur 2016; Radić Rossi & Nicolardi 2019.

Uranija, the Director of the National Museum in Zadar. The day of 13 September 1967 is marked in the history of Croatian archaeology as the date of official discovery of the Gnalić shipwreck (Radić Rossi et al. 2013, pp. 67-68; Radić Rossi, Nicolardi & Batur 2016, pp. 224-225; Radić Rossi & Nicolardi 2019, p. 31).

The public showed great excitement – newspapers were full of sensational titles mentioning a sunken galley loaded with precious items in the vicinity of Biograd na Moru. The first three rescue actions were executed from 7 to 10 October, from 23 to 31 October 1967, and from 13 to 28 October 1968. Even though the research was conducted over a very short period, it resulted in the recovery of hundreds of artifacts (Ministry of Culture of the Republic of Croatia, GN-KOZ-D021a, GN-KOZ-D165). During the first excavations, eight guns were recovered, from which two, the longest, bore the initials Z. A. and the year MDLXXXII. The initials refer to Zuane Alberghetti, member of a famous Venetian family specialized in gun casting, and 1582 marks the year of the production. Having the date of the casting of the guns, researchers recognized the ship could not have sunk earlier than 1582, so this year was used as a *terminus post quem* (Petricioli 1970, pp. 10-11). Exceptional cargo items recovered from the shipwreck included goblets, vases, bowls, mirrors, window panes and other types of glass, brass chandeliers and sconces, and raw materials and semi-processed products. Exquisite textiles were discovered, preserved in an ironclad chest: 54 meters of silk damask, three linen shirts and eight woolen caps (Radić Rossi & Nicolardi 2019, pp. 47-59). The artefacts recovered during the first excavation campaigns were conserved and restored by Božidar Vilhar, then placed on permanent exhibition at the Regional Museum in Biograd na Moru in 1970. During the following years, the general public was introduced to the site by several exhibitions held in Zadar, Zagreb, Ljubljana and Beograd (Petricioli 1981, p. 39; Radić Rossi et al. 2016, p. 230).

The initial problem during the early excavation projects was the lack of a professional team educated in underwater research, so the first actions could be described as attempts to rescue what was present on the seabed. The research team was composed of local divers who had no prior experience in underwater research and excavations. During the working day, the team members were assigned tasks to excavate or record the situation within the trenches. Afterwards, they were questioned by the director, art historian Ksenija Radulić, to describe the situation in the trench. The data given by the divers was written in the daily diary, and accordingly, the site plan was created.

Although having no previous experience in studies of naval architecture or ships' cargo and equipment, the researchers who directed the first campaign had incredibly strong awareness about the value of the information from the site. Comparing the shipwreck to terrestrial

archaeological sites, often disturbed by human activities in later periods, Ksenija Radulić noted the importance of this site, explaining: ‘...the find of this kind has a specific character in that it provides a section through the contents of an ordinary, everyday moment in the history at a certain point.’ (Radulić 1970, pp. 6-9).

After a break of several years, the excavations continued from 8 to 22 September 1972 and from 31 August to 10 September 1973. In 1972 an area containing barrels was reached; the divers started to uncover red and yellow content, as well as heavy cones in the casks. The director of the project, Ksenija Radulić, was concerned by the damage caused by cleaning with the water pump. The inability to feel for the fragile objects combined with the strong suction of the water pump resulted in divers pulling out the casks and barrels without maintaining their integrity. Data was irretrievably lost due to the absence of trained expert divers capable of doing delicate cleaning and recording of the archaeological context.

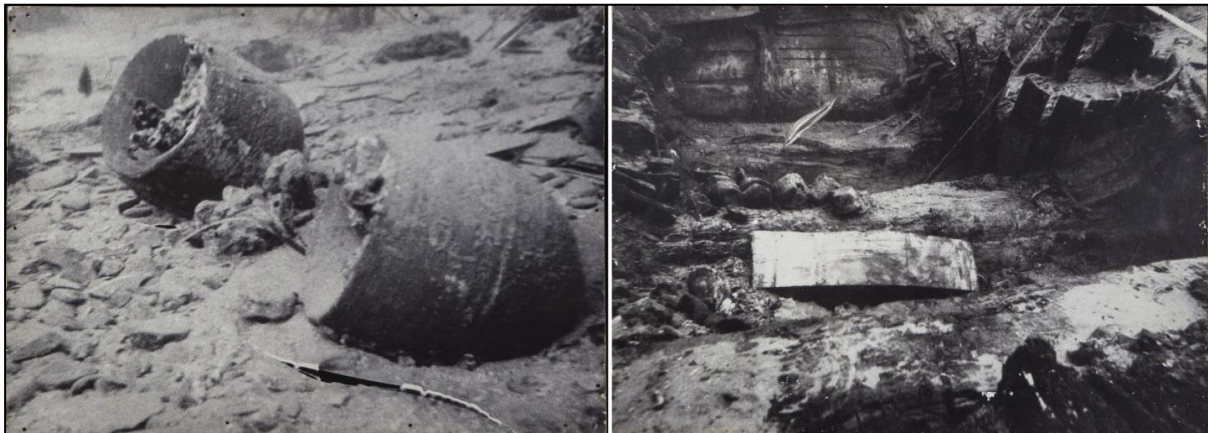


Fig. 5-2. and Fig. 5-3. Bells of mercury sulphide and a remarkably preserved barrel with contents (Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

After the first excitement of recovering attractively decorated objects, the following year brought up new questions. The 1973 excavations revealed the ship was, indeed, full of ‘mysterious and interesting materials’ (Figs 5-2. and 5-3.). In comparison to the 1967 and 1968 campaigns, the diaries of 1972 and 1973 are more detailed in describing the context of the finds. The curator of the National Museum in Zadar, Sofija Petricioli, who was actively involved in the research of the site and the artifacts, stated:

‘We discovered that our ship is of large size with different types of material, and identifying these materials goes far beyond our hydro archaeological abilities. We worked on the trenches where the concentration of the cargo was the largest, and we discovered numerous closed barrels full of various contents. We are no longer finding the

artifacts of fine manufacture (still, we discovered several complete glass vessels and from four to five kilos of glass beads), but instead various raw materials. While excavating, we ran into barrels with some intensive yellow colour, as well as barrels with red colour, which is, in contrary to the yellow, not soluble in water. Further, we discovered brown colour, brass rods, lead carbonate cones, sheets of white foil, cleaned almonds, a large lump of anise, and some heavy sand which, to us laypersons, looks like the ore from which mercury is extracted, as well as a large pile of stones which the divers are convinced is not of marine origin. We also recovered some sand that is not the same as the sea bottom.' (Personal archive of Sofija Petricioli).⁶¹

Although the raw materials were analyzed and their identifications were published by chemist Ivo Kelez in *Vrulje - Journal of the National Museum in Zadar* in 1970, the quantity and variety of material recognized on the seabed suggested the ship transported more materials than was originally thought. The ship, indeed, transported remarkable amounts of colouring materials. When the first analyses were completed, it was discovered that ship transported lead white, mercury sulphide, stibnite, mercury and sulphur (Kelez 1970).

In 1973 the director Ksenija Radulić was forced to stop excavations, as it was not possible to maintain the work on a complex site without having proper equipment and a trained team, supported by sufficient financial resources. With the enthusiasm of the public and the scientific world settled down, the famous "Venetian galley full of gold" was forgotten for a while. Had there been no Regional Museum of Biograd na Moru, which opened in 1970 with the aim to host a Gnalić exhibition, the site could well have been forgotten completely.

In 1996, Zdenko Brusić, the curator of the Archaeological Museum in Zadar, organized a brief attempt to recommence excavation at the Gnalić site. Zdenko Brusić had all prerequisites to successfully conduct excavation - he was familiar with the site because of his involvement in 1973 excavation campaign, but he also had an abundant experience in surveys, excavations

⁶¹ 'Otkrili smo da je naš brod tako velik i tako pun najrazličitijeg materijala da prelazi naše hidroarheološke snage. Radili smo na onome mjestu gdje je koncentracija tereta bila najveća, pa smo nalazili bezbrojne još neotvorene bačve pune svega i svačega. Više i ne nailazimo toliko na predmete umjetnog obrta /ipak našli smo nekoliko cijelih staklenih predmeta i oko 4-5 kg perlica/, nego više na razne sirovine. Tako smo naišli na bačve s nekom intenzivnom žutom bojom, bačve sa crvenom bojom koja se za razliku od žute ne otapa u moru, zatim neku tamno smeđu boju, mesing u šipkama, čunjiće olovnog karbonata, plitice bijelog lima, očišćene jezgre bajama /mandula/, veću grudnu anisa, neki teški pijesak koji nama laicima izgleda kao ruda iz koje se vadi živa, a naravno još je uvijek dolje velika hrpa šljunka za koju ronjaci tvrde da nije morskog porijekla. Također smo izvadili i pijesak koji nije jednak onome na dnu.'

and protection of underwater sites in the Eastern Adriatic.⁶² However, the excavation he started at the Gnalić site was soon cancelled by the Croatian Ministry of Culture.

Subsequently, in 2005 the cargo from the shipwreck was partially studied under the framework of the project *The Heritage of the Serenissima*, directed by Mitja Guštin (University Primorska, Koper), Sauro Gelichi (University Ca'Foscari, Venice) and Konrad Spindler (University of Innsbruck). The research activities were conducted within the European program Culture 2000, and each group studied a particular part of the artifacts from the Gnalić shipwreck site stored in the Regional Museum of Biograd na Moru. The project gathered international experts to study cargo and equipment from the sunken ship and resulted in several publications (Mileusnić 2004; Lazar & Willmott 2006; Guštin, Gelichi & Spindler 2006). Interestingly, the colouring materials were barely mentioned. At that time, it was not yet clear how much the identification and characterization of the raw materials could contribute to Venetian economic history studies, particularly with respect to the studies of the trade in colouring materials. In following years, the team directing the project *The Heritage of the Serenissima* tried to restart the underwater excavations in collaboration with Smiljan Glušćević from the Archaeological Museum in Zadar, but this initiative was never supported by Croatian Ministry of Culture (Guštin & Spindler 2006, p. 92; Radić Rossi & Batur 2019, p. 5).

Despite the unsuccessful attempts to restart the Gnalić shipwreck project, the Croatian scientific community remained very aware of the importance of the site. A significant step forward was made by gathering the experts at the roundtable meeting titled *The Gnalić Shipwreck – Research History, the Problems of Conserving Archaeological Finds, Plans for the Future and Application of Underwater Information and Communication Technologies*, held on 5 July 2011 in Biograd na Moru. The roundtable was an opportunity to start discussions about the relevance of the site and possibilities of restarting the project. The meeting in Biograd na Moru was followed by a workshop on the site, using cutting-edge technologies such as multibeam sonar, an autonomous underwater vehicle (AUV), and a remotely operated vehicle (ROV) (Fig. 5-4.). The workshop ended with fruitful results, establishing the foundation for starting the project of systematic research of the Gnalić shipwreck site.

⁶² Zdenko Brusić was recognized as one of the pioneers of Croatian maritime archaeology for the significant contribution his work left on the development of the discipline.



Fig. 5-4. The diver holding window glass in front of remotely operated vehicle (ROV) during the survey in 2011 (photo: M. Brzac).



Fig. 5-5. Exposing the ship's hull during the trial excavation in 2012 (photo: M. Belošević).

The excavations on the Gnalić shipwreck restarted in 2012 with a trial campaign organized by professor Irena Radić Rossi from the University of Zadar, in collaboration with Filipe Castro from Texas A&M University and other local and international institutions.⁶³ The aim of the trial research was to study the area already excavated by previous researchers in order to see how well the hull was preserved, and to determine if any artifacts remained to be recovered (Fig. 5-5.). The short campaign brought excellent results; it was confirmed that many artifacts remained on the site, as well as wooden hull construction in a quite good state of preservation in the area previously excavated in the 1970s. The ship's construction clearly contains unique information about Venetian shipbuilding at the end of sixteenth century.

The project continued during following years, focusing on studying old documentation from the first excavation, cataloging artifacts, and studying the ship's hull. In 2014 it became a part of the *AdriaS project – Archaeology of Adriatic Shipbuilding and Seafaring*, supported by the Croatian Science Foundation (HRZZ IP-2014-09-8211). Today, the research has gathered international experts to study the ship's hull and parts of the merchant cargo. Considering the rich cultural and historical context of the shipwreck, this study is significantly contributing to the general knowledge of life in the late Renaissance world. To use the idea of Ksenija Radulić, the shipwreck represents one moment in 1583, and it is astonishing how much information about manufacture, trade, seafaring and everyday life can be drawn from this valuable archaeological data.

⁶³ From 2015 onward the excavations were directed only by Irena Radić Rossi from the University of Zadar.

5.3. Identification of the shipwreck

The question of the wreck's identification was addressed by Astone Gasparetto in 1973, and his proposal was confirmed through detailed research conducted by Mauro Bondioli and Mariangela Nicolardi from 2012 to 2019.

The year of casting on the bronze gun (1582) and the approximate location of the shipwreck became the starting point for Astone Gasparetto, a historian studying Venetian glass production, to research documents in the State Archives of Venice. The glass artifacts were of particular interest for him, as they included a wide array of types clearly manufactured in the same period. His main goal was to identify the shipwreck to precisely date the glass collection (Gasparetto 1973, p. 83).

While doing research on deeds of assignment of the merchants who insured their goods in the office of the notary Giovan Andrea Catti, Gasparetto found documents regarding a ship named *Gagiana* (*Gagliana*) which sunk in the “waters of Murter” island in the vicinity of Gnalić islet. Giovan Andrea Catti's clients usually sold their commodities in the Eastern Mediterranean, and Gasparetto located three deeds of assignment related to the *Gagiana* (*Gagliana*), which mentioned the name of the captain, the final destination (Constantinople), and the location of the shipwreck. Unfortunately, the insurance documents did not include a list of the insured goods. Recognizing the fit to the Gnalić shipwreck, Gasparetto proposed the identification (Gasparetto 1973, pp. 80-81). The identification of the shipwreck was finally confirmed by the research of Mauro Bondioli and Mariangela Nicolardi in 2012. Finding an abundance of the window panes on the seabed was the main evidence that confirmed the identification. Those finds were connected with an archival document ordering 5000 window panes (ven. *rui*) for the renovation of the harem of sultan Murat III, signed by Giovanni Francesco Moresini; many of these panes were recovered from the site in the 1960s.

5.4. The lifetime of the ship: from construction to the depths of the Adriatic

The results of the research in the State Archives in Venice brought to light hundreds of documents related to the ship's history, the captain, and the merchants who loaded the cargo. Very few examples of ship studies from the Early Modern Period, such as *Mary Rose*, *Vasa*, and *La Belle* (Mardsen 2009; Hocker 2011; Bruseth et al. 2017), can reconstruct the full story based on archival resources. In addition to the great value of precise datation of the artifacts on the historical timeline, these documents provide vast information about the historical events,

personalities of main characters, and even diplomatic relations of that specific period. This subchapter provides a brief overview of the ship's lifetime – additional detailed information can be found in the recently published book *Brodolom kod Gnalića – Ogledalo renesansnog svijeta* (Radić Rossi & Nicolardi 2019).

The ship was built on behalf of Venetian nobles Benedetto da Lezze, Lazaro Mocenigo and Piero Bassadona. These three nobles founded a company in 1567 to conduct trade between Venice and the Iberian Peninsula, Flanders, and England. During the same meeting, they ordered around 650 oak logs, as well as Mediterranean pine and larch, to begin the construction process.

The ship was built by Francesco di Curzola, an experienced shipwright whose family moved to Venice after the Venetian-Ottoman war (1537-1540). Reflecting his skill and knowledge in shipbuilding, Francesco was even named as the foreman of the Venetian Arsenal. By managing the voyages of merchant ships, he gained extra revenue. After some delay waiting for a prohibition of sailing to expire, the ship was finally launched in September 1569. In archival documents, the ship was often referred to as *Lezza, Moceniga e Basadonna*, reflecting the last names of the owners. The tonnage of the ship measured 1200 *botti veneziane*, which is the equivalent of around 720 tons.

During the first years, the ship was in the service of the Venetian State, as Ottoman-Venetian relations worsened and eventually escalated into the Cyprus War. The ship was about to make its first voyage when the Venetian Senate obliged the owners to concede it to the State due to the necessity of transporting military troops and supplies to Cyprus. In the spring of 1570 *Lezza, Moceniga e Basadonna*, together with two other ships *Dolfina* and *Giustiniana*, completed voyages to Cyprus.

While serving the Venetian military in July 1571, the ship was attacked by an Ottoman fleet directed by Uluç Ali in the vicinity of the island of Corfu. The enemy's fleet managed to destroy the ship's rudder, mast, and rigging; water began to penetrate through the seams. The Venetian crew in *Lezza, Moceniga e Basadonna* was unable to fight back as the enemy was too numerous. After a long combat, the crew of *Lezza, Moceniga e Basadonna* succumbed to the enemies' attacks.

The ship's story is unknown during the period when it was under the ownership of Uluç Ali. It is even possible that, after being repaired in a nearby shipyard, the ship fought as part of the Ottoman fleet during the Battle of Lepanto in 1571. The first document mentioning the ship after its capture near Corfu in 1571 dates to November 1581, when Uluç Ali sold the ship to Odoardo da Gagliano, a merchant in Constantinople. Before known as *Lezza, Moceniga e*

Basadonna or Leze et Moceniga, now the ship was named *Gagliana*, according to the family name of the owner, and *grossa*, due to its large capacity.

In spring 1582, the ship *Gagliana grossa* finally started to execute trading ventures between Odoardo da Gagliano in Constantinople and his uncle Domenico da Gagliano in Venice. Sailing under the direction of the captain Alvise Finardi, the ship made three voyages from Constantinople to Venice.

In late October 1583, the ship was ready to depart from the port of Venice in the direction of Constantinople. The ship included a special cargo of 5000 window panes, loaded under the direction of Giovanni Francesco Morosini, Venetian *bailo* (resident ambassador) in Constantinople. The window panes were ordered for the renovation of the harem of sultan Murat III, which had recently burned in a fire caused by the carelessness of a servant. In addition, three bales of silk damask were sent as a gift to the sultan's mother, Nūr Bānū. The ship was also loaded with products of various European manufactures, and with the finest examples of Venetian glass as well. The complete list of the cargo is unknown, but the documents of the insurance companies provide a partial list of the merchants who loaded goods. For example, Antonio Platipodi from Athens loaded three bales of silk linens of medium quality, a bundle of green damask and crimson dyed textile, whereas Iseppo Balbio loaded anise and cumin. Unfortunately, the documents of insurance companies do not specify the goods loaded by other merchants.

The news about the unfortunate event of *Gagliana grossa* sinking in the vicinity of Murter and Biograd na Moru was delivered in Venice on 9 November 1583. Soon, the merchants made a request to notaries to confirm the loss of insured cargo, so they could receive reimbursement for their lost merchandise. In order to retrieve valuable cargo, a committee chaired by Piero della Moneta was formed to plan and organize a salvage operation.

To organize the action of the recovery, Piero della Moneta engaged experienced diver Manoli from Crete, nicknamed Fregata. Manoli was well-known for his ability to gather the right people and ships to efficiently complete such a complex action. He had already proved the success of his plans by organizing recovery of the armament of the sunken ship *Bonalda*. Upon successful completion of the *Gagliana grossa* salvage, Piero della Moneta promised to Manoli the profit of one third of the recovered value. Among various objects and textiles, Manoli and his team recovered the chest of the ship's notary. The chest soon revealed valuable contents: several bags of coins, along with jewelry, diamonds, pearls, and emeralds, originally sent by the Dutch merchant Guglielmo Helman to his agent in Constantinople, Antonio Peruta.

Based on the value of recovered items, Manoli requested a higher award for the completed work than was arranged at the very beginning.

The rescue operation stopped when all the merchants who requested a refund were pleased. It seems likely that most of the salvaged goods were recovered from the upper decks, while the heavy cargo remained inaccessible in the hold. Many of the crew members of *Gagliana grossa* survived the sinking, as some of them appear later in other documents not related to the shipwreck, or they were buried in graves dated later than 1583. However, several people did not manage to escape, as was demonstrated by the human bones recovered in the excavation campaign of 1973.

Insurance documents (*ven. cession*) provide essential information for the identification of sunken ships and reconstruction of the stories of their last journeys. Nevertheless, it is unfortunate that merchants were not obliged to list all loaded cargo. Having the names of the merchants who insured the cargo of raw materials would be a useful starting point to trace their origin, manufacturers or shops which originally sold them.

Finally, as already emphasized in published articles, the effort invested by Ksenija Radulić, Sofija Petricioli and Božidar Vilhar to excavate, study and conserve artifacts from the shipwreck was essential for keeping the collection preserved for future generations. Rejecting the initial idea to divide artifacts between the Archaeological Museums in Zadar and Šibenik, and instead founding the regional Museum of Biograd na Moru to host the exhibition, were crucial to keep the integrity of the collection. The results of the current excavation project continue to enrich the story about the shipwreck, in terms of archival research, artifact analyses, and ship construction studies. Fifty years ago, Ksenija Radulić noted the complexity of the site; today, her statement still rings true, even with contemporary facilities and equipment. As the project progresses and more trenches are opened on the excavation site, the Gnalić excavation team continues to cope with complex issues and new challenges.

6. Historical context of the Gnalić Shipwreck

As the ship *Gagliana grossa* headed from Venice to Constantinople in 1583, this chapter will introduce the reader to the historical context of the late sixteenth century, explaining which factors made Venice an important trading point, while also giving an overview of two important factors – conflict and trading relations with the Ottomans. The backbone of this chapter is the work of Alberto Tenenti (1959), Fernand Braudel (1992; 1992a; 1995; 1997), Frederic Lane (1973) and Eric Dursteler (2006), while more recent works about certain points will be used to supplement.

6.1. Venice: the trading hub on the crossroad of East and West

In the eleventh century, there was no attribute that would make Venice stand out from the other European regional powers. In fact, from 600 AD until 1000 AD few facts are known about the state built on the banks of the lagoon, but beginning in the thirteenth century⁶⁴, it significantly expanded its territories, becoming highly reputed for political manoeuvres of leading authorities and communally controlled capitalism. During the period from 1300 to 1600, the Venetian Republic was establishing strong trading connections, which, coupled with its economic growth, made it one of the most influential states in the Mediterranean (Lane 1973, pp. 1-2).

Along with the prosperity, the influence and the reputation of Venice in the Early Modern Mediterranean world, its visual appearance left visitors astonished while passing through the ‘most noble’ and ‘marvelous’ city (Rosaccio 1992, pp. 3-5) that ‘has the ocean for a pavement, the straits of the sea for a wall, the sky for a roof’ (Hills 1999, p. 4). Venetians appreciated luxurious materials, as can be seen from their finely crafted facades, where the artisans installed slabs of marble, or simply coloured bricks. Visitors could have the full experience of a metropolis, in its decorative expression as a result of Venetian taste for luxury and colour, influenced by different cultures which found their way to Venice (Hills 1999, pp. 12-15).

The Venetian Republic was constituted of its main city, Venice, the hinterland possessions, known as *Terraferma*, and the chain of maritime colonies known as *Stato da Mar*. In the sixteenth century, *Terraferma* encompassed the territory from Udine to the East, Verona to the North, Milano to the West and Ravenna to the South. *Stato da Mar* included Venetian

⁶⁴ Lane reports how only from 1000 AD Venetians became open towards the sea and began to experiment with navigation (Lane 1973, pp. 1-2).

maritime possessions in the Adriatic, Ionian and Aegean Seas, as well as Crete and Cyprus (Čoralić 2004, pp. 62-66). The chain of maritime colonies provided continuous safe routes for Venetian ships, keeping them safe from pirates, and allowing them to rest in the ports under the surveillance of the guards (Hocquet 2006, pp. 48-49). Maintaining a well-organized system of ports provided undisturbed sailing, resulting in successful trading and diplomatic ventures.



Fig. 6-1. Venice, *Terraferma*, *Stato da mar* at the end of the fifteenth century (author: V. Butorac, modified from Hocquet 2007, p. 39).

Until surpassed by the other European rivals, Venice had the reputation and the role of a central European market, a place where all the merchandise from Europe and Eastern Mediterranean was leveraged. The following sections will provide explanation of the factors that made Venice to stand above her contemporary Mediterranean counterparts and provide a supremacy over the sea routes.

6.1.1. Geographical position on the crossroads of the European and Mediterranean trading routes

Considering the size of the property of the Venetian Republic, the mainland did not occupy a large surface area (Fig. 6-1.). It was its strategic position that increased its chances to have control over the territory, a crucial place at the crossroads of the European and Mediterranean trading networks. Positioned at the highest point of the Adriatic, on the main natural crossings of routes connecting the East and the West, Venice used all the advantages of its strategic position to obtain absolute dominance and control over Mediterranean trade. All merchants coming from the West by land routes had Venice as the meeting point, and all the merchandise coming from the East was exhibited in the vibrant Venetian markets. It was well-known that European merchants were ready to travel a long way in order to purchase the merchandise available there (Howard 2007, p. 67).

The idea of Venice as the gateway to the Orient was present in all the nations of Western and Northern Europe, since this was the only way to obtain the valuable merchandise originating from the Orient. This vision can be traced in arts, manufacture, and architecture. While entering the city, first appears the facade of Doge's Palace facing the Grand Canal and the Piazzetta, built in the middle of the fourteenth century. Building the facade in an oriental manner is glorifying this idea, but it could be also interpreted as the announcement of a high peak of trade with Syria and Egypt at the time it was built (Mack 2002, p. 11; Howard 2007, p. 67).

6.1.2. Creation of trading chain within its maritime colonies (*Stato da Mar*)

Besides the strategic position of the city, Venice is greatly indebted to her network of colonies on the sea, *Stato da Mar*, for her success as protagonist of Mediterranean trade. This chain of trading colonies in the sixteenth century consisted of towns along the Dalmatian and the Aegean coasts, as well as Crete and Cyprus, which had a role of stations for shipping. These colonies created a chain of bases, helping Venice to commercially link trading posts, becoming famously known as the 'empire of naval bases' (Lane 1973, p. 42; Braudel 1992a, p. 132; O'Connell 2017, p. 107). Venetian connection to the east was enhanced by conquering Cyprus in 1489, and it was a secure spot on the way to the Levant (Tenenti 1967, p. xii).

One of the most accurate representations of sixteenth-century Venice, the woodcutting of Jacopo Barbari, not only delivers a birds-eye perspective view of the city, but also clearly

depicts the idea of the significance of the Venetian hinterland and overseas possessions through one detail (Fig. 6-2.). Above the representation of the city stands Mercury, the ‘god of trade’, bearing a title *MERCVRIVS PRECETERIS HVIC FAUSTE EMPORIIS ILLVSTRO* meaning ‘I Mercury, shine favourably above all other emporia’. Mercury, the symbol of trade and capitalism, being positioned above the centre of the Venetian Republic demonstrates that Venetians understood the importance of their possessions *Stato da Mar* and *Terraferma* (Howard 1997; Howard 2007, pp. 69-70).

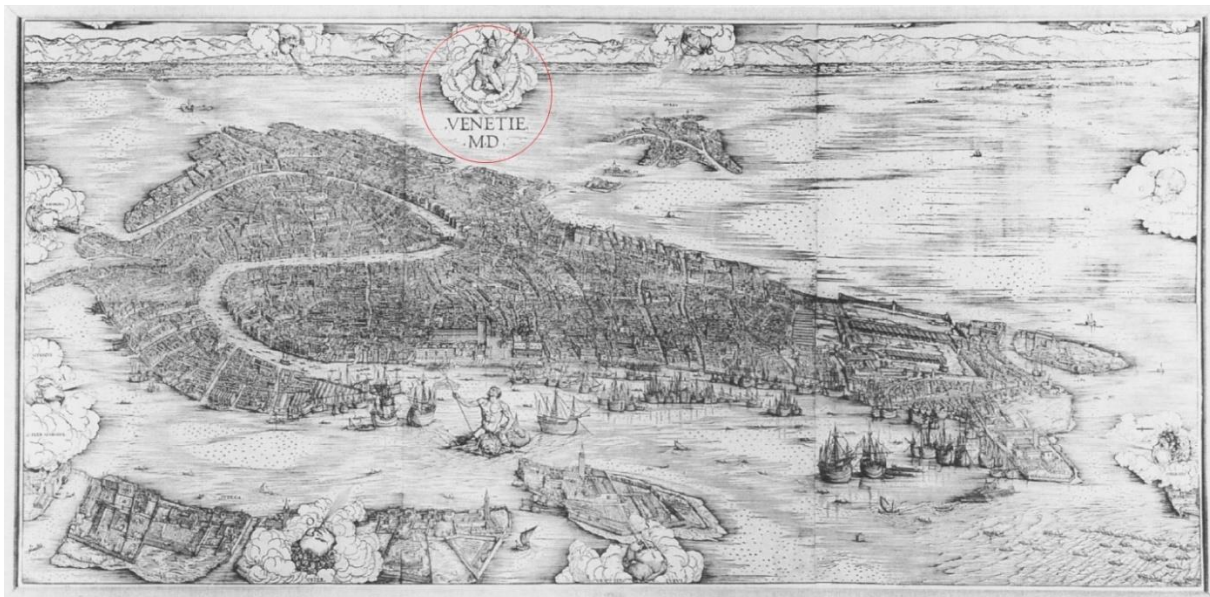


Fig. 6-2. Jacopo de' Barbari, Map of Venice, woodcut, six blocks, British Museum, London. The god Mercury is marked in the circle (Howard 1997, p. 102).

6.1.3. Ownership over the Adriatic Sea (ven. *Golfo di Venezia*)

The Venetian Republic claimed its absolute dominance over the Adriatic Sea, or as it was called, the ‘*Golfo di Venezia*’ (Fig. 6-3.). The sea which Braudel (1997) describes as ‘the most unified of all seas’ is a region of geographical differences. The north of the Adriatic is characterized by the shallow coast of Pesaro and Rimini (Fig. 6-3, left shore), the valleys from where it was facilitated to establish maritime contact. The Italian Adriatic coast or Western Adriatic (Fig. 6-3, low shore) stands in opposition to the well-indented coasts of the Eastern Adriatic, composed of Istria, Kvarner, and Dalmatia. The characteristics of the Western Adriatic coast are quite different than the rest of the Adriatic. The Italian shore is characterized by swamps bounded by the chain of the Apennines. On the other hand, the region of Dalmatia

presents a coast with islands, separated from the hinterland by the chains of Dinaric Alps (Braudel 1997, p. 135).

The feature that makes the Adriatic ‘unified,’ as Braudel states, is the Strait of Otranto, connecting the Cape of Otranto in Italy with the Cape of Linguetto in Albania, a breadth of 72 kilometres (Fig. 6-3., passage on the right). During history, it was well-known that whoever was eager to dominate the Adriatic must fight to control the Strait of Otranto. Indeed, this was one of the main points of interest for the Venetian Republic, as owning the Strait allowed her to unobstructedly perform the trading ventures towards the East, while having complete surveillance over the foreign ships entering and leaving the sea. However, the Strait was not always the property of the Venetian Republic. Some periods are marked with tenacious trials to gain or maintain the capes in their possession, with successful results in 1495 and 1528, and later in 1560 (Braudel 1995; Braudel 1997, p. 135)

Cinque Savii alla Mercanzia, the official state institution for the trade regulation, made a perfect description of the Venetian mission to dominate trade, stating ‘All the merchandise entering or leaving Adriatic had to be controlled by Venice’ (‘Ogni merce che entra nell’Adriatico o esce dall’Adriatico deve toccar Venezia’) (Braudel 1995, pp. 157-158).

Other powerful Mediterranean states of the sixteenth century did not readily accept the Venetian audacity and appropriation of the Adriatic, which commonly included cases of confiscation of ships. The ambassador of the Spanish king Philip II, Francisco de Vera, complained about the Venetian unfounded ownership over the Adriatic, stating:

‘For many years, without any reasonable foundation, the Venetian Republic claims its property over the Adriatic. As if the God did not create that part of the bay, as all others, to be used by everybody.’
(Braudel 1997, p. 135)

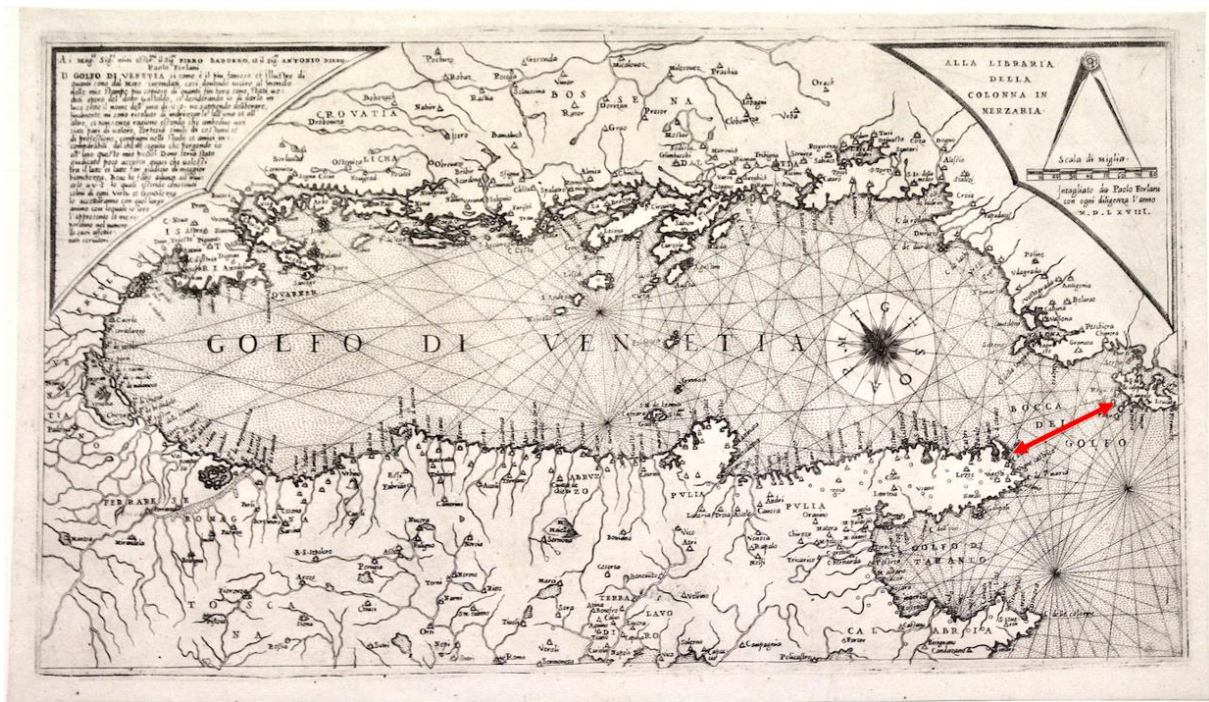


Fig. 6-3. The map of Adriatic Sea, published by Paolo Forlani in 1567. The Strait of Otranto is marked with the arrow (<http://www.libreriaperini.com/it/cartografia-antica-europa/adriatico---croazia---slovenia/il-golfo-di-venezia-si-come---il-pi--famoso-et-illustre-di-quanti-sono-dal-mare-inondati---/7054/dcm> February 1, 2020).

People living in the towns of the Venetian trading network, accustomed to Venetian supremacy, certainly supported Venice when necessary. Even inhabitants of Ragusa, the only other independent state in the Adriatic Sea, were patronizing to the Venetian Republic, which could be seen from the expressions of her merchants. In the dedication of a book by Benedikt Kotruljević, a fifteenth-century Ragusan merchant involved in international trade, Kotruljević states:

‘...you, Serene doge and glorious Senate, to you, I am saying, to you who are caring and having sovereignty over the things related to the sea, to you Venetians it is justified to call you the lords of the sea, and the sea is yours everywhere’ (Kotruljević 2005, p. 21).

In the further text, Kotruljević compares Venetian power to ancient Athens, Carthage, and the Roman Empire, stating how ‘none of them achieved eternal fame as a sea power save your Serene State’ (Kotruljević 2005, p. 21).⁶⁵

⁶⁵ “...vama, prejasni dužde i dični senate, vama, kažem, koji vodite brigu i imate suverenu vlast nad stvarima vezanim uz more, tako da se vi Mlečani s pravom nazivate gospodarima mora i more je svugdje vaše. Ta koja je država ikada postojala - nakon pada, da ne kažem propasti atenskog grada, za koji se pripovijeda da je nekada daleko vladao morem, ili nakon Kartazana koji su bili silno moćnim brodovljem i u pomorskim poslovima, ili

Lastly, even though Venice claimed absolute dominance over the Adriatic, there are several examples proving it was not always possible to control all networks directed towards Constantinople. When the Ottomans invaded and conquered the Balkans, the independent Republic of Ragusa established a land route to Constantinople. Florence, a main trading rival of Venice, found a way to avoid the time-consuming and expensive hub of Venice. Florentine merchandise was transported by land to Ancona, shipped across the Adriatic to Ragusa, and then transferred to Constantinople via the Ragusan land route. This example clearly shows some trading ventures, especially in the case of cross-Adriatic transport, were out of sight and could escape the control of Venice (Lane 1973, p. 302; Molà 2000, p. 65).

6.1.4. Controlling foreign merchants

The audacity of Venice is evident in the number of regulations introduced in order to control and benefit from foreign merchants. Using the advantages of all the predispositions for successful trade, such as favourable geographic position and ownership over ports and strait in the Adriatic, Venice set a number of rules and requests for all foreign merchant ships passing through Venetian waters. Even if the final destination of those ships was not Venice, it was mandatory to pass through Venetian customs with the aim of control. For example, all merchandise originating from *Terraferma* had to check into a Venetian port, regardless of the fact that the merchandise was destined for the markets of Sicily or England (Braudel 1992a, p. 139).

However, it was not only the Adriatic where Venice exercised absolute control. She controlled the trade gravitating by land routes from Northern and Western Europe by imposing numerous rules. Based on the enclaves for the Venetian merchants in Islamic states, Venice created *Fondaco de Tedeschi* (ven. *Fontego dei Tedeschi*), a quarter intended for the lodging of the German merchants. *Fondaco*, positioned in the building next to the market of Rialto, was active at least from the second half of the thirteenth century. With the German community

nakon Etoda, čija su se slava i pomorska vještina prenijele na Rimljane, ili nakon Rimljana, - koja je slavno i nepobjedivo ime tako slavnobitno sačuvala na moru kao vaša presvijetla država' (Kotruljević 2005, p. 21).

'..., serenissime dux et inclite senatus, vobis, inquam, quibus maritimarum rerum cura omnis et dominium est. Que enim civitas unquam antea fuit post inclinatum, ne iam dicam extinctamque Atheniensium, qui permultum classe maritimisque rebus valuerunt, aut Ethodorum, quorum usuque ad Romanos disciplina navalis et Gloria remansit, aut Romanorum – quę gloriosenomen invictum ita uti vestra gloriosissima civitas in mari triumphando servavit.' (Kotruljević 2005, p. 20).

settled at one location, the official state organization for trade regulation could easily establish surveillance over the trading activities of the German merchants. It was mandatory for the German merchants to store and sell their merchandise in a specific building, and no trading activities were allowed to be executed elsewhere. Although the idea of the building was made on the model of the already-existing *fondacos*, it was different through having strict control and by charging fees for the lodging (Constable 2003, p. 309). In fact, other cities had different systems of lodging foreign merchants in special neighbourhoods or quarters, where they could have their own permanent property, for example in Pera in Constantinople (Constable 2003, p. 311; Dursteler 2006, p. 154; O'Connell 2017, p. 114).

The German merchants had to follow strict regulations proclaimed by the Venetians. Firstly, no merchant was allowed to trade with the Venetians outside of the *Fondaco*, or north of Venice. It was not allowed to transfer goods by ships, so all merchants were forced to sell their goods in the *Fondaco* (Constable 2003, p. 319). This strategy built upon strict regulations was fruitful for the Venetian economy, as the Germans used earned money to purchase goods, then transported and delivered products of Italian, Venetian and Eastern Mediterranean manufacture to the German markets. In turn, the German merchants were forced to travel and return to Venice (Braudel 1992a, p. 139).

In 1516, the Venetian Government established the Jewish Ghetto, an enclave for Jewish merchants under the control of the state (Braudel 1992a, p. 139, Howard 2006, p. 64, O'Connell 2017, p. 114). Sources do not register a large presence of Ottoman merchants during the sixteenth century. Opening the *Fondaco dei Turchi* in 1621 is the attestation of the Ottoman growing presence in Venice (Dursteler 2002, p. 128).

6.1.5. Emerging spirit of capitalism in the sixteenth century

Venetian achieved success can probably be explained by the tight connections and tangled networks of the economic and mercantile worlds. In the fifteenth century, these two components were substantially depending on each other, as all the goods imported in Venice were considered communal property. O'Connell (2017, p. 103) states medieval merchant spirit was well depicted by medieval sources as 'greedy, self-interested, untrustworthy', but these virtues contributed to the development of 'entrepreneurial protagonists of an emerging capitalist spirit'. If there is a profoundly controlled system with strict regulations established by the state added to this particular character of the merchant, the accumulation of profits is ensured. Venice

intentionally created a system aimed to accumulate revenue from merchandise circulating through the city markets.

6.2. Venetian-Ottoman conflicts

The Early Modern Age in the Mediterranean was indeed a turbulent period characterized by coexistence of the two major powers of the Mediterranean, the Venetian Republic and the Ottoman Empire. The coexistence between these two powers has often been described as the constant opposition between ‘West and East, Christianity and Islam, Venetian and Turk, Europe and other’ (Dursteler 2006, p. 6). While the fifteenth century was characterized by minor conflicts caused mainly by the rapid growth of Ottoman power, at the beginning of the sixteenth century the situation significantly changed. Fearing a deterioration in relations as the Ottoman expansion neared Venetian maritime colonies in the region of Dalmatia, Venice practiced tolerance and maintained neutrality towards the Ottomans, pursuing collaboration rather than conflict (Dursteler 2006, p. 6).

This section will focus on the conflicts of Venetians with Ottomans (Tab. 6-1., Fig. 6-4.), known as Ottoman-Venetian wars, and will explain how they were reflected in their relations and the end, in regional trade. Open conflict with the Ottomans first began at the turn to the sixteenth century in 1499, when the Ottomans attacked Venetian possessions in the Aegean Sea, which were followed by harsh raiding of the regions of Dalmatia and Friuli. Finally, exhausted from continuous defence against the powerful Ottomans, in 1503 Venice signed a peace agreement and relinquished important colonies of *Stato da Mar* in the Aegean Sea to the Ottomans (Lane 1973, p. 242).

It took several decades for simmering arguments to again escalate into conflict. In 1537, Venetians and Ottomans had a conflict regarding the ownership of Corfu and the possession of some Venetian colonies in Greece. Venice finally decided to join the Holy League, under the direction of pope Paul III, composed of an alliance of the Vatican, the Holy Roman Empire, Spain, Genova, and the Maltese Order of St. John, aiming to prevent the Ottoman Empire from conquering European territories. The Venetian Republic initiated hostilities, in an attempt to retrieve the territories recently lost in encounters (Pavić 2014, p. 100). However, after three years of conflict Venice yet again ceded portions of the *Stato da Mar* to the Ottomans. The consequences of this conflict especially impacted Venetian territories in Northern and Middle Dalmatia, as the Ottomans conquered fortresses in Klis, Nadin and Vrana (Husić 2006, pp. 138-140; Pavić 2014, pp. 184-186).

Period of conflict / main battle	The cause of the conflict	Other states involved	Consequence	Reference
1499 - 1503 / the battle near islet Sapienza, 1499	Ottomans attacking Venetian possessions in Aegean Sea, raiding Dalmatia and Friuli	/	Signed peace agreement in which some colonies of <i>Stato da Mar</i> are given to Ottomans (Lepanto, Modon, Codon and coastal Makarska)	Lane 1973, p. 242; Čoralić 2004, p. 72; Pavić 2014, p. 100
1537 - 1540 / the battle near islet Levkada, 1537	Ottomans argue ownership over Corfu and the possession of some Venetian colonies in Greece	Holy League (Venice, Vatican, the Holy Roman Empire, Spain, Genova, and the Maltese Order of St. John)	Signed peace agreement in which some colonies of <i>Stato da Mar</i> are given to Ottomans (properties in Aegean Sea - Monemvasia, Nauplion; properties in Dalmatia – Klis, Nadin, Vrana)	Čoralić 2004, pp. 138; Husić 2006, pp. 138-140; Pavić 2014, p. 184-186;
1570 - 1573 / the battle of Lepanto 1571	Ottoman sultan Selim II requested Cyprus properties from the Venetian Republic	Holy League (Vatican, Genova, Malta, the Duchy of Savoy, Parma, Urbino, Genova, and the Grand Duchy of Tuscany)	Signed peace agreement where Venice lost Cyprus and had to pay 300,000 ducats of reparation; Bar, Ulcinj and Dalmatian territories (fortress Zemunik and Kamen) were lost in the battle	Čoralić 2004, pp. 139-140; Pavić 2014, p. 105-108

Tab. 6-1. Brief representation of Ottoman-Venetian conflicts in the sixteenth century



Fig. 6-4. Map of Ottoman-Venetian conflicts in the sixteenth-century and loss of the territories from Venetian side. The region of Zara lost Zemunik, Vrana, and Nadin in the period of last two conflicts is not on the map (author: V. Butorac).

During the almost half a century of peace that followed the conflict from 1537 to 1540, the Ottomans managed to strengthen their navy. Western Europe observed the growth from a safe distance, with a growing feeling of resentment coupled with the fear of deprivation of territories. Tension heightened when in February 1570, Ottoman sultan Selim II requested Cyprus properties from the Venetian Republic, giving historical evidence of the possession of Cyprus by leaning on the long tradition and history of Cyprus being part of the Eastern Roman Empire, and afterwards the Byzantine Empire. Not willing to lose one of the most prominent colonies crucial for trade with the Levant, but also aware of potentially entering into open combat with the Ottoman Empire, the Venetian Republic rejected the request (Šišić 1974, p. 39). Besides its strategic position, Cyprus was one of the crucial points of the economy of the Venetian Republic, as Venice relied heavily on Cypriot agricultural products and natural resources, such as copper, salt, cotton, sugar cane and wine (Costantini 2006, p. 73).

Although the Battle of Lepanto was the crucial exchange, several events preceded the battle itself. Confrontation began with Ottoman attacks on the fortress of Famagusta on Cyprus island, while simultaneously tasking part of the Ottoman fleet to pillage the Dalmatian islands of Brač, Korčula, Hvar and Vis (Šišić 1974, p. 39, Novak 2004, p. 22). As a result of the Ottoman attacks on Cyprus, the battle of Lepanto happened on 7 October 1571 (Fig. 6-5.).

Generally speaking, the battle was portrayed as the battle of Christians against Muslims, to prevent the infidel threat from expanding and conquering all of Europe. By attacking Cyprus, the Ottoman Empire brought the wrath of the Holy League, but also increased the fear and panic accumulated within European states. At this time, the Holy League was re-established by pope Pio V, with the majority of the fighting forces composed of the Venetian and Spanish naval fleets, but also including ships and soldiers from Genova, Malta, the Duchy of Savoy, Parma, Urbino, Genova, and the Grand Duchy of Tuscany (Novak 1974, p. 8; Pavić 2014, pp. 105-106). Although named the battle of Lepanto, it did not actually happen in the city of Lepanto, but in the adjacent Gulf of Patras. The Lepanto name was adopted due to two reasons: firstly, it was a reminder of the city of Lepanto, positioned at the entrance of the Gulf of Corinth, where the Ottoman fleet was gathering prior to the combat; and secondly, according to the Venetians, the Gulf of Corinth was named *Golfo di Lepanto* (Novak 1974, p. 9).

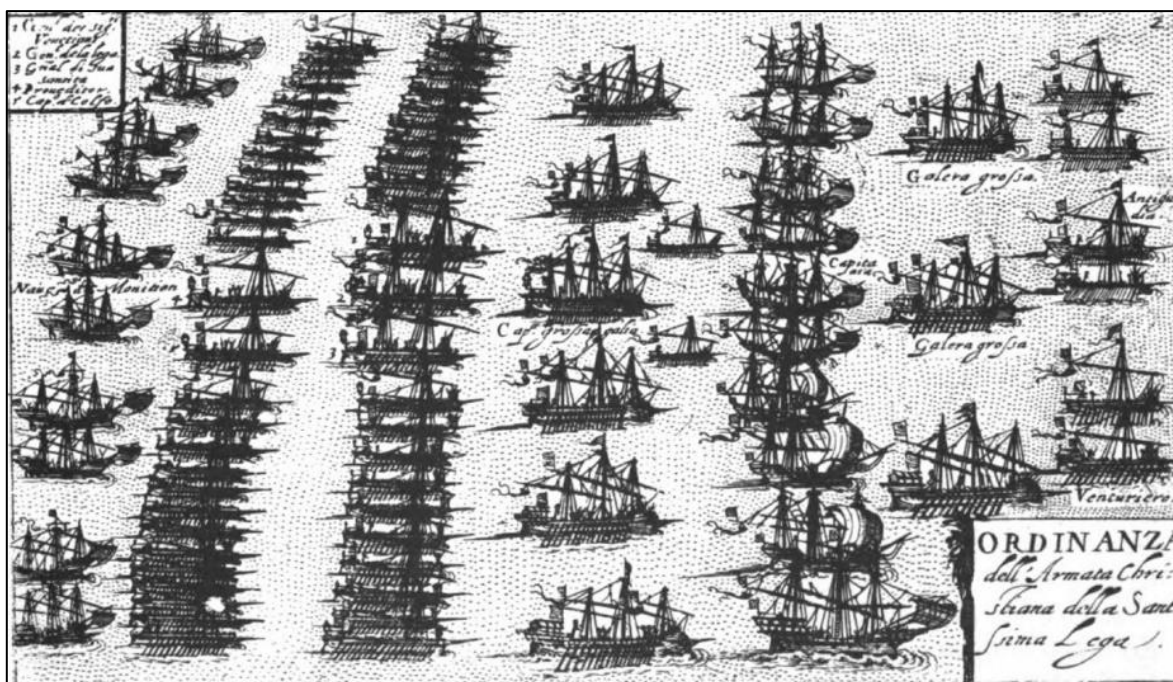


Fig. 6-5. Representation of confronted navies at the battle of Lepanto: on the left side is the Ottoman, whereas the right depicts the Christian navy or the Holy League (Rosaccio 1598, p. 36).

The battle ended with the victory of the Holy League, symbolically glorifying the Western world over the Ottomans, Christians over Muslims (Rosaccio 1992, pp. 35-38).⁶⁶ Subsequently, an agreement between the Ottoman Empire and the Venetian Republic was concluded on 7 March 1573, when Venice, although proclaimed as the winner within the Holy League, accepted the withdrawal of Cyprus from the *Stato da Mar*, agreed upon new land borders for the territory of modern Dalmatia in Croatia and Albania, and agreed to pay three hundred thousand ducats of compensation (Novak 1974, p. 10). The outcomes of this battle were perhaps best described by Mehmed-pasha Sokolović, Grand Vizier of the Ottoman Empire (Pavić 2014, p. 108; Duiker & Spielvogel 2015, p. 451):

‘There is a big difference between our loss and yours. In taking Cyprus, we have cut off one of your arms. In sinking our fleet, you only shaved our beard. A lost arm cannot be replaced, but a shorn beard grows back quickly to its prior magnificence.’

Depending on the perspective, the outcomes of the battle can be considered as ‘win/lose’ situations for every participant. While the Ottoman Empire lost the majority of its naval fleet, the naval fleet of the Venetian Republic was not entirely destroyed, as the Spanish fleet took a

⁶⁶ ‘...con l’aiuto di Dio restorno vittoriosi, e l’armata Turchesca destrutta non se n’essendo saluati piu...’ (Rosaccio 1992, p. 38).

major role in the battle (Pavić 2014, pp. 54, 88). Even if Venice lost Cyprus and Aegean Sea islands, redefining the borders in Albania and Dalmatia meant a decrease, but probably not the absence, of the fear that the Ottomans would continue their expansion into colonies of the Adriatic (Novak 1974, p. 8).

However, the situation dramatically changes after the battle of Lepanto (1571), when the Venetian-Ottoman contact became less intense. Seeing that Venetian economic power was waning, the Ottomans changed their attitude. They had less interest in boosting contacts with Venetians, instead opting for negotiations with the more powerful regents of Western Europe. Another reason for less intensive contact was a decline in shipbuilding in Venice, as many foreign ships from Western Europe began filling the role of transport between Venice and the Levant (Lane 1963, p. 328).

6.3. The role of Venice in maritime trade in the Early Modern Mediterranean

During the fifteenth and sixteenth centuries, most goods from continental Europe came by land routes coursing to the port of Venice. The merchants coming from Salzburg, Nuremberg, Ulm and Passau had to travel through Alpine passes, often reaching the Veneto via river routes (Lane 1973, p. 61; O'Connell 2017, p. 108). On the other hand, the exotic goods coming from the Eastern Mediterranean by merchant ships were marketed in the area of Rialto, available for purchase to Venetian or foreign merchants. From these markets, the goods were transported to Western and Middle Europe. Among the most common merchandise traded by German merchants were copper, tin, silver, zinc, gold, iron, timber, wool, and fustian cloth, as well as furs, hides, and objects made of horn and leather (Braudel 1992a, p. 139; Constable 2003, p. 319; Howard 2006, p. 64).

The role of intermediary between the East and the West made the Venetian market a place of gathering of all the people involved in the trading mechanism. It allowed them not only to buy products that were not available in their home countries/cities, but also to learn about other cultures, languages, and technological advancements, resulting in the exchange of practices and ideas. Venice was the melting pot of different cultures, and the merchants that established connections with the farther reaches of the world were the ones who first acquired knowledge of new technological developments. There is vast evidence that the increase in trade and travel was simultaneous with the large leap that happened in the change in decorative arts in general, encompassing metalwork, textiles, and architectural decoration (Mack 2002, p. 1).

Long-distance trading was both time and money consuming; traveling such great distances was possible to execute only once, or a maximum twice in the year, if the weather and political conditions were favourable.⁶⁷ Merchants could not afford to travel empty handed, as it was expected to earn a profit on every leg of travel. While carrying goods intended to be sold on the Eastern markets, merchants had to plan their return with cargo desirable in the markets of the West, most likely Venice.

6.3.1. The fifteenth century

In the second half of the fifteenth century, the trade between the West and the Levant gained significant importance, growing gradually by involving more agents and merchants in the trading network. This connection began to strengthen in parallel with the development of manufacturing in Western Europe. Increased production of metals and woollen cloth provided enough supplies to satisfy local demands while also allowing export to Venetian markets. Besides cheap woollen clothes and metals, the export of soap and glass products became common (Ashtor 1983, p. 440-448, 466). Venice immediately asserted itself as the intermediary of commercial exchange between the West and the East. Prior to being exported to the Eastern Mediterranean, merchandise was delivered to Venice by land routes. Upon arrival, it was bought by Venetian merchants, and further transported by ships or combination of ships and caravans to Asia Minor, Southeastern Europe, or the Eastern Mediterranean (Lane 1973, pp. 69-70; Constable 2001, p. 123).

Merchants always returned to Venice with a stash of goods bought on the vivid and colourful Eastern markets, including spices, textiles, and minerals. The regions of Western and Middle Europe had a high demand for the spices for seasoning meat, and their merchants found a main supply source in Venice. At the same time, European exporters sent raw materials via Venice, such as silver, copper and woollen cloth, all in great demand in the East. Thus, Venice became the primary intermediary between this East and West exchange.

Ashtor (1978, p. 13; 1983, p. 469-470) explains how the crucial factor in Venetian dominance over Levantine trade could be found not only in the necessity of importing raw materials, but in the decline of the economy in the Near Eastern countries. Their factories were not producing textiles, but instead importing cheaper fabrics from Venice, and the prices of spices became significantly lower thanks to the Venetian trade. This enhanced communication

⁶⁷ See appendix 6, *The journey from Venice to Constantinople*, for a more detailed explanation.

between Western Europe and Levantine cities, with goods passing through Venice and other Italian cities reaching a peak in the fifteenth century. For Venice, this trade and exchange was especially intensive in the period from 1420 until 1488, the year of the discovery of the Cape of the Good Hope (Lane 1973, pp. 69-70; Ashtor 1978, pp. 48).

6.3.2. The sixteenth century

The beginning of the sixteenth century bears a special designation as the century of Venetian despair caused by the Ottoman expansion, as this period marked the beginning of the clash of efforts between Western Europe and the Mediterranean states to obtain dominance over the profitable spice trade. This period of Venetian history is intriguing as, regardless of all the difficulties, including the eventual deprivation of territories by the Ottoman raids and the loss of Venetian relative importance due to the rise of Portuguese trading power, throughout the century Venice still managed to keep its high trading reputation and maintain profit from remarkable leverage of trading goods (Lane 1963, p. 332).

At the turn to the sixteenth century, Venice was one of the four largest cities in Europe. As goods were imported from the North and from the East, it is evident that it was the most prominent and prosperous centre in the Mediterranean. Two of the most common facets of the Venetian trade were spices and luxury goods. However, as the sixteenth century began, Venetian trade importance was already on the decline. This was in comparison to the power and status that Venice had created at the beginning of the fifteenth century, when she imported almost three-quarters of the spices in Europe. The other fraction of the spices was imported through the ports of rival cities such as Genoa, Catalonia, Marseille, and Ragusa (O'Connell 2017, p. 107-116).

Nevertheless, the events in the Atlantic Ocean, including the discovery of the New World in 1492 and the development of an alternative route to India around the Cape of Good Hope in 1488, did change the role of Venice in the trade of the Mediterranean. In retrospect, Venice had reached a peak in richness and wealth (Lane 1973, pp. 290-294). In the sixteenth century, Venice was exporting mostly textiles and metals (gold, silver, copper, and iron), and importing various spices, alum, textiles, honey, and wax from the Levant.

The appearance of a new naval power, Portugal, and its emergence within Early Modern Mediterranean and Oceanic routes, entirely changed the flow of the spice trade. In fact, the trade was interrupted by the Portuguese opening the *feitorias* market in Antwerp, allowing merchants of Western and Northern countries to have an open source of spices. The spice trade

no longer required merchants to complete long travels through the Alpine passes to Venice. As a result, Venice began losing its main clients and customers. The Venetian supremacy over the Levantine trade was also threatened, mostly due to the absence of the German merchants in *Fondaco dei Tedeschi* (Braudel 1992a, p. 139).

During the past centuries, Venice had already experienced how the absence of German merchants resulted in a decline of trade. During the war between the Hungarian Empire and Venice, from 1418 to 1422, the mountain passes were endangered by raids. This prevented the German merchants from going to Venice, resulting in a sharp decrease in the intensity of trade (Lane 1966, p. 114). Therefore, opening *feitorias* in Antwerp gave a clear indication that the newly opened markets in Western Europe would have large consequences on the profitable trade with the East. The Ottomans were in one way a deadly enemy, as they threatened the Venetian maritime colonies, but on the other hand, they were also faithful Venetian clients in trade. When the Portuguese appeared, Venice may have even considered the Ottomans as a possible ally against Portugal (Braudel 1992a, p. 153).

By the end of the sixteenth century, the Venetian Republic had lost its relative importance, but surprisingly, it continued to amass a great fortune through the trade that was going on inside of the city walls, especially in the case of the exchange offices, which allowed Venice to set high exchange rates in this central trading hub. Prudently played political manoeuvres kept the city balanced between all the major rulers of the Mediterranean of the late sixteenth century, keeping neutral to please the Ottomans, confronting them only in the cases when the support of other Mediterranean countries was keeping its back safe. Nevertheless, it became apparent that Venice's fortune and reputation were gradually losing their shine as the end of century approached. At the beginning of the seventeenth century, we can clearly state that the Venetian Republic, once influential and dominant, now was enjoying its last moment of fame. The main reason was that the merchant activities of the Mediterranean had switched from the East to the West. Now, Florence and Genova, who began competing for dominance in the fifteenth century, had taken over dominance, by creating trading posts along Europe and the Americas to help them build a strong merchant network (Braudel 1992, p. 425).⁶⁸

At the end of the sixteenth century the Venetian situation continued to change. New enemies approached from the Northern sea – the powerful Dutch and English fleets, but also the French – interrupting peaceful relations in the Mediterranean Sea and Indian Ocean (Lane

⁶⁸ Genova established connections with Spain and America, while Florence built its connections with Lyon (France), laid down trading posts in Spain, and reinforced her already strong connections with Germany (Braudel 1992, p. 425).

1940, p. 589; Constable 2003, pp. 356 – 359). Tenenti (1967, p. xii) claims that the problems started to be visible in the middle of the sixteenth century upon the crises caused by the lack of raw materials and the decline of shipbuilding. Lane (1991, p. 236) supports this theory by demonstrating that the decline in Venetian shipbuilding was even greater than the regression that happened in trade.

To summarize, Venice, as one of the most important Medieval and Early Modern centres of the Mediterranean, used its strategic position, maritime colonies and dominance over the Adriatic Sea to gain a monopoly over the Mediterranean trading routes. Her reputation as a great market and a place where all demands could be satisfied drew merchants to Venice. Nevertheless, the wealth of the city would not be so impressive had there not been an ambitious merchant spirit coupled with a profound system of foreign merchant control. With respect to both, circulating the goods within the city made the Venetians profit. Fees and taxes were levied based on the goods imported to the city, contributing to the growth of the state's wealth.

6.3.3. The decline of maritime trade and reflection on the land and maritime routes

During the sixteenth century, there were constant fights over the dominance of the Mediterranean Sea routes. As explained in sections 6.3.1. and 6.3.2., Venetian trade in the sixteenth century was facilitated by the glory days of the prosperous trade with the Levant in the fifteenth century. Losing colonies that once belonged to the *Stato da Mar* had consequences on trade routes, introducing changes in both sea and land itineraries. The Venetian maritime trade area became very limited in the second half of the sixteenth century, as it became oriented mainly on the Adriatic Sea (Fig. 6-6.).

In fact, it seldom happened that ships went beyond the borders of the Adriatic. The ships would reach Marche, Abruzzo, Puglia, Dalmatia, sometimes extending their path to the Venetian colonies of Corfu, Zante, Cefalonia, and Candia. Outside of the navigational route based on *Stato da Mar*, Venetian ships sailed towards Greece, Smyrna, Constantinople, Syria, Cyprus, and Alexandria. If remaining within the borders of the Adriatic, land routes were taken to continue transport of the goods. For example, if merchandise was unloaded in Abruzzo, the land route was taken to Naples. At the beginning of the seventeenth century, ships were sailing from Venice to Split or Ragusa, where they shifted to a land caravan route for continued transport to Constantinople (Tenenti 1959, p. 14-22).

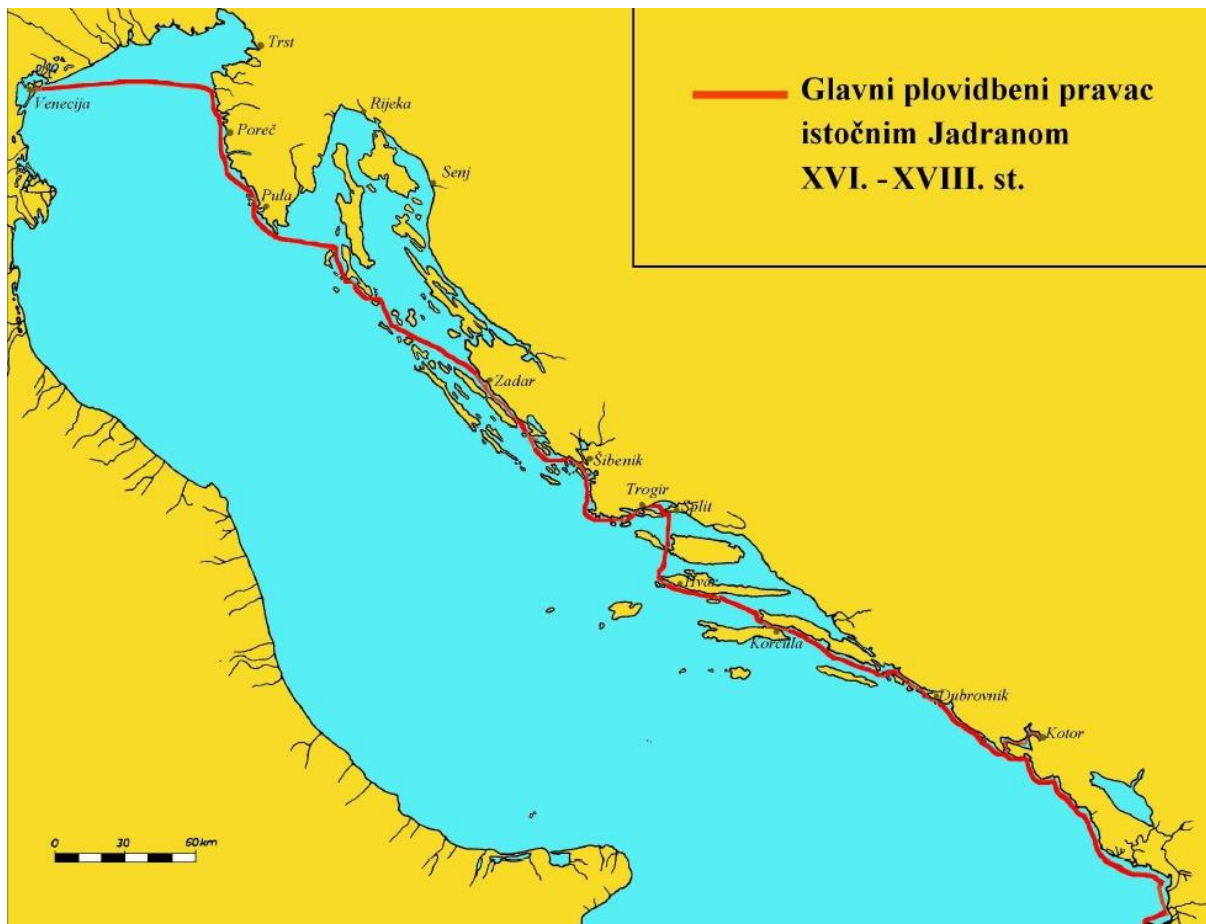


Fig. 6-6. The main seafaring route on the Eastern Adriatic, used from sixteenth to eighteenth century (Pavić 2012, p. 57).

Finally, it is important to mention that at the end of the sixteenth century, the Venetian operational area of navigation changes. Unlike the previous period, when owning a chain of colonies ensured dominance over Mediterranean routes towards the East, in the sixteenth century Venetian navigational control was present in the Adriatic only. This was reflected in the increasing prevalence of foreign ships in the region. In the 1580's, there were numerous foreign ships in the Adriatic, while from 1591, Venetian ships were almost not operating. At the beginning of the seventeenth century, foreign ships were even allowed to register with the *Cinque Savi alla Mercanzia* to legally travel in and out of Venetian ports, although they were still required to pay taxes and were forbidden to register with a foreign name (Tenenti 1959, p. 14-22; Dursteler 2002, p. 114).

6.4. The Venetian Republic, the Ottoman Empire, and trade

When trying to explain Ottoman-Venetian relations, it is important to mention that the tensions always existed, but during the sixteenth century, they escalated into open conflict only

three times. The Venetian loss of Modon and Codon in 1499 to the Ottomans can be seen as foreshadowing of the territory deprivation that will accompany the sixteenth century (Lane 1973, p. 242). As the sixteenth century progressed, the Ottomans were getting closer to the Venetian border, causing the feeling of insecurity, while depriving Venice of *Stato da Mar* assets in Dalmatia. This general overview of the series of events related to the Ottoman presence near the borders of Venetian possessions allows the conclusion that not only did the Venetian Republic lose a series of their colonies, but that they were also blocked from further expansion. In the second half of the sixteenth century, the area of contemporary province of Dalmatia was divided between three rulers: the Venetian Republic (as the part of the *Stato da Mar*), the Habsburg Monarchy, and the Ottoman Empire; the borders met in Northern Dalmatia in the hinterland of Zadar, Croatia (Figs 6-7. and 6-8.). By conquering fortresses in Vrana and Nadin, the Ottomans established their troops in Dalmatia, only twenty kilometres away from Zadar, the main political, cultural, and economic centre of the Venetian province Dalmatia. The presence of Ottomans in the vicinity of the heart of Dalmatian part of *Stato da Mar* represented a real threat to Venetian prosperity.

Although one might think this course of Ottoman-Venetian conflicts changed the state of the trade in Mediterranean, the opposite is true. The growth of Ottoman power did not impact Venetian supremacy in the Levantine trade (Lane 1963, p. 332). The Ottomans had a full respect towards the agreement made in 1479 that allowed the Venetians to sail safely to conduct their business with the Levant.⁶⁹ In fact, their international trade relations remained friendly, as both had personal interests, which were especially seen in maintaining maritime trade and diplomatic relations during this period of strong international competition (Hocquet 2007, p. 44, 49).

In addition to conflicts with the Ottoman Empire, the late sixteenth century was a turbulent period for the Venetian international maritime trade, as Venice started to lose dominance over the trading routes. Although the discovery of the New World changed the area of focus from Mediterranean to the Atlantic navigational routes, the Venetian Republic decline in power was coupled with the ascendance of Portugal as a rival power, aided by the discovery of the Cape of Good Hope, which became an alternative route to southern Asia. Although these events impacted the Venetian role in international trade, Venice still managed to keep her status

⁶⁹ The urgency for the agreement appeared after several attacks on Venetian galleys trading in the Black Sea. Finally, Venice had to pay damages of 100,000 ducats, and beginning the following year, an annual tribute of 10,000 ducats, to sustain the trading networks without being interrupted by the Ottomans (Hocquet 2007, p. 44, 49).

as an important intermediary in regional international trade (Lane 1963, p. 332), until the end of the sixteenth century.

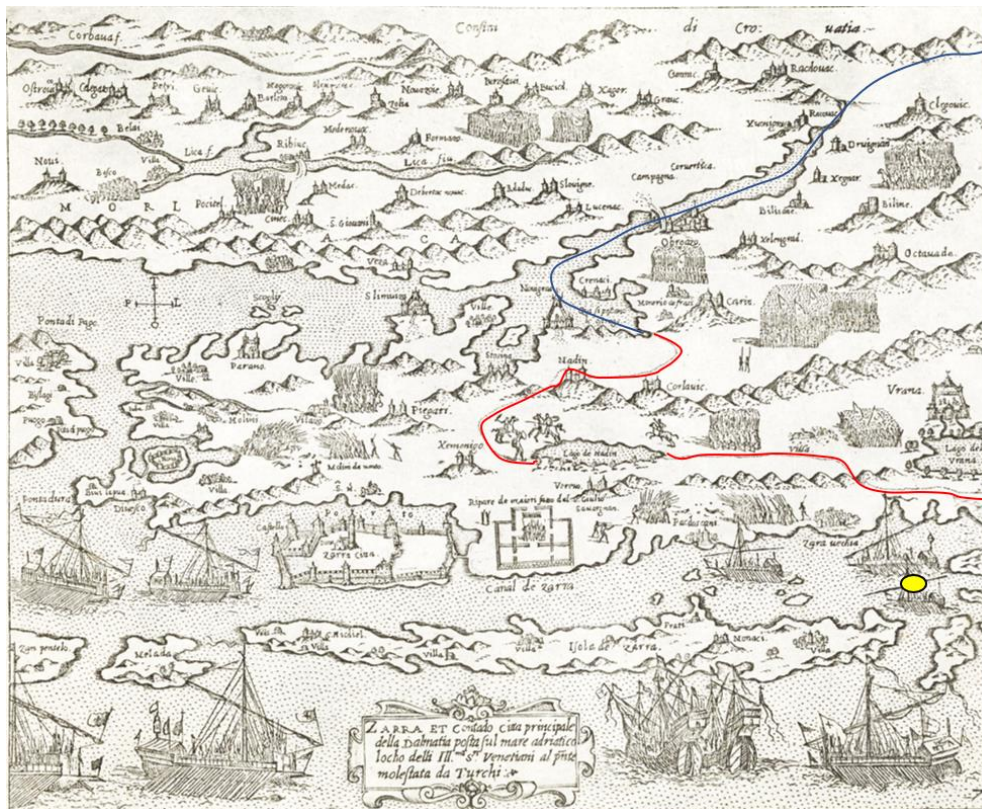


Fig. 6-7. Representation of the Ottoman – Venetian frontier in the hinterland of Zadar region. Above the red line is the Ottoman Empire, below it, are Venetian territories, including the city of Zadar and surrounding islands. Blue line, passing through the sea of Karin, represents the border with the Habsburg Monarchy. Yellow dot is the location of the Gnalić Shipwreck (Camocio & Bertelli 1757, p. 21).⁷⁰

6.4.1. The *Gagliana grossa*

The *Gagliana grossa*, or *Lezza, Moceniga e Bassadona*, the ship's name at the time when she was built, can be observed as an instrument of both communication and conflict between Ottomans and Venetians.⁷¹ The ship was launched in 1569 in Venice. Although it was a trading ship, soon it was engaged by the Venetian State to transport military troops and supplies for the Ottoman-Venetian conflict which started with the occupation of Cyprus in 1571. However, on the way to Cyprus the ship became a victim of an Ottoman ambush near the island of Corfu. The ship was probably incapable to navigate in that year due to combat damage, but there is also a possibility that it was repaired in time to participate in the battle of Lepanto in October of 1571, but on the Ottoman side. During the next ten years, the ship was in

⁷⁰ It is assumed that the print was made ca. 1757, but the representation depicts the frontier between the Venetian Republic and the Ottoman Empire along the Venetian coast during the period between 1570 and 1573.

⁷¹ Entirely described in the chapter five, section 5.4.

possession of Uluç Ali, admiral of the Ottoman fleet. The ship's operations are not known within this period. In 1581, the ship was sold to Odoardo da Gagliano, a Venetian merchant situated in Pera, Constantinople. Odoardo had an uncle, Domenico, in Venice, and the two of them actively traded over the Venice – Constantinople route (Radić Rossi & Nicolardi 2019, pp. 95-120).

The last trading venture of the ship happened in 1583, just before the period depicted by historians as a decline of shipbuilding and trading connections. Interestingly, the ship *Gagliana grossa* was a player in one Venetian-Ottoman conflict, and perhaps a participant in the battle of Lepanto, one of the crucial battles that changed the flow of Ottoman-Venetian relations. After being captured by Ottomans and later sold to a Venetian merchant, the ship switched its role. Instead of being a medium for conflict, she played the role as a connection between these two regional powers by trading between Venice and Constantinople.

The *Gagliana grossa* ended her last venture by sinking near the islet of Gnalić at the exit of the Pašman channel. She rested at a depth of 26 to 30 metres in the vicinity of Biograd na Moru, only ten kilometres away from the Vrana fortress, a position where the Ottomans and Venetians, after a series of combats, had established a border (Fig. 6-8.).

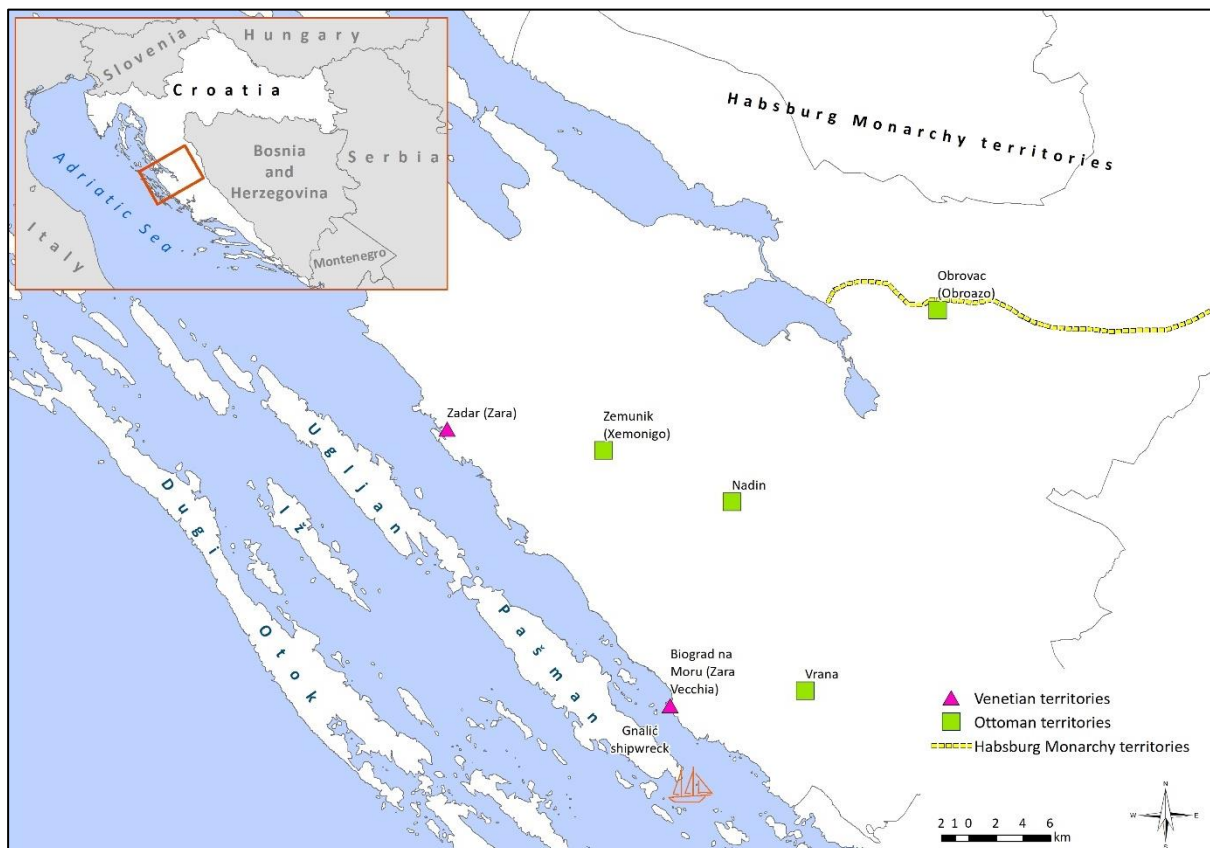


Fig. 6-8. Map of Zadar region representing the location of Venetian, Ottoman and Habsburg Monarchy territories, in relation to the Gnalić Shipwreck (author: V. Butorac).

By looking at the lifetime of the *Gagliana grossa*, the dynamic events of her operational life are intertwined with Ottoman-Venetian relations – collaboration and conflict, combat and trade. The archaeological evidence, supported by archival sources, demonstrates how the relations of the Ottomans and the Venetians were prone to rapid changes during the sixteenth century.

The greatest importance of the site is that the cargo of the sunken ship provides a unique insight into material culture of the late sixteenth century: the products made in the finest workshops of European cities and Venice, but also the great variety of the objects that were in demand and fashionable in the Eastern Mediterranean. On its last voyage in autumn 1583, the ship transported a vast array of finely produced goods, intended to be traded, including the shipment of five thousand decorative window panes for the renovation of sultan Murad III's palace, along with gifts of three bales of precious damask for his mother, Nūr Bānū. The trading goods consisted of various glass types, brass chandelier and sconces, small objects for everyday use, raw materials and semiproducts. Although ships with this kind of inventory were common during the sixteenth century, by the last decades of the century they are becoming rarer. Besides a decline in shipbuilding, the reasons are of a sociological nature. After the battle of Lepanto, the Ottomans do not see any great advantage in keeping good relations with the Venetians, turning instead to other emerging powers of the Western World. In this period, the Venetians do not insist on sending gifts to the sultan and his mother, and the diplomatic voyages are not such a common case.

Taking in consideration the rarity of the archaeological sites with well-studied historical background, coupled with the excellent preservation of the entire ship's hull and the artefacts, the *Gagliana grossa* is a remarkable testament of material culture and Ottoman-Venetian relations of the late sixteenth century. Future studies of the recovered artefact shall supplement the knowledge of both.

7. Production and trade with colouring materials in Venice

7.1. Manufacture, processing and colouring material refining

Colouring materials can be of synthetic or natural origin. Since Prehistory, humans created colouring materials from the resources available in nature. Soil, minerals, charcoal, insects, and plants – all of these were used in the first attempts to express creativity, paint their bodies during rituals, or even as remedies. As the colouring materials went into more common use, and nature could not always provide satisfactory amounts, humans learned how to improve the properties of the available colouring materials, and how to artificially create colours by synthesis.

It is quite understandable that all ores extracted from nature require processing, as raw colouring materials almost never occur in pure form, thus always require refining or cleaning from impurities. Different notes appear in the texts of ancient authors, such as Vitruvius or Pliny the Elder, mentioning methods of processing and conversion of metals into colouring materials (see *e.g.* of cerussite Roy 1997, p. 67). During the Middle Ages, these procedures were treated as a confidential secret, and were sometimes executed in discretion by monks. The books titled '*secretii*' describe the various recipes revealing the procedures to obtain a colour of a good quality, and also provide commentary regarding reactions between the materials, or how to obtain a particularly desired hue. Sometimes those manuscripts are problematic in terms of precise datation, as the recipes were collected over centuries, copied, and passed on to the next generation (Pulsifer 1888, p. 247).

Another source of recipes are alchemy experiments. These are often shrouded in mystery, giving information about peculiar transformations of metals. Biringuccio (1942) often criticizes 'the art of transmutation', mentioning the experiments and conclusions with illegitimate arguments given by alchemists. For example, as they were seeking to produce gold, many experiments strived to create gold out of metals such as brass or tin (Biringuccio 1942, pp. 36-40). Even if most of the experiments did not end successfully, alchemy had an influence in the development of technical knowledge.

The treatises on metallurgy (Biringuccio 1942, Agricola 2018) and painting (Merrielfield 1967) created in the sixteenth century, coupled with current research on manufacture of specific pigments (Berrie & Matthew 2011), are providing an idea of how the colouring materials were extracted from the deposits, manufactured, and refined.

The manufacturers processing minerals existed in Venice, and during the sixteenth century they had the knowledge and the required skills to refine and create ready-to-use products. The research done on documents in archives are testifying how colour seller shops could also act as manufacturing sites, which is explained in the following section (7.2). It is known that Venetian manufacturers gained a high reputation for their skills in colour processing; there is evidence that raw materials were even imported to Venice, to be processed by highly specialized manufacturers and further exported and sold as a Venetian product (Matthew 2011, p. 311).

The manufacturers in Venice developed this high level of expertise because there were a number of individuals and artisans who had a strong demand for quality colouring materials, like glass makers, painters, ceramists, etc. The manufacturers had an important role of creating high-quality materials for the arts and crafts. As Smith and Gnudi (1942, xv) stated in the foreword of the translation of Biringuccio's *De la Pirotechnia*, the manufacturers were 'true scientists of this period', as their practical knowledge led to discoveries of chemical reactions whose relevance was recognized many years later.

Production and refining represent an interesting aspect of the research on colouring materials. It is not the main occupation of the dissertation, since it is highly specialized, requiring proper equipment and access to historical sources. This dissertation delivers only a brief overview of information about manufacture and processing information available in the bibliography. Known techniques of manufacture and refining of colouring materials identified at the Gnalić shipwreck is represented briefly in the sections of chapter 9. The procedures that are familiar to scientists nowadays are described, with the aim to demonstrate that the terminology of colouring materials was not simple, as sometimes raw materials adopted different titles depending on their production or processing method.

7.2. Colour sellers (*vendecolori*)

7.2.1. Who were colour sellers (*vendecolori*)?

The shops of merchants (*merciai*) and textile producers (*drapieri*) were located in the city center in the Venetian lagoon from the Middle Ages to the Modern Age. Trade was actively executed in the city center, but it must be taken into account that the center would not operate easily without its connection to the hinterland. While the center was the trading hub offering specialized products and services, with many shops (ven. *botteghe*) and storages (ven. *magazzini*) around the area of the Rialto, the hinterland had the essential role for procurement of semi-finished and raw materials (Cecchini 2017, pp. 68-69).

The works of Biringuccio (1942) and Agricola (2018) provide an overview of how the minerals were obtained and processed. The question that logically follows is – where were those raw materials delivered, refined into colour, and sold? Unlike other cities in Italy, where the colouring materials were sold by pharmacists, at the end of the fifteenth century, Venice had developed a particular profession specialized only in colour selling.⁷² It is not surprising to find that this profession appeared particularly in Venice, due not only to the large number of artists working actively in the city, but also to support requirements for raw materials in the Venetian dyeing and glass industries (Matthew & Berrie 2006, p. 302; DeLancey 2011, p. 200).

Regarding paintings, it is known that the number of painting artworks increased from 1480 to 1530. A major factor is the introduction of oil painting in the middle of the fifteenth century. During this period, the variety of formats and materials grew, and painters were feeling uplifted to express their creativity. The characteristic palette for Venetian painters was made of vivid colours, including the presence of arsenic sulphide-based pigments, vermilion, and red lakes, while other shades and hues were made by the use of lead white. It is important to note that the wide array of materials mentioned in the written sources, such as treatises and inventories of colour seller shops, were attested by the painters of the Venetian Renaissance school (Matthew & Berrie 2006, p. 302).

The profession of colour sellers, or *vendecolori*, encompassed specialists highly engaged in manufacture and selling of various colouring materials and artists' tools. Their shops could offer a wide array of colouring materials of local and foreign origin, but they could also

⁷² A similar situation is documented in Antwerp, with the development of colour sellers called *verfvercopere* or *marchand de couleurs* (Vermeylen 2010). This is not surprising, as Antwerp in North-Western Europe had an important strategic position and trading role, just as Venice had for the Mediterranean. Matthew and Berrie (2010, p. 245) state that colour sellers appeared in Venice at least half a century earlier than in other parts of Europe.

be specialized in refining or manufacturing of one substance. Their customers were mainly painters, but also glass blowers, pottery makers, dyers, apothecaries, makers of *terrazzo* floors, plaster makers, book binders, and all representatives of specialized manufactures who used colouring materials in their daily activities (Matthew & Berrie 2006, p. 302; 2010, p. 245; DeLancey 2010, p. 195)

Although this profession has only been recently discovered, the research carried out by historians and art historians has already yielded interesting data which is helping to understand their appearance and identity. Scholars have studied the inventories, wills, partnership contracts, judicial proceedings, and other documents where *vendecolori* were the protagonists. Noteworthy research has been done by Louisa Mathew (2002), coupled with scientific approach in co-authorship with Barbara Berrie (2010), unveiling not only the identity of the merchant but also the Venetian palette (Berrie & Matthew 2005). Julia DeLancey located the position of colour sellers within Venice (2011) and researched the most influential colour seller families (2017), while Roland Krischel published complete inorganic (2002) and organic (2010) assortments of the colour seller Jacopo de' Benedetti's inventory. This section is entirely based on the work of the abovementioned authors, who all made a significant contribution to understanding the colour seller trade in sixteenth-century Venice.

Colour sellers (*vendecolori*) co-existed in parallel with confectioneries and shops offering candles and soaps, so called *spezieri da grosso*. Although the colour seller profession never gained a status of a special guild, they clearly had their identity, as they were recognized in society as involved in material refining and colour selling.⁷³ The earliest known recognition of the *vendecolori* profession occurred in 1493, when the title '*dai colori*' appeared next to the name of Francesco de Bartolamio, who had just been accepted into the confraternity Scuola Grande di San Marco (Matthew 2002, p. 680). During the sixteenth century, the number of merchants that held the title '*dai colori*', and in rare cases '*a coloribus*', increased, and their shops are mentioned in various types of documents, such as contracts between merchants, dowries, wills, and inventories (Matthew 2002, p. 681; DeLancey 2011, p. 197).

The colour seller did not necessarily need to have a shop offering colouring materials. Some of them had a status just to legalize their activity of colour selling, because they were primarily registered as apothecaries or mercers, but they offered colours as well (DeLancey 2011, p. 199). However, if a shop existed, it usually had space for selling the goods (*bottegha*), as well as storage (*magazen*), which could either be adjoined or in the vicinity. Rarely,

⁷³ The exact roles and status of the colour sellers are not clear enough and require further studies (DeLancey 2011).

additional space was mentioned in documents in later periods as separate buildings and rooms – the place for grinding (*masena*), or the area which had the function to produce, and possibly sell lead white (*biaccharia*). The activity in the shop was directed by the head (*capo*), and there were always several apprentices (*garzoni*) present, and if necessary, the person in charge of production of specialized colouring material (for *e.g. maestro di biacharria / sbiacharria*, which means specialist in lead white manufacture) (DeLancey 2010, pp. 199-200).

The highest concentration of the shops known to have existed in the sixteenth and seventeenth centuries is recorded in the market area in the vicinity of the Rialto bridge, especially in the street called *Calla dei Stagneri* (DeLancey 2010, p. 201). These shops could operate on different levels – there are numerous instances of their involvement in retail, wholesale, and international trade. For example, the shop of Jacopo de’Benedetti operated at a retail level, offering a wide array of the both metal-based and organic colouring materials, as well as artists’ tools (Krischel 2010).

Colour seller shops could offer a wide range of products which were ready to be used, or they could be specialized in processing/producing a certain type of material. If a shop was engaged in the manufacture of colouring materials, it required special rooms where the colouring materials would be refined, as well as an employed person who would be in charge of providing the recipe, monitoring the process and supervising the work.

Shops could specialize in manufacturing just one or a few colouring materials. For example, the shop owned by Hieronymo Sulimadi was known for selling lead white, mercury, mercuric chloride (in Appendix 8 under title *solimado*), and potassium nitrate (in Appendix 8 under title *sal ammoniac*), while Giovanni Griffalconi owned a shop specialized in lead white production. From the inventory of Griffalconi’s shop, we know it was equipped with tools for washing, grinding and refining lead white, and he also had 31 barrels of lead white in his storage. Griffalconi’s importance among his contemporaries supports the direct evidence of the list of the colour sellers who were in debt for purchasing lead white (Matthew 2002, p. 681; Matthew & Berrie 2010, p. 247).

What is of interest in this dissertation is the involvement of *vendecolori* in international export. Colour sellers typically established partnerships to trade internationally. For example, Matthew and Berrie (2010, p. 247) deliver information on the partnership formed in 1550 by Zuan di Nicolo and Marco da Corphu to internationally export pigments, especially brazil wood, brazilin lake, minium, vermilion, and verdigris. This is only one example that *vendecolori* were actively involved in international trade, not only as sellers of the colours which they manufactured, but also as intermediates. To gather the information about

international maritime transport, the author coupled published bibliography about *vendecolori* and the book of maritime insurances and accidents at sea (Tenenti 1959).

7.2.2. Analyses of maritime insurance documents and active *vendecolori*: families Bosello and Gradignan della Scala

Based on available information, J. DeLancey created a database of active colour sellers from the beginning of the fifteenth century to the end of the seventeenth century (DeLancey 2010, pp. 210-219). It was used to extract information of the colour sellers active in Venice at the end of the sixteenth and the beginning of the seventeenth centuries (Appendix 9).

Further, the author turned to the ship accidents listed in Appendix 8, which represents the lost ships carrying colouring materials of great variety or considerable amounts. The names of the merchandise owners and insurers responsible for loading are provided in Tenenti (1959). Table 7.1. extracts specific information from Appendix 8.

ID number	Type of the ship, name and year of accident	Direction	Accident at sea	Colouring materials	Owners of the goods⁷⁴
2 / 3	saetia <i>Salvaressa</i> , 1592	to Messina	shipwreck near Lissa (cro. Vis)	vitriol (11 casks = 600 pounds); cerussite (5 casks); arsenic (2 casks = 1000 pounds) sulimadi	Francesco Salvaressa, Zuan Maria Canevali
3 / 10	saetia <i>Vidala</i> , 1592	from Alexandria	shipwreck in Porto Muneghe	cerussite (400 casks)	Giacomo Giachinopulo, Stefano Martinelli
42 / 399	nave <i>San Giuseppe et San Bonaventura</i> , 1600	to Constantinople	captured by Sicilian ship and taken to Messina	cerussite (100 casks)	Augustin de Giacomo
46 / 475	nave <i>Martinella</i> , 1601	to Constantinople	captured by Sicilian ship in Archipel	cerussite (20 casks); cerussite (150 casks); mercury (for 1400 ducats)	Lorenzo et Francesco Nobilloni
56 / 608	marciliana <i>Barozza</i> , 1603	to Valona	shipwreck near Curzola (cro. Korčula)	<i>terra bianca</i> (2 boxes); alum (200 pounds); arsenic (100 pounds); mercury (1 box); sulima (1 box); crimson(13 pounds); arsenic (100 pounds)	Caim Maza, Vital de Lunel

⁷⁴ Tenenti (1959) delivers the names of the merchants' insurers, but they are not listed in the table.

ID number	Type of the ship, name and year of accident	Direction	Accident at sea	Colouring materials	Owners of the goods ⁷⁵
70 / 788	nave <i>Perastana</i> , 1605	to Alexandria	accident in Alexandria	minium (4 casks); or <i>pinente</i> (probably orpiment) (2 boxes); vert-de-gris (and silk <i>de peneli</i> 1 box); cerussite (50 small casks); arsenic (4 casks);	Giacomo Buselo (Bosselo)
77 / 868	nave <i>Zena</i> , 1607	to Constantinople	captured by corsairs	<i>verzin</i> (brazilin?) (290 pounds); <i>terra rossa</i> and crimson (2500 ducats); sal ammoniac; vert-de-gris; minium ordinaire; <i>verzin lake</i> ; <i>verzin intero</i>	Gabriel and Alvise della Scala

Tab. 7-1. Large shipments of metal-based colouring materials (selected from Appendix 8; see the appendix for definitions of terms). Names in bold are matching with the database of Venetian *vendecolori* published by DeLancey (2011)

⁷⁵ Tenenti (1959) delivers the names of the merchants' insurers, but they are not listed in the table.

The author searched for matches between the names of active colour sellers and merchants who owned the goods loaded on the ships (Appendix 9 and Tab. 7-1.). The research identified the name Stefano Martinelli, possible owner⁷⁶ of cerussite loaded on the ship *Vidala*, which sunk in 1592 in Porto Muneghe on the island of Mali Lošinj, Croatia; the name Giacomo Bosello, the owner of minium, verdigris, cerussite, and arsenic on the ship *Perastana*, which sunk in 1603 near the island of Korčula, Croatia; and the names Gabriel and Alvise della Scalla, the owners of verzin, terra rossa, crimson, sal ammoniac, verdigris, minium, lake brazilin and 'entire' brazilin loaded on the ship *Zena*, which was captured in 1607 by corsairs.

Although Martinelli matches with the last names of the staff of the shop which operated under the sign of Corona, the dates of shop activity, from 1604 to 1660, do not coincide with the date of the shipwreck (1592), so it was excluded from the study.

On the other hand, Giacomo Bosello and Gabriel and Alvise della Scala were family members of the most influential colour seller families active in the late sixteenth and seventeenth centuries in Venice, with shops situated in the *Calla dei Stagneri*, a vivid merchant street in the vicinity of the Rialto bridge. The Bosello family operated in the shop with the sign of 'Madonna' or 'Santa Maria Virgine'. This family's activity in the colour seller business was recorded from at least 1577 until the early seventeenth century. Archival documents attest that in 1594, the shop was directed by *capo* Giacomo Bosello, in cooperation with Marco Esperti, along with *garzone* and two other workers (DeLancey 2011, pp. 212-213).

The representatives of the Gradignan della Scala (abbreviated della Scala) family were main figures in the colour selling business in the sixteenth century. Under the sign of the 'ladder', the family operated from 1534 to 1664 (DeLancey 2011, pp. 216-217). The family name of della Scala had a strong tradition and reputation in colour selling, and there is a vast amount of archival documentation regarding their business in the shop under the sign of the Ladder in *Calla dei Stagneri* (DeLancey 2011, p. 206).

The last names of both families are mentioned in the context of intermarriage. Marina, the daughter of Iseppo Bosello, married Gabriele Cabaretti, nephew of Alvise Gradignan della Scalla, *q.*⁷⁷ Domenico. The occurrence of intermarriage is interpreted as an act of creating a tight connection between families Bosello and Gradignan della Scala, with the aim to create a strong bond, improve wealth and enhance reputation (DeLancey 2011, p. 205).

⁷⁶ It is not certain whether the ship owner was Giacomo Giachinopulo or Stefano Martinelli.

⁷⁷ 'q' is abbreviation from lat. *quondam*, which means 'from deceased'. In this case, Alvise della Scala from deceased father Domenico.

The shop at the sign of the Ladder was first mentioned in the inventory of Domenico Gradignano in 1534. It is known that Domenico was successfully maintaining the workshop, a wealthy man selling both colours and lead. As the sixteenth century progressed, under the direction of Alvisè Gradignan della Scala the Ladder specialized in selling lead-based materials, especially lead white and minium, and there is a possibility it also sold tin. In the last decades of the sixteenth century, the shop had permission to manufacture lead white and minium, and in the seventeenth century two storages were specifically identified for the storage of lead white (DeLancey 2017, pp. 20-21).

The Ladder shop continued to develop and grow when Alvisè started to export internationally, unlike his father Domenico who kept the business only within the city walls. It is necessary to point out that Alvisè did not sell only the colours that were manufactured in his workshop. He also had a role of intermediate who obtained pigments of the best quality in the region, which he offered to his international clients. In the period when Alvisè della Scala was in charge of the shop, the Venetian painter Tizian and his son Orazio arranged an order of pigments to supply the Spanish royal court. If Alvisè himself supplied the Spanish royal court with the highest quality pigment materials of various colours, his network of colleagues and manufacturers must have been large. The shipments to the court of Spain in 1572 must have enhanced the reputation and prosperity of the Gradignan della Scala family (DeLancey 2017, p. 26). When colouring goods destined for Constantinople were loaded on the nave *Zena* in 1607, the Ladder shop was still operating with success.

Alvisè *q. Domenico* appears in a portrait painted by Tiziano (Fig. 7-1.). For a long time, the subject in the portrait was under debate; the box with pigments on the figure's right-hand side suggested that he could be a painter, apothecary, or colour seller. Identification was helped thanks to a description on the back, stating that the painting was made in the year when the person was the main figure holding office of the Scola Grande in di S. Rocco. The fact that Alvisè della Scala was in charge of the offices of Scuola Grande confirms how influential and important a figure he was in the second part of the sixteenth century (DeLancey 2017, pp. 15-16).

Finally, while *vendecolori* are important in the study of local, regional and international trade with colouring materials, existing inventories provide insight into materials available in contemporary Venice (Appendix 7).⁷⁸ This valuable information provides an overview of the materials which were available locally, as well as those that arrived through numerous Venetian

⁷⁸ Only metal-based and composite colouring materials are included in the table. The table is a modified version of the one published in Batur & Rossi 2019.

trading connections – from the Middle and Western Europe, or from the Eastern Mediterranean. Also of interest is the variety of materials available in the workshop, especially when considering different types of the same colour. For example, the inventory of Jacopo de’Benedetti mentions different types of iron oxide-based and arsenic sulphide-based colouring materials, providing information on how those were sold in different forms, as presented in Appendix 7 (Krischel 2002, pp. 112-113).



Fig. 7-1. The portrait of Alvise della Scala by Tizian (online collection of the Staatliche Kunstsammlungen Dresden – SKD, Germany, Gal.-Nr. 172 <https://skd-online-collection.skd.museum/Details/Index/4099809>).

Bosello's ownership of the colouring materials loaded on the nave *Perastana* in 1605 and della Scala's ownership of the colouring materials loaded on the nave *Zena* in 1607 are clear evidence that the *vendecolori* operated on an international scale of trade. Evidence of international export can also be seen in the partnership of Zuan di Nicolo and Marco da Corphu, established with the aim to internationally export colouring materials (Matthew & Berrie 2010, p. 247), and in the story about Alvise della Scalla supplying the Spanish royal court with pigments. Based on these facts, it is proposed that the colouring materials from the Gnalić shipwreck originated from the shops of Venetian colour sellers. With respect to the large amount of lead white recovered from the Gnalić site, it is possible that a Venetian colour seller specialized in production of lead white, similar to the workshop the Ladder owned by della Scala. In fact, due to the high popularity and activity of the workshop, this lead white could have been manufactured in the workshop of della Scala. However, no systematic study on the producers of lead-based colouring materials has been undertaken for the given period, so it is not known how many were active in Venice in the late sixteenth century. The wooden head of one lead white cask bears the stamp of 'the ladder' (Appendix 12); however, no studies have been done on Venetian barrel markings, as this material is largely unknown.

This chapter proposes that, since archival information demonstrates the involvement of *vendecolori* in international trade, it is reasonable to conclude that the colouring materials from the Gnalić shipwreck were represented as merchandise offered in their shops. This proposal is supported by the strong evidence that the most influential families involved in the colour selling business were launching large international shipments of colouring materials (Tab. 7.1). However, this hypothesis should be taken with caution. The colour sellers could offer a variety of different materials, which they provided as intermediates; they also may have had a shop specialized in refining certain products. This chapter only considered some of the questions that require a comprehensive study in the State Archives of Venice. Additional archival research is required to bring a reliable understanding of involvement of colour sellers into international trade with colouring materials.

8. International trade with colouring materials: cargo, trade, shipping

With respect to the goods circulating in the Mediterranean during the sixteenth century, the greatest importance was supplying cities with shipments of cotton and sugar (Lane 1973, p. 298), while spices made up only a small portion of the total flow of goods (Braudel 1992, p. 206; 1997, p. 465). However, the spice trade had such a value and importance that it made an impact on the political situation during the first part of the sixteenth century. Competitors who were able to reach the spices in India and offer them for cheaper prices in Europe worked to dominate the maritime trading routes, as discussed in section 6.2.

It is important to note that the term ‘spice trade,’ used to describe the competition over the trading routes, usually referred to spices originating from India, such as pepper, cardamom, cinnamon, cumin, cloves, nutmeg, mace, etc. (Tenenti 1959). However, the term ‘spice’ actually had a different meaning in the period of the fourteenth to the sixteenth century in comparison to its contemporary meaning.

In the fourteenth century, Francesco di Balduccio Pegolotti, in *La pratica della mercatura* (Florence, 1310 – 1340), diversified general spices from ‘minute spices’. Within the list of general spices given by Pegolotti, there are similarities with the cargo of colouring materials from the Gnalić shipwreck: lead white⁷⁹, mercury, cinnabar, tin of Venice, tin of Provence⁸⁰, tin sheets, minium, red orpiment, yellow orpiment, fine ochre, fine realgar, Spanish realgar, compact madder of Romagna, ground madder of Romagna, madder of Alexandria, madder of Byzantine Empire, and madder of Cyprus. According to Pegolotti’s diversification, it is interesting to note that during the fourteenth century, the bulky raw cargo of metals and other raw materials was addressed as spices, including the raw materials mentioned above, while more valuable fine seasonings, medicines, pigments made of rare minerals, and dyes were named ‘minute spices’ (Constable, Lopez & Raymond 2001, pp. 109-114).

In the late sixteenth century, the word “spice” still had a very general meaning; it could be considered as an addition to the meal, as a component for dyeing textiles, or as a medicine supply (Braudel 1992, p. 206; 1997, p. 465).⁸¹ Although the spice trade often meant small packages of valuable seasonings, merchants had a preference for this cargo due to the high value (Rogers 1990, p. 60).

⁷⁹ Listed two times – lead white of medium quality, and the lead white with the braiding.

⁸⁰ Tin and cupreous raw materials are not included in the dissertation due to the fact that they do not appear as items on the inventory lists of Venetian colour sellers.

⁸¹ The author did not find the confirmation that during the sixteenth century, the same classification that Pegolotti applied in fourteenth-century Florence existed in Venice.

As the broad category of goods considered under the heading ‘spice trade’ included dyes, they must be taken into account when giving general conclusions about the trade with colouring materials. Multiple uses of the materials in the Medieval and Renaissance periods makes it difficult to suggest their specific purpose when loaded on board. For example, saffron and curcuma (table of cargo items in Appendix 8) were considered as spices and seasoning, dye and medicine.

The aims of the following sections are threefold. Firstly, to gather the information about the circulation of the colouring materials to and from Venice. Secondly, to study archival information about the international trade with colouring materials focusing on just one, very limited source - the insurance documents for international transport issued by notaries G. A. Catti and A. Spinelli from 1592 to 1609 (Tenenti 1959). Thirdly, to discuss whether the colouring materials attested in the documents issued by G. A. Catti and A. Spinelli could be present at underwater archaeological sites.

8.1. International trade with colouring materials according to the historical documents

If an historian would like to have a thorough review of the goods being exported or delivered to Venice, he or she would target this sort of documents: lists of the ship’s cargo or the bills of lading (ven. *carichi*), customs records, and insurance documents issued in the case of maritime accident⁸². Among these sources, the most comprehensive data for systematic studies would be obtained from bills of lading. Unfortunately, there are very few examples of bills of lading preserved in the State Archives of Venice for the period of the sixteenth century (Matthew 2013, pp. 302-303).⁸³ Another aggravating factor is the absence of the documents corresponding to both sides of the trade: the archives in Venice, and the archives at various locations in the East where the goods were delivered (Tenenti 1959; Rogers 1990, p. 61). Nevertheless, historians have been collecting pieces of data, merging them to gain understanding, and creating a picture of international and regional flow of colouring materials. A brief overview of what is known will be presented in the following paragraphs.

Venetian markets and colour seller shops had a broad spectrum of organic and inorganic materials to offer. Therefore, it is not surprising at all that Venice was called ‘the city of colour’,

⁸² For example, maritime insurance documents issued by G. A. Catti and A. Spinelli used within this dissertation (Tenenti 1959). Matthew (2011, p. 302, 303) mentions that correspondence between merchant and diplomats, or judicial proceedings can yield an information.

⁸³ O’Connell (2017, p. 103) states that the evidence about Venetian economic history in the State Archives of Venice is scarce in comparison to wealthy documentary sources preserved in the cities of Northern Europe.

and considered as a trading hub, especially when it came to the supply of colouring materials. The advantage of buying colouring materials in Venice was the wide selection of materials originating from the Eastern Mediterranean and Northwestern Europe. Painters' documents frequently mention traveling to Venice to purchase the pigments, especially blues, with the greatest demand for lapis lazuli (Mathew 2002; Krischel 2002; Matthew & Berrie 2010; Matthew 2011).

Venice was well known for the production of lead white, which was exported in large amounts together with vermilion and lake pigment to the East (Matthew & Berrie 2010). Other colouring materials delivered to the Eastern Mediterranean were verdigris, orpiment, hematite, realgar, minium, lampblack, powdered silver and gold (Berrie 2012).⁸⁴ Regarding local supplies of raw materials, Venice relied on earths from the region of Veneto, such as green, yellow and red earth (*terra verde di Verona, terra gialla di Verona, rosso Veneziano*), while smalt and lake pigments could be imported, but also produced locally as by-products of developing industries (Lazzarini 1983; 1987, p. 118).

Venice imported large amounts of arsenic sulphides and dyes (kermes, lac, indigo, brazilwood, gallnuts), as well as artists' materials such as alum, resins, and borax from the East. Precious lapis lazuli originating from the mountain of Badakshan in the Kotcha Valley in northern Afghanistan was delivered to Venetian workshops, which processed the mineral, turning it into deep-blue hued ultramarine (Matthew 2011, p. 303; Lazzarini 1983; 1987, p. 118).

The import from the North was important as well, providing materials such as azurite, vitriol, silver, lead, and tin. Crucial routes for trade included imports from Hungary and Flanders coming to Venice over both land and sea routes. According to archival documents, Flanders supplied *zalla da fiandra* (probably lead-tin yellow) and Flemish smalt (Matthew & Berrie, 2010, p. 246). In the direction of contemporary Netherlands, Belgium, and Luxemburg were exported various materials such as ultramarine, azurite and various dyes (Lazzarini 1983; 1987, p. 117; Matthew & Berrie, 2010, p. 245; Vermeulen 2010, p. 360).

The textile industry in Venice flourished and its products were cherished in the Ottoman Empire. Stunning colours of textiles were obtained with the dyes made of plants and insects. Great demand existed for the dyes made of plants, with brazilwood (ven. *verzino*) being one of the most important; this dye had been imported from India since the thirteenth century. Besides *verzino*, other pigments originating from plants used during the Renaissance were madder (ven.

⁸⁴ Information is based on very limited research on works of art in Islamic paintings, discussed by Berrie (2007, p. 142).

robia) and orchil (ven. *oricello*). The dyes called lac (ven. *lacca*), grain (ven. *grana*) and kermes (ven. *cremisi*) were produced from insects (Lane 1973, pp. 298-299; Molà 2000, pp. 107-120).

The dyes in use in Venice came from different parts of Europe and Asia until the discovery of the New World, when the sources of plants and insects changed. The discovery of the New World introduced a new sort of dye in Europe around 1520: scarlet dye cochineal. The main source for this dye was an insect living on the prickly pear cactus. Soon, New World cochineal replaced Old World cochineal, as well as the dyes made of oak trees kermes in Crete and Morea, and became the preferred dye. During the second half of the sixteenth century, so called ‘New World cochineal’ was already commonly used in Venice, and it was transported even to Northern and Western Europe (Molà 2000, pp. 107-120; Kirby 2015, pp. 174-176).

8.2. International trade based on the insurance documents issued by notaries G. A. Catti and A. Spinelli

In order to get insight into trading with colouring materials in the late Renaissance, the work of historian Alberto Tenenti (1959) *Naufrages, corsaires et assurances maritimes à Venise, 1592-1609*, was consulted. The backbone of Tenenti’s work was the insurance documents issued by the notaries G. A. Catti and A. Spinelli, from which Tenenti counted the number of 1021 accidents on the maritime routes.⁸⁵ While the document date range is from 1592 to 1609, it is still possible to obtain a small data set to help to understand maritime trade in colouring materials, the amounts of the various materials that were traded, and the destinations where they were transported.

With the goal of better understanding the trade flow of colouring materials, the author has developed a list of colouring materials lost on shipwrecks. The author’s wish is to demonstrate that these colouring materials were traded internationally and were common among the cargo inventories. Therefore, during underwater excavations, there may be evidence of their existence on shipwreck sites. The methodology of the work is explained in Appendix 8, coupled with associated tables.

The category of artists’ materials was additionally added to the dataset, to demonstrate how resins, varnishes, waxes, and oils appear in the cargo inventories of shipwrecks. Among many different purposes that could be given to those materials, it is important to note they can

⁸⁵ After an accident happened, on request, notaries issued the document of insurance (ven. *cession*). The purpose of this document was to transfer the claim from the owners to the insurers, with the aim of insurance collection (Radić Rossi et al. 2013, p. 87).

be interpreted as artists' materials as well. Some insurance documents mention the boxes of colours, as well as drugs and various merchandise. These items were also listed in the database, as the possibility of their use in conjunction with colouring materials cannot be excluded.

It is necessary to point out that colouring materials are traded in different conditions. For example, tin, lead, and cupreous cargos are not colouring materials, but they could be used for the production of pigments by exposing them to appropriate chemical processes. Those materials are not included in this research. Based on the documents, it is evident that merchants and notaries are mentioning the titles of colouring materials individually, such as cerussite, indigo, arsenic, cinnabar, mercury, etc. while only once did the very general description of 'colori' appear (see Appendix 8, table listing shipwrecks and ship's accidents, shipwreck numbered with 13 / 112).

Besides pure raw materials, it has to be taken into account that semi-refined products or finished products also appear in the lists. In this context, it is important to state how the same material could be transported in different conditions, which reflects the different techniques of production. For example, brazilin, the dye made of brazilin wood, is mentioned in different contexts: as a verzin, which probably refers to the dye; as a verzino wood, which perhaps refers to the logs of brazilin wood; and as verzin lake, referring to verzin. Another adjective that appears is 'verzin intero' (entire verzin) (Tenenti 1959, pp. 82, 243, 496), but the exact meaning of this term remains unknown to the author.⁸⁶

According to the data delivered by Tenenti, the ships were exporting cerussite, arsenic sulphide, red ochre, turpentine, saffron, mercury, vitriol, sulimado, and varnish to the West and East. They were importing grana, indigo, saffron, brazilin, *terra ghetta* (or litharge), alum, and orpiment from the East. Each term mentioned here is explained in the table of cargo items of Appendix 8. It is particularly interesting how much cargo of indigo and grana colouring material is being imported to Venice from the Eastern Mediterranean.

As this dissertation studies mostly metal-based colouring materials, similar cargo has been tried to be separated within the whole database. It is especially interesting that when colouring materials appeared, they were grouped together within the cargo lists. Of note, several especially large shipments of cerussite were sent to Constantinople and Alexandria (Tab. 8-1.). The noticeable amounts of lead white (cerussite) cargo were almost always transported in *nave* ships, which was the merchantman of large capacity.

⁸⁶ Verzin 'intero' and lake verzin are listed in the document insured by the merchant Alvise della Scala and loaded on nave Zena in 1607 (Tenenti 1959, p. 496). Verzin 'intero' might be used to distinguish lake pigment from 'entire' brazilin, which could be either dye or the wood.

The analyses of the cargos in Appendix 8 demonstrate how the materials that were traded had multiple uses and sometimes it is just not possible to conclude what their main purpose was based solely on the title in the document.

However, we have to be careful with drawing conclusions based solely on the documents of the notaries studied by Tenenti. The documents studied by Tenenti were issued by two notaries only, while there were a dozen other notaries active in Venice at the end of the sixteenth century.⁸⁷ The fact that the data is from ships that had been lost through accident, without having an overview of the inventory of all ships coming in and out of the port, also limits the research. It is likely that some lists of insured goods did not survive, and that others are incomplete. Another limitation is that it was common practice to smuggle valuable goods and avoid listing them in an insurance document. Therefore, it is surprising to find the lapis lazuli listed in the documents (table in Appendix 8, 47 / 483). Because of these limitations, the data provided cannot be used to obtain a comprehensive picture of international trade of colouring materials.

⁸⁷ Personal correspondence with Mauro Bondioli (December 2019).

ID number	Ship's name	Type	Year	Direction	Accident at sea	Colouring materials
2 / 3	<i>Salvaressa</i>	<i>saetia</i>	1592	to Messina	shipwreck near Lissa (cro. Vis)	vitriol (11 casks = 600 pounds); cerussite (5 casks); arsenic (2 casks = 1000 pounds) sulimadi ⁸⁸
3 / 10	<i>Vidala</i>	<i>saetia</i>	1592	from Alexandria	shipwreck in Porto Muneghe ⁸⁹	cerussite (400 casks)
42 / 399	<i>San Giuseppe et San Bonaventura</i>	<i>nave</i>	1600	to Constantinople	captured by Sicilian ship and taken to Messina	cerussite (100 casks)
46 / 475	<i>Martinella</i>	<i>nave</i>	1601	to Constantinople	captured by Sicilian ship in Archipel	cerussite (20 casks); cerussite (150 casks); mercury (for 1400 ducats)
56 / 608	<i>Barozza</i>	<i>marciliana</i>	1603	to Valona	shipwreck near Curzola (cro. Korčula)	<i>terra bianca</i> (2 boxes); alum (200 pounds); arsenic (100 pounds); mercury (1 box); sulima ¹⁰⁶ (1 box); crimson(13 pounds); arsenic (100 pounds)

⁸⁸ Equivalent to solimato.

⁸⁹ *Porto Muneghe* is positioned on the island of Veli Lošinj.

ID number	Ship's name	Type	Year	Direction	Accident at sea	Colouring materials
70 / 788	<i>Perastana</i>	<i>nave</i>	1605	to Alexandria	accident in Alexandria	minium (4 casks); d'or <i>pinente</i> (probably orpiment) (2 boxes); vert-de-gris (and silk <i>de peneli</i> 1 box); cerussite (50 small casks); arsenic (4 casks);
77 / 868	<i>Zena</i>	<i>nave</i>	1607	to Constantinople	captured by corsairs	<i>verzin</i> (brazilin?); (290 pounds); <i>terra rossa</i> and crimson (2500 ducats); sal ammoniac; vert-de-gris; minium ordinaire; <i>verzin lake</i> ; <i>verzin intero</i>

Tab. 8-1. Large shipments of metal-based colouring materials (selected from Appendix 8)

8.3. Evidence of historical documents: what can be expected at the archaeological site?

Now that the previous two sections have given an overview of available data about the spice (and within it, colouring materials trade), it is possible to predict a pattern of the merchandise that can be expected upon discovery of an underwater archaeological site dating to the end of the sixteenth or the beginning of seventeenth century. Since the term colouring materials itself encompasses a wide array of pigments, dyes, and medicines, the author decided to make categorizations within the group.

While working on underwater sites, archaeologists do not have a high expectation of finding the evidence of the spice trade, since this type of cargo consists mainly of organic compounds. However, the question of organic materials preservation is more complex than it seems. The spice trade evidence can be preserved, but there must be certain conditions to enhance the preservation.

To avoid simplifying things and state that organic evidence of the spice trade cannot be preserved underwater, the author introduced a division. The main criteria are the physical and chemical properties of the colouring materials. They can be divided into inorganic materials, which includes metal-based colouring materials; organic materials, including various plants and insects, as well as organic dyes; and composite materials, such as organics which have been precipitated on hydrated salts (lake pigments).

The purpose of the division within the dissertation is to point out how the evidence of spice trade can be preserved in different forms. Guided by the examples of the Gnalić shipwreck finds, it helps archaeological researchers to pay more attention to the possible preserved evidence while removing the sediment with the dredge. This division is introduced to facilitate the discussion about preservation.

It is almost impossible to find evidence of trading goods of organic origin at underwater archaeological sites, as the long exposure to marine environment normally results in their rapid disintegration or their being dissolved into the sea. With respect to sixteenth-century shipwrecks, the cargo that most often survives is typically bulky and resistant to disintegration - cupreous, lead, tin and iron-based materials. These inorganic materials, preserved in the surface layer, often contribute to site discovery and also frequently propose approximate shipwreck datation, even prior to applying destructive methods of removing archaeological layers.

The publication of the shipwreck Sveti Pavao near Mljet discusses the most commonly transported merchandise on the ships that were passing through the Adriatic based on the data

in the registers of G. A. Catti and A. Spinelli, stating how common cargo of organic origin will most likely disintegrate in the marine environment (Beltrame, Gelichi & Miholjek 2014, p. 151). It is, indeed, expected that most organic goods, especially organic-based colouring materials, will not be preserved underwater. However, this statement should not be taken for granted, as some evidence of organic-based and composite colouring materials, that on some lists can be considered as spices, were preserved at the Gnalić site. The following examples are provided as evidence.

The reports from the Gnalić shipwreck from the year 1973 mention that organic materials were preserved beside the lead white barrels – shelled almonds, and a plant that resembled anise (lat. *Pimpinella anisum*) or fennel (lat. *Anethum foeniculum*) (Radulić, unpublished report, 1973, p. 6). Unfortunately, these materials do not exist in the contemporary collection in the Regional Museum of Biograd na Moru, but the reports and diaries written in 1973 are detailed enough to understand the context of the finds. Anise and fennel were used as dyes, medicine, and seasoning, and justifiably attest as evidence of spice trade (Constable, Lopez & Raymond 2001, pp. 109-112). Both almonds (Tenenti 1959, p. 130) and anise (Tenenti 1959, p. 130) appear in the registers of G. A. Catti and A. Spinelli.

The other example of the excellent preservation of organic materials attested at the Gnalić site is the find of red lake pigment, which is described in detail in section 3.3h. Since the main components of the lake pigment are the roots of plants or the tissue of insects, it is obvious to think that this material will not be preserved underwater. However, the alumina or alum substrate on which these materials are precipitated by the method described in section 9.3.8.4. helped to preserve the organic matter.

Thus, preservation of organic matter is indeed possible, but under specific conditions: if the material is covered with a thick layer of metal-based materials or a thick layer of sediment which create a sort of protective shield from the marine environment, as in the case of the preservation of almonds and anise at Gnalić, or in the case of composite materials, where organic materials are precipitated on hydrated salts.

After review of the records of Catti and Spinelli, the author has counted 84 shipwrecks with a cargo of colouring and artists' materials from a total of 1021 ship which had an accident at sea. Of these 84 wrecks, seven sunk along the Eastern Coast of the Adriatic in the period from 1592 to 1609 carrying a cargo of colouring materials (marked bold in the table in Appendix 8). Shipwrecks are marked on the map in chronological order (Fig. 8-1), starting from the ship *Salvessa* which was lost in 1592, and finishing with the *Barozza* which sunk in 1607. The locations of the accidents cannot be precise, as maritime insurance documents are very

scant with the information; if the location is mentioned, it usually states briefly ‘in the waters of island...’ or ‘in the vicinity of city...’ (table in Appendix 8).

The division of the sites is made according to metal-based colouring materials cargo, marked with full red dots, and organic-based colouring materials cargo, marked with hollow dots. Only three of these wrecks carried a massive cargo of metal-based colouring materials, marking them as more likely to be discovered in the future. If these shipwrecks should be found and excavated in the future, the existence of organic-based and composite colouring materials should not be overlooked, as their preservation has been attested at the Gnalić shipwreck.



Fig. 8-1. Map of the Adriatic Sea with marks of the sunken ships with a cargo of colouring materials. The codes in the brackets refer to the identity number given in Appendix 8. Red indicates a large cargo of inorganic colouring materials, likely to have survived on the sea floor.

Description: 1) saetia *Salvaressa* (2 / 3); 2) saetia *Vidala* (3 / 10); 3) nave *Canevala* (10 / 88); 4) marciliana *Poma* (24 / 193); 5) marciliana *Rigola* (32 / 237); 6) nave *Martinenga* (37 / 329); 7) nave *Pozza* (44 / 454); 8) marciliana *Barozza* (55 / 608).

9. Colouring materials from the Gnalić Shipwreck

Since divers visited the site for the first time in 1967 and conveyed their impressions and observations to art historians present on board, it was recognized that interpretation of the cargo would be a full challenge. Sofija Petricioli reported that besides many objects that are of fine manufacture, ‘the ship is full of mysterious materials’ of different physical properties, as well as sand that definitely does not belong to the local marine environment.⁹⁰ However, researchers were aware that recognizing the merchandise was beyond the capabilities of the Yugoslavian research facilities. Today we might miss the information and the samples of the materials that were still on the site when the first divers were working, but we continue to admire the detailed descriptions, devotion and will which these early researchers showed while searching for answers.

This chapter provides an overview of the situation at the site and interpretation of results of analyses done on recovered colouring materials. The beginning of the chapter introduces the reader to the description of the situation on the site when the project was restarted in 2012. In order to obtain as complete information as possible, the excavation reports from 1967-1973 were consulted to determine the disposition of the cargo within the hold. Further, this chapter individually represents each type of colouring material present as a part of the merchant cargo of the ship, giving information about the appearance at the site, amounts present, and the interpretation of results of characterization analyses. This text is followed by additional information on the colouring materials properties and historical information. The colouring materials, packaging methods and amounts are briefly listed in Appendix 10, while characterization analyses results are provided in Tab. 9-1. and Appendix 21.

⁹⁰ Quoted in chapter 5.

9.1. Archaeological context of colouring materials

In the excavation campaign of 2012, a metal grid with squares of dimension 2x2 meters was constructed, with a total area of 16 m², oriented north-south based on visible traces of ship's hull protruding above the surface of the sand (Radić Rossi et al. 2012, p. 90). As the excavation seasons progressed, being conducted for at least two months annually, the grid was adjusted to encompass a larger surface area. The columns of the grid from west to east were progressively marked with numbers starting with 15, while the rows of the grid from north to south were labelled by letters Z, A, B, C, and D (Map 6). The metal grid was placed for the needs of accurate documentation, but also to facilitate the orientation of the divers. Moreover, it is easier to clean the ship's hull while having a sturdy support for the diver and dredge, avoiding any physical damage to the wooden hull. The sediment was removed with dredges powered by water pumps, making it possible to see the outlines of the ship within the grid more clearly. When cleaning delicate objects, such as barrels and casks, the addition of a flexible tube on the dredge was used.

Over the years, various barrels were excavated, recorded, recovered, and exhibited, but unfortunately, for many of them no trace survives either on the bottom or in the documentation. In the area marked with A - B 17 / 18 / 19 on Map 6, where the ship was excavated in 1973, several types of barrels were present, as can be seen on the drawing of the site plan situation by Ksenija Radulić (Fig. 9-1). The following section will provide the comparison of the colouring materials disposition based on reports from 1967 to 1973, 1996 and the recent excavations (2012 – 2019). To follow the comparative description, the author suggests following the site plans attached in the back of the dissertation (Maps 1 – 7).

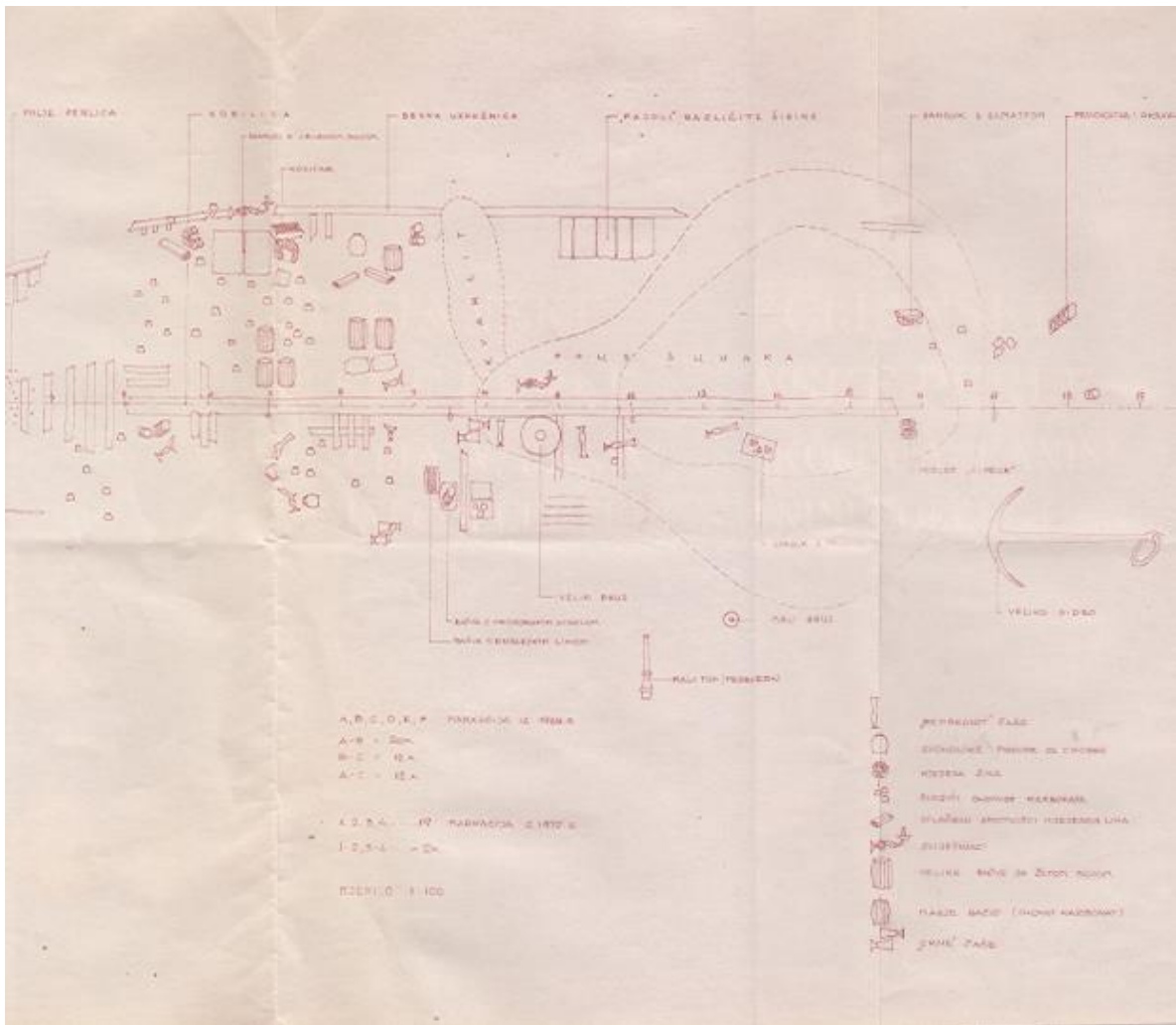


Fig. 9-1. Section of the site plan from 1973, encompassing information from 1967, 1968 and 1972 (Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

To the far north in the vicinity of the keel, tin, brass, and mercury sulphide bells were discovered (numbered with 5 and 6 on Map 1; within squares A - B 17 on Map 6). Nearby were two accumulations of red colour which preserved the shape of their original chest-shaped packaging.⁹¹ Going deeper, approximately two meters towards the south, the accumulation of various materials was present (numbered with 3, 4 and 7 on Map 1; within squares B 17 / 18 / 19 / 20 on Map 6). To the west were massive amounts of the lead white cones which fell from the broken casks and scattered on the site. The whole layer was full of small artefacts, especially window pane sherds and glass beads. After removal of the layer of sand, ingots and small artefacts, well-preserved ship's hull was revealed together with quite damaged casks containing

⁹¹ Analyses of composition were never executed.

remains of lead ingots, along with two long barrels and the remains of one ovoid cask with red powder content⁹² (Map 6, located between B 17 and B 18).

In the same level as the scattered ingots, but towards the east, were the casks filled with yellow colour. According to the joint site plan (Fig. 9-1.) and photos from the site from 1972 and 1973, it is possible to conclude that at least three casks filled with yellow colour existed when the excavation was going on. That area corresponds to today's Z 19 (one cask) and B 20 / 21 (two casks). It is possible that two additional casks of yellow colour were located in C 19.⁹³ The excavation reports are descriptive only, stating 'yellow colour' or 'sulphur (?)' (Figs 10-1., 10-2., 10-3., and number 7 on Map 1). At least one ovoid cask was recovered during the excavation season of 1972 (Appendix 13), as it is on display in the Regional museum today, but the notes from the excavation diary state 'two bottoms and joint staves recovered'.

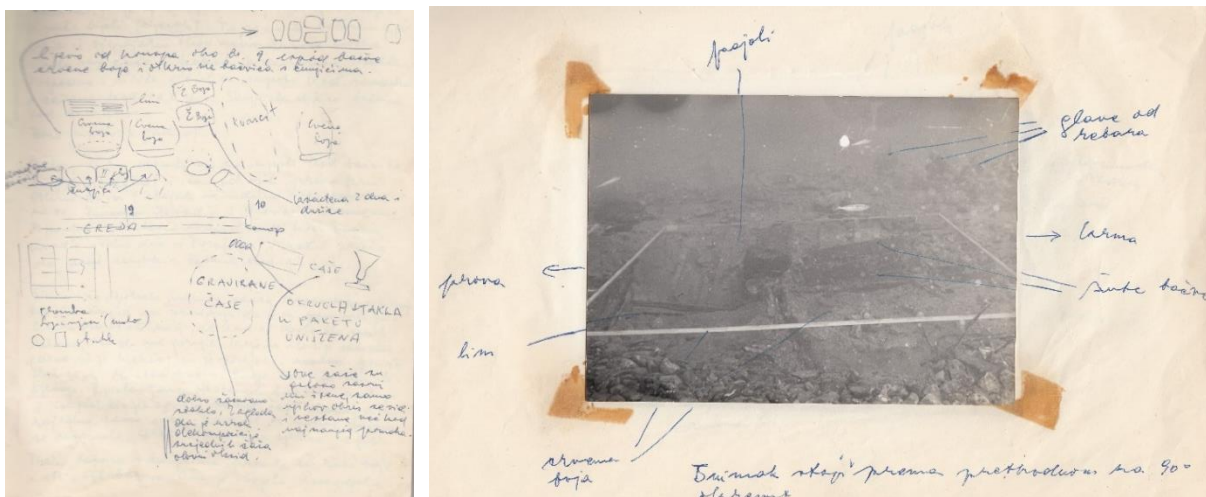


Fig. 9-2. and Fig. 9-3. The sheets from the diary of Ksenija Radulić, indicating the disposition of the cargo in the barrel area in 1972 (Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

None of the abovementioned casks existed on the bottom when the excavation restarted in 2012. While one cask was recovered in 1972 (Appendix 13), no other casks of yellow colour were preserved, but the marks of their original positions could be seen on the bottom in the large accumulation of yellow particles in the fine sand, as well as in the yellow stains on the wooden hull (see yellow stains on the hull on Maps 5 and 7, corresponding to north of A 18 / 19, south of B 19 / 20, and south east of C 19 on Map 6).

Further, one meter deeper to the south is the so-called 'barrel area' (Fig. 9-4.). Most of this surface was covered with pebbles, scattered lead white, and ballast stones at the beginning

⁹² Red content of the long barrels revealed in 2014 has never been sampled.

⁹³ The existence of these two casks is unclear as the records are contradictory.

of the 2012 excavation season. In the excavation season of 2013, underwater work was focused on the barrel area. After cleaning with the dredge powered by a water pump and removing the layer of scattered ingots, pebbles and sand, the outlines of barrels became visible, so they were assigned individual numbers (Maps 2 and 3). This work was continued in 2014; two excavation seasons of removing heavy layers uncovered the following: in the eastern part of B 15 / 16 / 17, nine damaged casks of lead white, one oval and two long barrels filled with unknown red powder⁹⁴, and two damaged barrels with unknown composition. In the northeastern part of C 16 / 17 / 18 / 19 and the western part of C 20, the situation was even more complex, as the area revealed six oval barrels filled with red ochre, one long barrel with unknown red powder⁹⁵, and 30 both partially and completely preserved lead ingot casks (Fig. 9-4. and Map 3).

All partially preserved casks and barrels from B 15 / 16 / 17, as well as casks in the northeast part of C 16 and the eastern part of C 17 were recovered due to the necessity of reaching and recording the ship's hull. Additionally, these casks were in such a bad state of preservation that the staves could not be kept in place, and there was real danger of further destruction caused by divers' movements. The preservation was poor in this area because it was previously excavated by researchers in the 1960s and 1970s. All recovered casks and their lead white contents were stored in the laboratory. Two barrels that had unidentified red content were recorded in the laboratory and returned to the site for *in situ* preservation.

The numbering scheme for the barrels is shown in Maps 2 and 3. The red ochre contents were entirely removed from barrels 1 and 3, and partially from barrel 7, and stored in the laboratory. The contents of barrels 2, 12, 13 and 21 were not sampled, as unfortunately they disappeared over time due to divers' movements and dredging. Besides barrels with red content, and casks with yellow content and lead white, the report from 1973 mentions two discoveries: shelled almonds, and a plant that resembled anise (lat. *Pimpinella anisum*) or fennel (lat. *Anethum foeniculum*) (Radulić, unpublished report, 1973, p. 6). Based on the report, the probable location was the southern part of square C 17 (Map 6).

⁹⁴ Red contents of the barrels have never been sampled.

⁹⁵ Red content of the barrel has never been sampled.



Fig. 9-4. Barrel area during 2014 excavation campaign (photo: S. Govorčin).

In the 2015 season the excavation did not continue in the barrel area, but in the follow-on excavation seasons of 2016, 2017 and 2018 several barrels were removed. Barrel 1 was recovered, recorded on the research vessel, sampled, stored in a plastic box and returned to the site. Barrel 2 was inadvertently dislodged by mooring lines of the research vessel. The logistics for recovery were not available, so the barrel was stored safely in the box on the underwater site. Barrel 3 and cask 29 were removed from the site by applying a recovery method of carbon fibre support, a special technique developed by the Institute for Conservation and Restoration in Rome, Italy which aims to preserve wood integrity when a delicate object is moved from its original position (Appendix 14). Both barrel 3 and cask 29 are stored in the laboratory.

9.2. Position of colouring material barrels within the ship's hull

The ship sunk onto the slope of the island on its starboard⁹⁶ side at a depth of 26 to 30 meters. Heavy cargo, composed of the barrels and casks stowed in the hold of the ship, were scattered to the south. During this accident, many lead white casks, particularly those on the port side of the ship, fell out of their original position. Over time, these casks became demolished, most of them disintegrated, while the lead white remained scattered on the surface. In addition to the cargo scatter, it also has to be taken in consideration that the shapes of ship elements and curves are distorted, and it requires thorough study to reconstruct the original shape of the hull and the original position of the barrels.

Of many discoveries described in a recent publication (Radić Rossi & Nicolardi 2019), the most important was understanding how the ship was oriented on the seabed. Instead of the ship sinking vertically⁹⁷, it was concluded that the ship sunk and leaned on its starboard side, with its bow to the east. Finally, the disposition the cargo on the sea bottom was understandable; alongside the lowest ship element, identified as the keel, was an accumulation of ballast stones, then came heavy barrels filled with raw materials, and above that an element which might be a deck beam, indicating the beginning of the first deck where the cargo of fine glass artefacts had been distributed (Map 4).

The main area excavated since the first excavations began in 1967 encompasses the aft starboard part of the ship and the area along the whole length of the keel (Map 7). The most dominant feature here was the barrel area, where 6 barrels filled with red ochre and 23 casks of lead white were stowed. During the summer of 2019, the excavation revealed one cask of lead white near the beginning of the barrel area, at the forward part of the starboard side of the ship (marked on Map 7). Therefore, from marked barrel, 8 square meters⁹⁸ towards the East is expected to uncover another barrel area.

Above mentioned area described the position of the mercury sulphide bells, barrels filled with red ochre, lead white and missing casks of yellow pigment within the hold of the ship. The exact location of the other colouring materials found in smaller amounts cannot be precisely determined, as they could have been easily packed in textile or leather bags and loaded on the

⁹⁶ Looking from the stern to the bow, the right side of the ship.

⁹⁷ Previous researchers thought that the ship laid down on the seabed sitting vertically on the keel, with the bow to the west and the stern to the east (as presented in Map 1), which is opposite of the interpretation of the hull by Radić Rossi & Nicolardi (2019).

⁹⁸ Calculation made based on the situation in the aft starboard of the ship.

either the first or the second deck. Maps 5 and 6 represent⁹⁹ the sampling position, but besides colouring materials from barrels and casks, it is not possible to claim where others have been stored. Samples as antimony sulphide (GN-2017-CM52), red lake pigment (GN-2017-CM15/CM16), small lumps of mercury sulphide (GN-2017-CM33) rested on their final position probably after the upper decks of the ship had disintegrated.

Total approximate¹⁰⁰ number of the barrels on the side is 47 casks and 10 barrels, not including barrels that were recovered in excavation from 1967 to 1973, conserved and exhibited in the Regional Museum of Biograd na Moru (Fig. 9-5.). The barrels and casks consisted of wooden staves, held in place with wooden hoops. These wooden hoops were locked into place with bindings made of unidentified vegetable material. Some of the barrel heads are marked with initials, but it is not yet clear whether these initials denote the cooperage workshop, or if there was a system of marking the merchandise with the stamp between merchants, used with the aim to distinguish loaded goods. The mark most often appearing is a monogram with the letters S, Z and a cross, typically found on the heads of barrels filled with lead white ingots; it is not yet clear to whom this monogram belonged. Other barrel heads are marked with numbers, like 97 and 37. The symbols can be more illustrative, like the ladder, the head in profile, and palm prints (Fig. 9-6.). Unfortunately, no comprehensive barrel head mark studies have been done on sources in the State Archives of Venice. Even if some studies are done, the whole system of marking cooperage products is unknown and it will take research from multiple aspects of trade to be able to suggest a marking system.¹⁰¹ Future studies will hopefully help understand the complexity and variety of the signs on the barrels.

⁹⁹ The description on the map avoided excessive details so the samples are marked with the plain number, without the entire code.

¹⁰⁰ Each excavation season's catalogue of recovered artefacts includes a number of loose barrel staves and hoops. Because of this disintegration, it is not possible to calculate an exact total number of both barrels and casks present at the site.

¹⁰¹ I am grateful to M. Bondioli and J. DeLancey for correspondance.



Fig. 9-5. and Fig. 9-6. Stamps on the lid of the barrels (left: eds Filep, Jurdana & Pandžić, p. 43; right: personal archive of S. Petricioli).

9.3. Colouring materials present in the cargo of the ship

Colouring materials found at the Gnalić site are a snapshot of Venetian export to the East in the late sixteenth century. Just as *vendecolori* inventories present the lists of goods available in their storage or shop areas (Appendix 7) and insurance documents preserve the variety and amounts of loaded goods (Appendix 8), the Gnalić shipwreck site contains a picture of materials that were exported from Venice, known for its strong colour selling industry and its broad availability of foreign origin products. This is unique archaeological evidence of Venetian trade with colouring materials, with the materials loaded in raw form.

To identify the colouring materials, the author performed a series of characterization analyses. The aim of all these analyses was to identify the materials, to enable their study in the context of the trade in colouring materials in the sixteenth century. Another aim was to collect the results of the analyses of these materials to create a comprehensive database. Upon completion of the project, the results will be accessible for comparative studies within various fields, such as archaeology, art history, geology, and conservation science. The results of these analyses will be the foundation for the reference collection of Gnalić colouring materials, which will be established in the future.

Not all type of analyses was used for all samples; current results of characterization and interpretation give an overview of what has been done so far. Many questions opened after the results were compared with bibliography sources and online databases, so future research will focus to thoroughly research these questions.

As the excavation of the Gnalić shipwreck was restarted in 2012, and progressed during following years, soon it became necessary to conduct analyses of the colouring materials recovered from the shipwreck. Sampling and analyses became urgent after reaching the area of the barrels and casks stored in the cargo hold of the ship. Preliminary analyses were done in collaboration with Vladimir Bermanec from the Faculty of Science, Department of Geology, University of Zagreb. The results of the modern analyses showed the presence of materials not recognized in the studies done by Ivo Kelez in 1970.¹⁰²

Sampling of the colouring materials was performed at the site in parallel with the excavations and the studies of the hull. Characterization analyses were conducted in the spring of 2018 in *Centre Interdisciplinaire de Conservation et de Restauration du Patrimoine* (CICRP), Marseille, while in the spring of 2019 the analyses of lead white, arsenic-based and iron-oxide based colouring materials were performed in *Ateliergebouw*, Amsterdam (Department for Conservation and Restoration, Cultural Heritage Agency of Netherlands, Rijksmuseum). Special assistance was required for the analyses and interpretation of the lake pigment, since recognizing organic components of different hues of scarlet colour demands knowledge and specialization in operating ultrahigh performance liquid chromatography (UHPLC) and an access to databases of dyes and lake pigments, such as the one in the possession of the Cultural Heritage Agency of Netherlands, Amsterdam, Netherlands.

Each colouring material is presented individually. The results of all characterization analyses are summarized in Tab. 9-1., while Appendix 21 represents the data. The titles are combination of the term used in the dissertation, and suggested historical name of the colouring material (in brackets).

¹⁰² The materials not sampled by Ivo Kelez and published in Vrulje includes arsenic sulphide-based colouring materials (orpiment and realgar), minium, red ochre, red lake pigment.

Tab. 9-1. The results of the characterization analyses (Appendix 21)

Explanation of abbreviations: LE (light elements in XRF); n/a (analyses not executed or cannot be applied). Explanation of fonts: **major**; *minor*; traces.

Colouring material	Sample number	Colour / Condition	XRF	SEM texture	SEM-EDS chemical elements ¹	XRD	FTIR	RS	UHPLC	Interpretation
Lead white	GN-2017-CM36	White / Ingot: powder from the white core	n/a	Irregular crystals from 100-200 µm and fine grains	Pb , Mg, Al, Cl, Ca	Almost 100% cerussite and one minor component present	n/a	n/a	n/a	Cerussite , Calcite less than 5%
	GN-2017-CM39 (SP-01)	Black / Alteration layer from the ingot	Pb: 38.76 LE: 24.97% S: 14.02% Fe: 12.54% As: 4.21% Ca: 3.81% Si: 1.37%	Irregular bright crystals from 100-200 µm and fine black grains	Pb , Na, Ca, Fe, As	n/a	Cerussite	Cerussite, Galena	n/a	Cerussite, Galena
	GN-2017-CM39	White / Ingot: powder from the white core	n/a	Irregular bright crystals from 100-200 µm	Pb , Al, Ca, Fe	n/a	n/a	Cerussite, Calcite	n/a	Cerussite, Calcite
	GN-2017-CM42	White / Ingot: powder from the white core	n/a	Irregular bright crystals from 100-200 µm	n/a	n/a	n/a	Cerussite, Calcite	n/a	Cerussite, Calcite
Red ochre	GN-2017-CM02	Red / Powder	n/a	Fine-grained	Al, S/Pb, Fe Si, K, Na, As, Mg, Ca, As	n/a	Red ochre (hematite and quartz)	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, clay minerals) possible contamination with sulphur (pyrite?)
	GN-2017-CM04	Red / Powder	n/a	Fine-grained in combination with irregular and round-irregular sand-like particles	Al, Si, Ca, Fe Na, Mg, Cl, P, S, K, As	n/a	Red ochre (hematite and quartz)	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, clay minerals) contaminated by the sand (sand bag for <i>in situ</i> protection of the barrel)

¹ Oxygen (O) and carbon (C) are always recorded with SEM-EDX. As those could be the pollution from the air in the chamber, here are only mentioned when existing in large amounts.

Colouring material	Sample number	Colour / Condition	XRF	SEM texture	SEM-EDS chemical elements	XRD	FTIR	RS	UHPLC	Interpretation
Red ochre	GN-2017-CM05	Red / Powder	LE: 46.27% Fe: 23.30% Al: 8.37% S: 3.52% Si: 4.52% Pb: 2.43% K: 1.23% Ca: 0.66%	Fine-grained	Al, Fe, Si, Ba, Na, Mg, P, Cl, K, Ca	Hematite (53.7%) Alunite (36%) Quartz (2%)	Red ochre (hematite and quartz), calcium carbonate	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, alunite, clay minerals)
	GN-2017-CM06	Red / Powder	LE: 49.48% Fe: 26.27% Al: 9.45% S: 3.78% Si: 4.83% Pb: 2.03% K: 1.46% Ca: 1.65%	Fine-grained	Al, Si, Fe, S, Cl, Na, Mg, P, K, Ca	Hematite (50.0%) alunite (34.8%) quartz (15.2%) magnesite (?)	Red ochre (hematite and quartz), calcium carbonate	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, alunite, clay minerals) magnesite calcium carbonate
	GN-2017-CM14	Red / Powder	n/a	Fine-grained on rounded particles	Al, Si, Fe, S, Cl, Ca, Na, Mg, P, S, K, Ba	n/a	Red ochre (hematite and quartz), calcium carbonate	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, alunite, clay minerals) calcium carbonate
	GN-2017-CM31	Red Powder	n/a	Fine-grained	Al, Fe, S, Si, K, Ba, Na, Mg, P, Cl, K, Ca, As	n/a	Red ochre (hematite and quartz), calcium carbonate	Red ochre (hematite, silica, clay)	n/a	Red ochre (hematite, quartz, alunite, clay minerals) calcium carbonate
Mercury sulphide (type-B)	GN-2017-CM33	Scarlet / Lump: powder taken from the core	Hg: 55.67% S: 23.4% LE: 11.37% P: 1.7% Si: 1.46% K: 1.23% Ca: 0.66% Ca: 0.59% Pb: 0.11% Fe: 0.1%	Regular-shaped particles of size 300-500 µm	Hg, S, Al, Si	Mercury sulphide (100%)	n/a	n/a	n/a	Mercury sulphide

Colouring material	Sample number	Colour / Condition	XRF	SEM texture	SEM-EDS chemical elements	XRD	FTIR	RS	UHPLC	Interpretation
<u>Minium</u>	GN-2017-CM35a	Orange – red / lump, powder taken from core	Pb:54.88% LE: 22% S: 15.55% Ca: 2.06% Si: 1.98% As: 1.37%	Fine-grained texture, on SEM are visible irregular longitudinal particles, size 5-20 µm	S/Pb, Na, Mg, Al, Ca	Minium (40%), Quartz (34.6%), Hydrocerussite (16.4%), Plattnerite (8.9%)	n/a	n/a	n/a	Minium, Quartz, Hydrocerussite, Plattnerite
	GN-2017-CM35c	Dark grey / lump, powder taken from alteration layer	Pb: 45.03% S: 23.6% LE: 20% S: 15.55% Ca: 7.78% Si: 1.5% As: 1.13%	Irregular flaky, crystals, approximate size 150 µm, with fine grains. Heterogenic texture and different hues visible	S/Pb, Ca, Mg Al, Cl	Cerussite (50.9%), Lead sulphide / galena (49.1%)	n/a	n/a	n/a	Cerussite Lead sulphide / galena
<u>Arsenic sulphides</u>	GN-2017-CM18	Yellow / Mixed with sand	LE: 60.35% Ca: 13.13% Si: 9.56% Mg: 7.5% S: 2.51% Al: 2.39% As: 1.9% Fe: 1.74%	Fine-grained powder mixed with round-irregular sand-like particles	Mg, Si, Al, S, K, Ca, As, Na, Fe	n/a	n/a	Realgar	n/a	Realgar
	GN-2017-CM08	Yellow / Mixed with sand	LE: 44.15% Fe: 23.3% Al: 11.59% S: 10.39% Si: 4.4% Pb: 2.16% K: 1.52% Ca: 1.09%	Fine-grained powder mixed with round-irregular sand-like particles	Mg, Si, Al, S, Fe Na, K, Ca, As	n/a	n/a	Realgar	n/a	Realgar
<u>Antimony (III) sulphide, stibnite</u>	GN-2017-CM52	Grey with lustre / Lump: powder taken from the core	Sb: 51.31% Ca: 22.35% S: 13.43% LE: 10.13% Fe: 0.92%	Bladed grey crystal of various sizes, 10-100 µm	S, Sb, Al, Si, Fe	Almost 100% antimony (III) sulphide and one minor component present	n/a	n/a	n/a	Antimony (III) sulphide, stibnite

Colouring material	Sample number	Colour / Condition	XRF	SEM texture	SEM-EDS chemical elements	XRD	FTIR	RS	UHPLC	Interpretation
Red lake pigment	GN-2017-CM15	Dark purple with lustre / ball embedded to epoxy resin	n/a	Fine-grained heterogeneous powder	C, Al, Si, S, Na, K, Ca, Fe, Cu, N, Mg, P, Cl	n/a	n/a	Cochineal, Quartz	n/a	Cochineal, Quartz
	GN-2017-CM16	Dark purple with lustre / ball grinded to powder	LE: 79.55% S: 5.32% Al: 4.68% Si: 2.4 Ca: 2.12% Fe: 2.11% Pb: 1.59%	Fine-grained heterogeneous powder	C, Al, Si, S, Mg, Ca, Fe Na, K, Cu, Hg	Alunite (80.4%) Quartz (12.1%) Gypsum (7.5%)	Wool?	n/a	Brasilein, Carminic acid, Kermesic acid, Unknown orange component, Alizarin, Purpurin, Several unknown components, probably not colorants	Red lake pigment (cochineal, madder and brazilin), Alunite, Quartz, Gypsum?

9.3.1. Lead white (*cerussa*)

9.3.1.1. General information

Lead white was a favoured white colourant since Antiquity; its excellent covering capabilities and its ability to mix with other colours to create different hues were the reasons why it remained in intensive use until the twentieth century; in the nineteenth century, it was partially replaced by zinc oxide, but it entirely went out of use later in the twentieth century when titanium oxide was introduced as a pigment (Roy ed. 1993, pp. 68-69). It has been widely used in cosmetics, and it has been found within the funeral contexts of finds from Egyptian, Greek, and Roman periods (Beck et al. 2018). Historical sources mark its use as a remedy, and it also appears in the repertoire of pharmacies, such as *spezeria* in Santa Maria della Scalla in Rome as discussed in chapter 2 (Cavallo & de Ágredos Pascual, 2018, p. 2).

The multiple uses of lead white were presented by Biringuccio (1942). Although he used the title ‘lead’, it can be suggested that his observations were made on lead white, as he referred to whiteness, and making dark women white:

‘In addition to these very useful effects, lead has a power to serve man in many other ways; the doctors also make use of it in many sicknesses. Women in particular are very indebted to it, for, with art, it disposes to a certain whiteness, which, giving them a mask, covers all their obvious and natural darkness, and in this way deceives the simple sight of the man by making dark women white and hideous ones, if not beautiful, at least less ugly.’ (Biringuccio 1942, p. 55)

The use of lead white was particularly intensive during the Early Modern period. Lead white proved to be a favorable material applied to paintings after the introduction of the painting with oil technique. Lead white is known for its excellent covering capabilities and opacity. It could be used for priming of paintings, and it was a crucial material to obtain different lighting in paintings (Pulsifer 1888, p. 203). Consequently, it became widely used in parallel with the development of art and manufacture. This was especially emphasised in Venice, where the pigment adopted the title ‘Venetian’ and became noted for its quality (Berrie & Matthew 2011, pp. 295-296).

9.3.1.2. Archaeological context

The most numerous colouring materials recovered from the sunken *Gagliana grossa* are lead white ingots (Figs 9-7., 9-8., 9-9. and 9-10.). All of them are conical-shaped, but the weight and size vary. The ingots have an average height of 5.5 cm, a diameter at the top of 6.3 cm, and a diameter at the bottom of 2.6 cm, while average weight is 390 g.¹⁰³ Different types and sizes of conical shapes are presented on selected samples in Appendix 15. This shape is obtained by pottery pots used for the manufacture of lead white, to create the shape of ‘loaves’ (Berrie & Matthew 2011, p. 296; Stols-Witlox 2011, pp. 285-288).

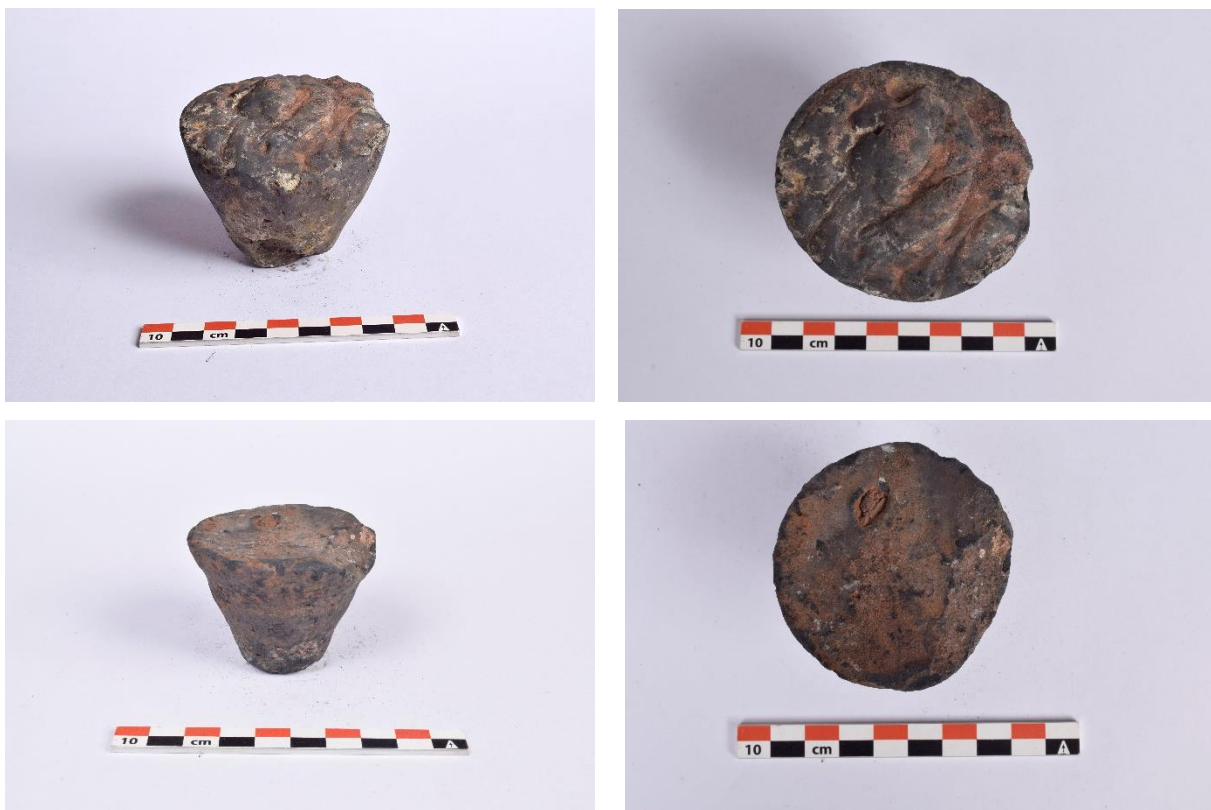


Fig. 9-7., Fig. 9-8., Fig. 9-9. and Fig. 9-10. Lead white ingots from the Gnalíć shipwreck (photo: K. Batur).

The external surface of the lead white ingot is usually coloured, due to the contact of lead with the other substances which were present in the cargo. The thickness of alteration layer can vary, from 2 mm to 15 mm and sometimes even more (Fig. 9-11.), depending upon how long and under what condition the lead white cone was in contact with the substance which caused the reaction. Lead white was exposed to the powder of arsenic sulphide-based and iron

¹⁰³ Average calculation is based on selected lead white cones marked in the Appendix 20. The number of lead white cones is over one thousand, and they require special laboratory conditions for recording.

oxide-based (red ochre) colouring materials. Since lead is reactive with sulphur, the external surface probably reacted with arsenic sulphide-based colouring materials or other sulphur-containing components at the site. This reaction initiated conversion of the lead carbonate (PbCO_3) into lead sulphide or galena (PbS) (Kelez 1970, p. 44; Pearson 1987, p. 243).¹⁰⁴

Marine growth was often spotted on the lead white scattered on the surface layers, sometimes resulting in damages made of millimetre-size holes (Fig. 9-12).¹⁰⁵ This damage could allow water to penetrate to the core. The layer of galena on the external surface might have had a role of a protective layer to the core of the sample, but at the same time the cracks which appeared as a result of the interaction with organic acids from marine growth could allow the water to penetrate. As no study of alteration product was done on the artifacts, the results of characterization analyses should be taken with great caution. Some mineral phases and chemical elements present perhaps do not belong to the original matrix, but could be the result of reactions with the marine environment.

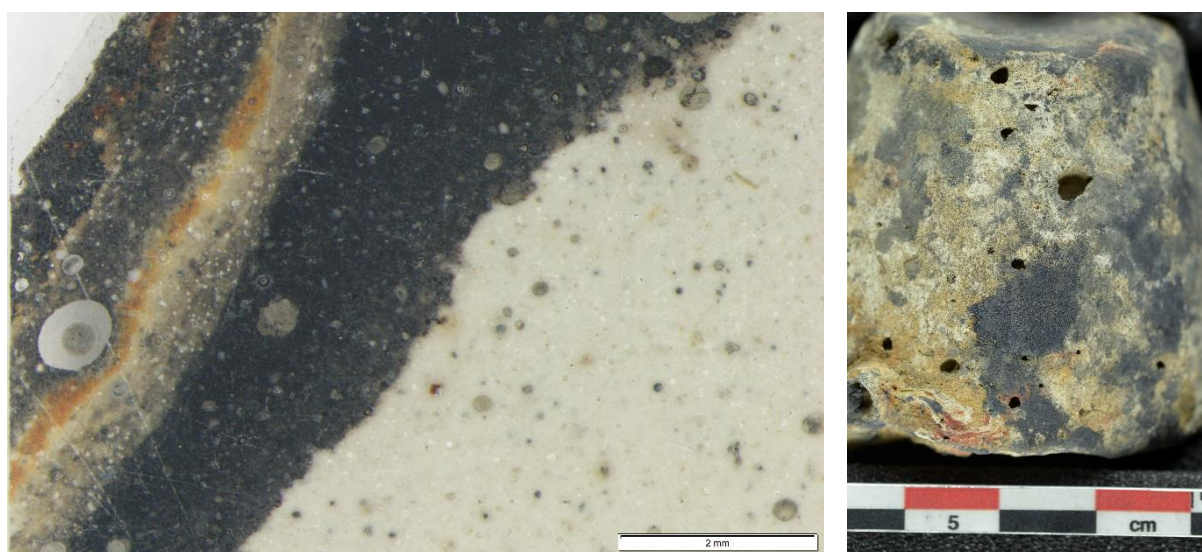


Fig. 9-11. and Fig. 9-12. represent an alteration layer created in contact with the underwater environment. Left photo: the thin section of GN-2017-CM39 (photo: K. Batur); right photo: the surface layer of lead white ingot CM-2017-CM46 (photo: O. Guillon).

While this study delivers the results of the characterization and identification only, future studies should perform multiple analyses of the core, alteration layer and the sediment from the environment to understand whether the reactions with the environment had any impact on the matrix in the core of the lead white.

¹⁰⁴ Also identified by Kelez (1970, p. 44). Black crust on the surface of the ingot is several millimetres thick, and is made of lead sulphide, which was created due to the high presence of hydrogen sulphide on the site.

¹⁰⁵ Lead can be damaged heavily by organic acids from the sea. These acids can be from marine growth or other organic materials in the vicinity which decompose (Pearson 1987, p. 244).

Regarding packaging methods, it might be assumed that all lead white ingots could have been wrapped in organic materials, such as leather-like material. However, this has never been attested in the upper layers of the barrel area. After the recovery of barrel 3, which was originally filled with red ochre, an interesting find appeared. Sealed under barrel 3 were three lead white cones, wrapped in material that is presumably leather with remains of straw attached (Figs 9-13. and 9-14., Appendix 16). It is not known whether lead white ingots were normally wrapped when transported in ships, and if they were, which materials were the most common. Later sources dating to the eighteenth century mention wrapping lead white in blue paper, as it was believed that would preserve a cooler tone of white colour (Pulsifer 1888, p. 269; Stols-Witlox 2011, p. 285).

Lead white ingots are packed in wooden casks of approximate height from 43 to 45 cm and an average head diameter of 30 cm (Fig. 9-15.). Some lids bear a mark on the top. These marks vary, and they can include letters S, Z and cross; the sign of ladder; letters G, P and the profile of head (Appendix 12). Ingots were placed in the barrels and secured by straw-filling. Early excavation reports mention a complete cask of lead white ingots taken out, which weighed 33 kg (Petricioli 1981, p. 44).¹⁰⁶



Fig. 9-13. and Fig. 9-14. Lead white wrapped in leather (photo: M. Martinčák).

¹⁰⁶ This cannot be confirmed by recent excavations. No complete barrels have been recovered.



Fig. 9-15. Barrel filled with lead white, Regional Museum of Biograd na Moru (photo: I. Asić).

Barrels are found entirely or preserved only in section (Fig. 9-16.); many lead white ingots that were carried on the port side collapsed onto the starboard side. Excavation of the starboard side revealed there were at least 41 casks. The amounts of lead white cones recovered from the site exceeds 1500, and there are still more lead white ingots covered with layers of sand or scattered on the site.



Fig. 9-16. Remains of casks filled with lead white in the position of B16. On the right side are long barrels, with unidentified contents (photo: S. Govorčin).

9.3.1.3. The results of the characterization analyses

For the aim of characterization analyses, samples GN-2017-CM36, -39 and -42 were used, while additional samples were taken from the group of lead white sampled in 2018 for the purpose of performing lead isotope analyses (Appendix 20). In order to reach the core of the sample, selected lead white cones were cut in half (Figs 9-17. and 9-18.). In the case of sample GN-2017-CM39 analyses of the samples included two different sample locations – the alteration layer and the core. GN-2017-CM39 and -42 were embedded in epoxy resin afterwards, while GN-2017-CM36 was sampled in powder.

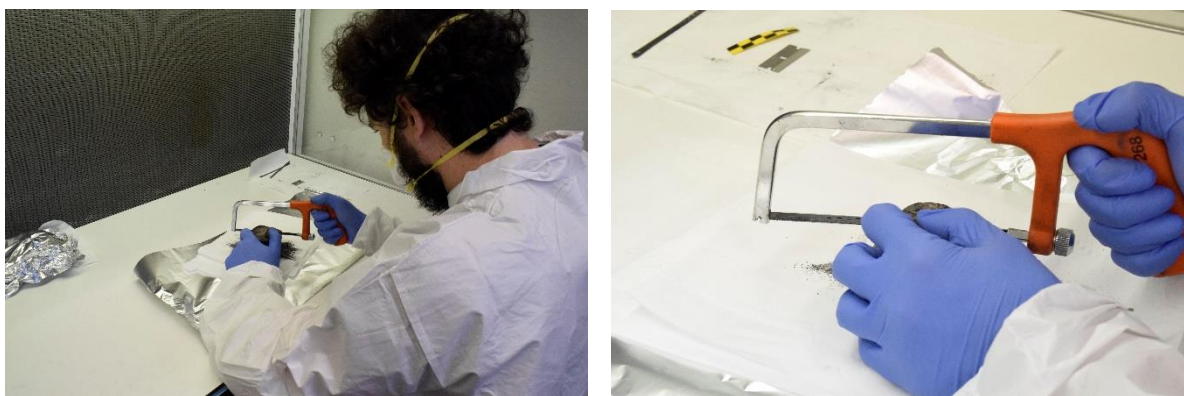


Fig. 9-17. and Fig. 9-18. Cutting lead white ingots at the Department for Geochemistry, Vrije University, Amsterdam, Netherlands (photo: K. Batur).

a) Alteration layer

The alteration layer is made of a combination of cerussite, which was part of the original composition of lead white, and galena, which was created by a reaction of lead with a sulphuric environment. Microscope photos of GN-2019-CM39 (SP-01)¹⁰⁷ clearly show the difference between crystals of cerussite and galena (Appendix 21, GN-2019-CM39).

The characterization analyses are based on the results of XRD, FTIR and RS. SEM-EDX was used to make observations on morphology particles within the sample, while it was impossible to use it to understand the difference between cerussite (PbCO_3), hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, and galena (PbS), as there are overlapping X-Ray wavelengths between the peaks of Pb and S¹⁰⁸ and the software is usually not able to distinguish chemical elements. The

¹⁰⁷ The sample of grey alteration layer was named SP-01 according to French *section polie* (eng. cross-section), to designate that this sample was taken before the lead white was embedded in epoxy resin.




¹⁰⁸ Wavelengths are overlapping on S ($K\alpha_1 = 2.309$ keV, $K\beta_2 = 2.465$ keV), and Pb ($M\alpha_1 = 2.342$ keV, $M\beta_2 = 2.444$ keV) (from www.bruker.com/hhxf).

spectra of SEM-EDX have shown additional trace elements within the sample, which could be the product of contamination from the environment.

b) The core

The core of the ingot is made of either pure cerussite, or made of a combination of cerussite and hydrocerussite, depending on the ingots studied (Tab. 9-2.). There are samples which contain calcite, which was used as an extender.¹⁰⁹ If calcite existed in the sample, it was at a concentration of less than 5%, which means it cannot be recognized by XRD. According to results presented in Tab. 9-3., all the lead white ingots selected for analyses were adulterated by a small percentage of calcite.

It is possible that sea water penetrated through cracks and holes of the lead white structure and created inner bright-grey alteration layers (see figures of GN-2018-LW3 and GN-2017-CM36 in Tab. 9-2.). It is not entirely clear if the presence of hydrocerussite was obtained by original recipe or is the result of contact with water. Hydrocerussite could have been a part of the original matrix or resulted as a consequence of contact with the marine environment.

GN-2018-LW2	GN-2018-LW3	GN-2017-CM36
Cerussite 35% Hydrocerussite 65%	Cerussite 100% Minor component present	Cerussite 100% Minor component present
		

Tab. 9-2. The results of XRD analyses¹¹⁰ of GN-2017-CM36, and samples additionally selected in 2018 – GN-2018-LW2 and –LW3. Arrow marks possible inner alteration layers (photo: K. Batur).

¹⁰⁹ The only information available about the composition of the lead white was published by Kelez (1970). The ingot sampled by Kelez (170, pp. 43-44) in section revealed the composition of 65.5% Pb, 6.1% Ca, 0.8 % Mg, traces of other metals and the remains of CO₃ and OH ions. Stoichiometry calculation resulted in the presence of 82% hydrocerussite and 18% calcite.

¹¹⁰ Analyses performed by Victor Gonzales, Rijksmuseum.

Sample number	SEM / EDX	XRD	FTIR	RS	Results
GN-2019-CM36	C, O, Pb Mg, Al, Cl, Ca	Almost 100% of cerussite, unidentified minor component present	n/a	n/a	Cerussite, calcite
GN-2019-CM39 (SP-01)	C, O, Pb/S Na, As, Ca, Fe	Cerussite, galena	Cerussite	Cerussite, galena	Cerussite, galena, calcite
GN-2019-CM39	C, O, Pb Fe, Ca, Fe	n/a	n/a	Cerussite, calcite	Cerussite, calcite
GN-2019-CM42	n/a	n/a	n/a	Cerussite, calcite	Cerussite, calcite

Tab. 9-3. Characterization analyses done on the alteration layer GN-2019-CM39 (SP-01) and the core (GN-2019-CM36, -CM39, -CM42). Explanation of fonts and abbreviations: **Bold**: Major, *Italic*: Minor; Normal: traces of chemical elements; n/a: analyses not conducted)

9.3.1.4. Production and processing

Lead ore is impure in nature, so it requires smelting in order to separate the lead from other substances. Biringuccio (1942, pp. 56-58) describes several procedures, with the most common smelting lead ore in rectangular furnaces. These furnaces had openings on the top and in front to allow draft to enter. The bottoms of furnaces had a slope which acted as a channel; these could direct melted lead to canisters. After cooling off in canisters, the lead took the form of cakes.

Lead ore often appears in nature associated with silver ore. These deposits were collected mostly with the aim of procurement of silver. The ore was placed in furnaces and heated, and since lead has a low melting point, it would separate from the silver. This process is known by the name of cupellation, and lead-based material was a by-product of this process (Fabian & Fortunato 2010, p. 427). The lead ore of cerussite, commonly used as a colouring material, appears in the nature as a secondary mineral, an alteration product of galena.

As lead white came into common use, and demand increased for lead white of great quality, the procedure for production of a synthetic variant of cerussite was invented. The

production of the synthetic variant is based on conversion of metallic lead (galena) into cerussite and hydrocerussite, and the earliest testament to its synthetic production dates back to Classical Antiquity (Beck et al. 2018). The Early Modern period marks a large increase of production centres, whose products gained a popularity in Europe (see examples of Venetian, Dutch and English lead white given by Pulsifer 1888, p. 214).

In the sixteenth century lead white started to be massively produced. The process that was used for the production required a large amount of well-sealed jars to be placed in one room, giving the manufacture process the name ‘stack process’. After a production explosion in the Netherlands in the seventeenth century, the process earned the title ‘Dutch process’ (Gonzales et al. 2018). Pulsifer (1888, p. 269) states that although the name ‘Dutch process’ was widely accepted, the manufacturing process originated in Italy.

There is no thorough study about lead white production and the capacity offered by Venetian lead white colour sellers. Historical sources that mention the lead white from Venice usually refer to it as a material of great quality. By making an overview of pigments identified on the layers of Renaissance paintings and data from the historical documents referring to colour sellers, Berrie and Matthew (2011) suggested which procedure might have been used to produce lead white in Venice. It can be assumed that the process was similar to the ‘Dutch’ or ‘Stack’ process. The metallic lead, in the shape of sheets or rolled into cylinders, is placed most often on the wooden twigs above pottery pots filled with vinegar and well-sealed with a ceramic or lead lid (Berrie & Matthew 2011, p. 295).

After cerussite is created on the surface of the lead sheets, it could be scraped off, collected and refined by various processes. Berrie and Matthew (2011, p. 297) deliver additional information from the inventories of colour sellers specialized in the manufacture of lead white, where we can see which tools and storage containers were available for lead white processing. The tools appearing within these inventories allow us to assume that the lead white was first heavily smashed, then ground, then soaked in water and repetitively washed. Within this process of washing, the particles were left to settle down, while the finest particles were collected. In the end, the finest particles collected from the mass were placed in conical ceramic moulds, so called loaves, known by the Italian name ‘pane’ (Fig. 9-19.).

To sum up, the production of lead white in Venice was based on procedures which stimulate corrosion on the surface of the lead-based material, in the presence of organic acids and carbon dioxide. This is done by exposing metallic lead to vinegar fumes while surrounded by horse manure, tan bark, urine in decomposition, or mineral poured in vinegar. While lead in reaction with vinegar results in the creation of lead acetate, the presence of carbon dioxide helps

to convert lead acetate to lead carbonate. The processes described in historical sources have been discussed and tested by scientists, resulting in the conversion of lead to cerussite and hydrocerussite (Gonzales et al. 2018). Experimental synthesis has proved different phases of creation corrosion on the metallic lead occurred, with the aim of reconstructing the manufacture process (Gonzales et al. 2018).

Historical recipes suggest how to refine the lead white to make it of great quality, by washing, decanting, soaking in vinegar and drying in the sun. Stols-Witlox, Megens & Carlyle (2012) performed multiple experiments to reconstruct these procedures on lead white. The authors concluded that the particle size and mineral phases present in the material depend on whether the lead white was ground and washed with vinegar or water. The results of procedures were analysed through BSE images of SEM-EDX, thus giving a scientific explanation of procedures described in historical sources. The success of the procedure depended on many factors, such as the source of raw materials and the condition under which the corrosion appeared (Stols-Witlox, Megens & Carlyle 2012, p. 112).



Fig. 9-19. Lead white was manufactured in conical ceramic moulds. This example represents the lead white mould from the mill ‘De Rob’, Koog an de Zaan, Netherlands, collection of Mollenmuseum (Stols-Witlox 2011, p. 288).

9.3.1.5. Trading with Venetian lead white

In the sixteenth century, Venice was a centre for the manufacture lead white, and it exported large amounts of lead white towards the Eastern Mediterranean. Maritime insurance documents issues by G. A. Catti and A. Spinelli reflect how in the transition from the sixteenth to seventeenth century especially large shipments were sent to Alexandria and Constantinople

(Tenenti 1959, numbers 3/10, 42/399 and 46/475 in Appendix 8). Venetian lead white gained its popularity, and it was distinguished among merchants. For example, in a Frankfurt trade catalog from 1582, lead white appears as ordinary (*bleyweiß*), Venetian (*cerussa Veneta*, *Venedisch bleyweiß*) and Antwerp or Netherlandish lead white (*cerussa Antverpiana*, *Niederländisch bleyweiß*) (Heydenreich, 2010, p 305).

It is known that sixteenth century Venice had active manufacturers of lead white. The number of active producers is unknown, but according to the published research (Matthew and Berrie 2010; Berrie & Matthew 2011), manufacture of lead white can be associated with colour sellers (*vendecolori*). It was attested that at least two shops specialized in the manufacture and refining of lead white existed in Venice in the second half of the sixteenth century: one was owned by Giovanni Griffalconi, and was active as early as 1551; the second was owned by the Gradignan della Scala family (the Ladder sign), which, besides lead white, specialized in selling other substances, such as mercury, and perhaps tin. Not much information about their production is known, for *e.g.* manufacture capacity, which facilities they owned, and how the lead white was produced. It is a problem that can be researched from various aspects, and it requires a thorough comprehensive study by a team of scholars to learn more about the lead white production in Venice.

Berrie and Matthew (2011, p. 296) suggest that more than one type of lead white was produced in Venice during the sixteenth century. The painters were aware of the properties of different lead white materials, and they might have had preferences over different source or different manufacture techniques. The main argument involved layers of paintings, which allowed the master to choose lead white with different ratios of cerussite and hydrocerussite. The choice depended upon the layer of the painting – different hues of lead white were applied in priming and painting – but also in regard to the desired effect to be achieved.

9.3.1.6. Discussion

Lead white was an indispensable raw material used in art, manufacture, and everyday life. It is one of the products that defined sixteenth-century Venice. While Venetian lead white is known from historical sources and a limited number of analyses done on Venetian paintings, lead white from the Gnalić shipwreck provides a unique insight into its appearance, transport and manufacture capacity.

Based on the difference in terminology used by manufacturers and the results of scientific analyses on paintings, scholars (Berrie & Matthew 2011; Stols-Witlox 2011) suggest that the painters either had access to, or knew how to prepare, different types of lead white. By studying the lead white from the Gnalić shipwreck, the author can pose the question – was there a difference in composition in lead white present in the cargo, and if yes, how were these different compositions distinguished? It can be suggested that there was a system of separating lead white according to the conditions of production and the refining process.

Separating lead white according to composition and/or quality could perhaps be done by using moulds of different size and shape during manufacture, or by packing different lead whites in different barrels. Studying the shape of the lead white in relation to different ratios of cerussite, hydrocerussite and calcite may give an answer to whether different types of lead white were segregated on board.

However, before taking the composition of lead white in Tab. 9-2. and 9-3. as representative, a study of alteration products has to be done. For *e.g.* the fact that the hydrocerussite might be created due to the penetration of seawater, or even the tap water which was used to wash the surface of lead white upon recovery, should be considered.

The characterization analyses have provided results for the selected samples, but in the context of the manufacture, trade and use of the Venetian lead white, they raise more puzzles which can be solved by future research projects.

9.3.2. Red ochre (*terra rossa*)

9.3.2.1. General information

Being one of the colouring materials studied extensively, red ochre has been found as a raw material and as a pigment in Prehistoric cave and tombs paintings from all around the world. The oldest attestation of its use comes from South Africa. The earliest use of red ochre is marked in the Middle Stone Age¹¹¹, which makes it one of the first materials humans used for purposes of artistic expression, dyeing, decoration, body painting, funeral practices and healing properties. The well-known examples of use are from the Middle Stone Age layers of Diepkloof Rock Shelter, Western Cape, South Africa, where the complete process of red ochre use was recognized – from obtaining the raw material, to ore processing, and finally use (Dayet et al. 2013, p. 2). Red ochre pieces from the Middle Stone Age layers in Blombos Cave, South Africa, dating to 75 000 – 100 000 BP, are the earliest known artifacts testifying to human cognitive thinking and deliberate efforts to create decorative patterns (Henshilwood, d’Errico & Watts 2009).

Red ochre use for its healing properties was reported by early explorers in the eighteenth century. It was applied internally and externally; it was noted by explorers that clay-eating was a daily routine of societies, while external application was mainly oriented on healing wounds. Therefore, it is not excluded that prehistoric tribes had awareness of red ochre’s properties and thus applied it often in medical purposes (Velo 1986, pp. 230-231).

Throughout history, red ochre was often used as a painting material due to its great covering abilities, permanence, and compatibility with other pigments. Considering the Renaissance, it has been mostly attested on frescos.¹¹² Kirschel (2002, p. 103) reports that it has been used by Venetian painters Titian and Veronese, while Bassano used it to paint boxes. Presumably, as it was relatively common and did not require complex refining techniques, red ochre must have been available at a low price.

¹¹¹ Blombos cave, South Africa (Henshilwood, d’Errico & Watts, 2009).

¹¹² There are numerous examples of red ochre used in wall-painting. For *e.g.* see Rossi-Manaresi, Tucci & Nonfarmale 1990.

9.3.2.2. Archaeological context

Red ochre from the *Gagliana grossa* was preserved as a fine powder, composed of hematite, alunite, quartz, and clay minerals. Red ochres were stored in oval barrels of 80 to 90 cm length, with a lid diameter from 60 to 65 cm. All the barrels were stored in the hold of the ship, surrounded by the casks of lead white ingots and arsenic sulphides (Fig. 9-20.). When the ship sank, it came to rest on its starboard side, along the underwater slope of the sea bed. As the ship's hull buckled over the centuries and put pressure onto the cargo, the barrels collapsed where the wood was not supported by the contents of the barrel. Therefore, the barrels containing red ochre are only partly preserved (Fig. 9-21.); however, studying the surviving sections can help us to understand their original volume, and therefore suggest how much red ochre was originally in the containers.

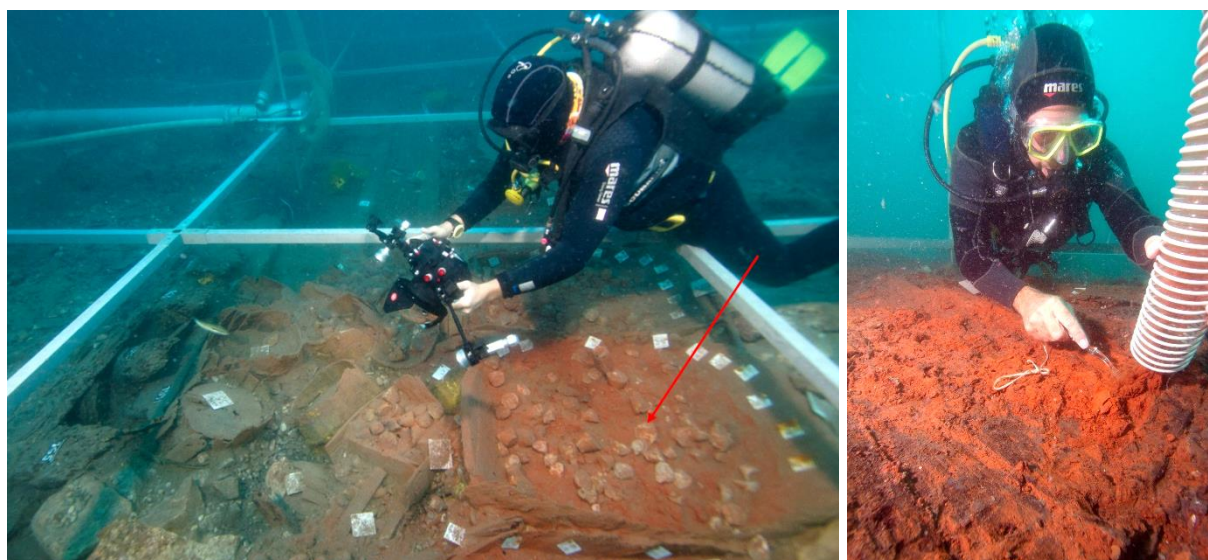


Fig. 9-20. and Fig. 9-21. Barrels filled with red ochre. All barrels were partially preserved, thus some materials from upper layer, especially lead white ingots, rested in the barrels, as presented in the left photo (photo: S. Govorčin).

There were at least six large oval barrels within the hold of the ship filled with red ochre. There might have been more, based on the descriptions recorded by previous researchers, such as an accumulation of red colour which had preserved two rectangular shapes (Radulić, unpublished report, 1973). Long barrels with red contents, numbered with 2, 12, 13, and 21 in the recent excavations, have not yet been sampled, so it is likely that sampling during future excavations will increase the known number of barrels containing red ochre.

9.3.2.3. The results of the characterization analyses

Samples were taken from barrels filled with red powder in the summer of 2017. Sample locations included barrels numbered 1, 3, 4, 5, 6 and 7 (Maps 2-4). Barrel 1 was sampled from the wooden stave (GN-2017-CM02), while barrels 4 (GN-2017-CM14), 5 (GN-2017-CM04), 6 (GN-2017-CM05) and 7 (GN-2017-CM06) were sampled underwater. Since barrel 3 was emptied in 2014, the sample was taken from its contents stored in the laboratory (GN-2017-CM31). It is important to note that the barrels were only half-preserved, just like most of the casks of lead white ingots. This means that, even if the amount of material in the barrel was large, it was still potentially contaminated with the remains of the materials that collapsed from the upper deck or rolled into the area from the port side (Fig. 9-20.).

However, all samples are consistent in composition. The pattern obtained by the results of XRD analyses on GN-2017-CM05 and -CM06 suggest the impart of hematite (around 50%), alunite (around 35%) and quartz (less than 15%). Clay minerals are present, which is suggested by the background XRD patten not attached to zero. Differences are noticeable, logically, in the barrels which contained other inclusions, either materials from nature or those introduced by archaeologists during underwater work. For example, sample GN-2017-CM04 from barrel 5 contained some of the sand used for *in situ* protection of the site. It is also possible that sample GN-2017-CM04 was contaminated by sulphur (S), possibly from the arsenic sulphides which were packed in the casks nearby. Calcium carbonates present in samples GN-2017-CM06, -CM14, and -CM31 reflect contamination from the sea environment. It is particularly interesting to note the presence of barium (Ba) in samples GN-2017-CM06, -CM14 and -CM31, which is unusual and its origin is unknown.

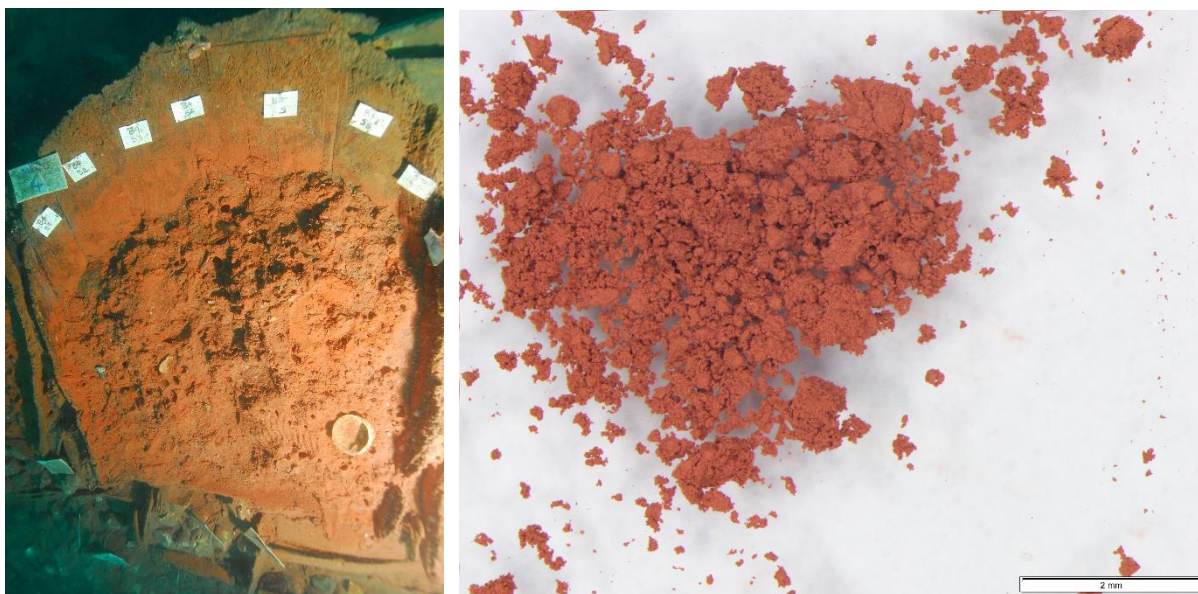


Fig. 9-22. and Fig. 9-23. Barrel filled with red ochre (GN-2017-CM14 / barrel 4). Fine grains of red ochre under binocular (GN-2017-CM05 / barrel 6) (left photo: S. Govorčin; right photo: K. Batur).

There was an unidentified component present in almost all samples, with peaks at 119 and 243 cm^{-1} of the Raman spectroscopy. These peaks are typical for lead-based components;¹¹³ however, lead was not attested in significant amounts in the mineral phase of the XRD pattern.

9.3.2.4. Production and processing

Minerals in the iron oxide group¹¹⁴ commonly appear in nature and are widely available on planet Earth. Iron (III) oxide or hematite is the major component of red ochre, with addition of clay and quartz (Dayet et al. 2013, p. 3). Biringuccio (1942, p. 77) categorizes ochres as ‘semi minerals’, which are applied as painting materials, but he does not provide any description of how red ochre ore was refined. It is known that ochre, after being recovered from the deposits, was ground while still wet (Eastaugh et al. 2008, p. 326). When the grinding produced a fine-grained structure, it was a sign that the ochre was refined and ready-to-use.

Even though hematite, a major component of red ochre, was readily available in nature, humans learned how to synthesize it. During history, it was well known that hematite, iron (III) oxide, can be produced by heating goethite, an iron oxide hydroxide. Researchers managed to reconstruct the process of heating at a temperature from 250 to 700°C, and observed the changes

¹¹³ According to lead based components in IRUG database (<http://www.irug.org/search-spectral-database/spectra-index>).

¹¹⁴ The iron oxide group encompasses the iron oxides, iron hydroxides, and iron oxide hydroxides. The iron oxide group includes, amongst other minerals, hematite, magnetite, maghemite and wüstite (Cornell & Schwertmann, 2003).

in the crystal structure. They suggested in several cases that, if the material is heated to the abovementioned temperature, the synthesized crystal structure can be distinguished from natural hematite (Périnet & Onoratini 1987, p. 51). In this way, sometimes it is possible to determine the production process (Pomiès, Menu & Vignaud 1999; Salomon et al. 2012).

According to the author's knowledge, there is a complete absence of information about the production and refining processes of iron-oxide based colouring materials used in Renaissance Venice. However, since red ochre was available locally, it can be assumed that no synthesis by heating goethite was required for production. Further analyses of mineral structure with the Transmission Electronic Microscope (TEM) are required to support the statement about the production.

9.3.2.5. Trading with red ochre

There are very scarce sources which can be taken as evidence for trade with red ochre. Nevertheless, it was known there was no need to import red ochre to Venice, as it was readily available in the vicinity of Venice.¹¹⁵ At the site of Badia di Calavena in the high Illasi Valley region of Veneto was a well-known deposit of Venetian red ochre, known by the names *Rosso Veneziano* or *terra rossa* (Lazzarini 1987, p. 118).

Cavallo, Pia Riccardi & Zorzin (2016, p. 221) report how the Lessini Mountains hold the deposits of several earths (*terre coloranti*): green (celadonite), red (hematite-based) and yellow (goethite-based) earths, as well as black (carbon-based) earths. Earths from the Veneto region have been exploited and processed probably from Prehistory, until the second half of the 20th century. Nevertheless, the absence of any link between the earth deposits and actual Renaissance artefacts or paintings is problematic for the hypothesis of red ochre being used as a source of colouring materials throughout history and particularly during the Renaissance. Characterization analyses on cultural heritage artefacts would provide a scientific reference to confirm the hypothesis of red ochre use in decorative purposes and artwork.

Regarding trade, *terra rossa* was one of four iron-oxide based materials available in the shop of Jacopo de' Benedetti in 1594 in Venice. Krischel (2002, p. 102) reports that the *terra rossa* was delivered to Venice through German *Fondaco dei Tedeschi*. The registers of G. A. Catti and A. Spinelli report that *terra rossa* was exported internationally; it was part of a

¹¹⁵ Other earths available locally in the region of Verona were green earth (*terra verde di Verona* or *tufo verde*), extracted from Malaga Tretto on Mount Baldo, and yellow earth (*terra gialla di Verona*), found between the Avesa valley and Valpantena (Lazzarini 1987, p. 118).

colouring material shipment which originated from the Gradignan della Scalla shop, loaded onto the *nave Zena* sailing to Constantinople in 1607 (77 / 868 in Appendix 8).

9.3.2.6. Discussion

It can be assumed that many more barrels of red ochre than currently exist were present on board *Gagliana grossa*, as more barrels and accumulations of red colour were recorded in reports. Other red colours that could have been part of the cargo are ground red arsenic sulphide / realgar or lead tetraoxide / minium. However, both of these substances would probably have had a light orange colour, and the underwater reactions would be as follows: arsenic sulphide would probably have dissolved in water, and been preserved as traces on the ship's hull only (see sample GN-2017-CM08 and -CM18), while minium would probably create the layer of galena (see sample GN-2017-CM35).

Since the composition of the *terra rossa* seems to be 70% hematite and 30% clay (Lazzarini 1987, p. 118), it is possible to suggest that the Gnalić Shipwreck finds can be taken as a reference of red ochre from Badia di Calavena in high Illasi Valley, Lessini mountain, Veneto, Italy. Confirmation that the Gnalić shipwreck red ochre is *terra rossa* from Monte Lessino would provide a valuable link between archaeological finds and mineral deposits exploited during the Renaissance. However, this hypothesis has to be taken with caution, because this material was available in several forms, as can be seen from the four red iron oxide-based materials listed in de' Benedetti's inventory (Appendix 7, Krischel 2002, pp. 102-103). Since the *lapis rosso* which originates from the East existed in four different forms (Krischel 2002, p. 102), it is great evidence that, even though the mineral was available locally, there was still import of similar materials from abroad. The reason might be a need for different hue, material properties or simply the fashion of owning the material from the Eastern Mediterranean.

While the author is suggesting the identification of Gnalić shipwreck red ochre with the *terra rossa* from Badia di Calavena in the Lessini Mountains, characterization analyses and provenience studies are required to test this hypothesis. The sampling and research done on Lessini Mountain *terra rossa* recently (Cavallo, Riccardi & Zorzin 2015; 2016) represents a great potential to obtain a reference sample and make the comparison between the natural deposits and the red ochre from the Gnalić shipwreck.

9.3.3. Mercury sulphide (*cinabro*)

9.3.3.1. General information

The earliest use of mercury sulphide is attested on wall paintings and in graves in the vicinity of Almadén in Spain, which was a main source of raw materials since Prehistory (Kroustallis, Bruquetas & Gómez 2011, p. 277). Probably the most well-known example is the use of mercury sulphide in the remarkably preserved frescoes in the Villa of the Mysteries in Pompeii, Italy (Coarelli, Foglia, & Foglia 2005, p. 354).

Mercury sulphide can be found in Renaissance paintings,¹¹⁶ very often mixed with lead white to obtain flesh tone. A madder glaze was sometimes added on top to obtain a glittery finish. Historical sources provide recipes of how to prepare mercury sulphide for miniature painting (Merrieffield 1967, p. 664), but it was also highly preferred in wall painting and furniture decorations (Krischel 2002, p 104). The qualities of mercury sulphide are evidently its great covering power, stability, and compatibility with other pigments (Alexander 1992, p. 29), which allowed painters to combine it with other materials and experiment. Mercury sulphide has a characteristic alteration of darkening which happens when the pigment is exposed to halogens¹¹⁷ and light (Eastaugh et al. 2008, p. 111), and this darkening is enhanced by the presence of moisture (Hochmann 2015, p. 178).

9.3.3.2. Archaeological context

The finds from the Gnalić shipwreck include two forms of mercury sulphide. The bell-shaped form, or so-called type A, has a weight from 80 to 100 kg (Figs 9-24. and 9-25.). All the dimensions of the entirely preserved artefacts are consistent. The diameter of the widest part and the height is 27 cm. The bottom diameter is 21.5 cm, and there is a conical indentation with a funnel-shaped channel going through the body of an approximate diameter of 1.8 cm. The outer surface is not entirely smooth, but partly ribbed (Fig. 9-26.). In total, fourteen bell-shaped mercury sulphide bells were recovered during the excavation seasons from 1967 to 1972. Today, there are seven entirely preserved, three split-pieces and five fragments (eds Filep, Jurdana & Pandžić 2013, p. 113). The ingots have an alteration grey-coloured alteration layer, with the thickness of several millimetres (Figs 9-27. and 9-28.), and some of the pieces are still

¹¹⁶ Especially adored by Tizian, Lotto, Tintoretto and Veronese (Krischel 2002, p. 104).

¹¹⁷ Fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At).

covered with marine incrustations. Even through this surface alteration layer, it is possible to notice wavy layering and crystallization in the section of the mercury sulphide (Fig. 9-25.).

The second form of mercury sulphide found, designated type B, were in the shape of lumps, with a visible needle-like internal structure (Figs 9-29. and 9-30.). The lumps vary in size and weight, from small fragments found in sediments, to lumps of pointed and rectangular-like shape of weight of almost 1 kg. Analyses are not complete, so it is not conclusively determined whether these two types of mercury sulphide were produced by the same method into a different form, or if their methods of production were different.

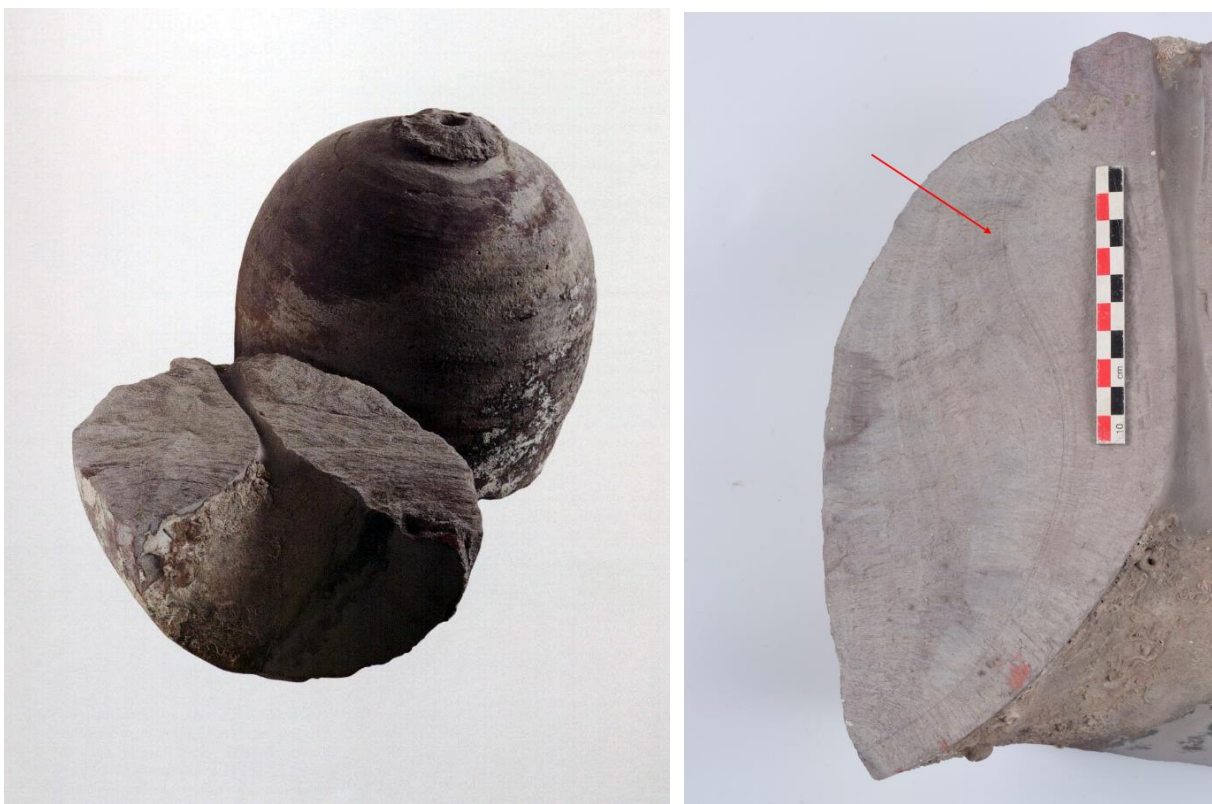


Fig. 9-24. and Fig. 9-25. Mercury sulphide, type A. Right photo is representing layers formed on the body of the lump as a result of the production process (left photo: from personal archive of prof. Zdenko Brusić; right photo: N. Ćuk).



Fig. 9-26. Ribbed surface of bell-shaped mercury sulphide, type A (photo: N. Čuk).



Fig. 9-27. and Fig. 9-28. Grey alteration layer of bell-shaped mercury sulphide, type A (photo: N. Čuk).



Fig. 9-29. and Fig. 9-30. Mercury sulphide, type B (photos: S. Govorčin).

9.3.3.3. The results of the characterization analyses

The characterization analyses were done only on the mercury sulphide, type B. The XRD analyses results confirmed the type B ingots were composed of mercury sulphide. The mercury sulphide, type A, was sampled (Figs 9-31. and 9-32.) but not analysed as access to the instruments was not possible. The chemical analyses done on one of the bell-shaped artefacts (type A) in 1970 identified the material as mercury sulphide (Kelez 1970).



Fig. 9-31. and Fig. 9-32. Sampling mercury sulphide, type A, in the Regional Museum of Biograd na Moru¹¹⁸ (photo: N. Čuk).

¹¹⁸ Sample not analysed.

9.3.3.4. Production and processing

In nature, mercury (II) sulphide is a scarlet red mineral known as cinnabar which occurs in massive forms, typically in areas with characteristic volcanic activity and hot springs. It is common to find cinnabar along with stibnite, marcasite, gypsum, quartz, and calcite (Eastaugh et al. 2008, p. 111). There were two main deposits active in Europe during the Renaissance: Idria in Slovenia, from the official discovery in 1493 (Leskovec 2008), and Almadén in Spain, with a long tradition of exploiting mercury sulphide sources (Broquetas Galán 2011, p. 294). When recovered from the deposits, the cinnabar mineral is intensive red, dark brown or black coloured (Bermanec 1999, p. 48). The raw material requires purification. The process includes washing crushed mineral in sieves and then drying the mineral in the sun. After this phase, the mineral is ready to be placed in the heat of a furnace in order to make a division of non-purified compounds (Leskovac 2008).

Mercury sulphide was one of the colouring materials that humans learned very early how to synthesize (Crosland 1962, p. 112). It is considered that the oldest synthetic production of mercury sulphide was introduced in Europe during the Roman period (Eastaugh et al. 2008, p. 111). Mercury sulphide was produced by heating mercury and sulphur, the method for which is believed to have been invented in the Almadén mines (Broquetas Galán 2011, p. 294). From the seventeenth century onward, the difference between natural and synthesized mercury sulphide is emphasized by the nomenclature 'cinnabar' to indicate natural mercury sulphide, as opposed to 'vermilion' to designate synthesized mercury sulphide. In sixteenth-century Venice, the historical name 'cinnabar' was applied to both natural and manufactured mercury sulphide (Krischel 2011, p. 103).

The manufacture of cinnabar in Venice has not been studied systematically, but there is evidence that intensive manufacturing began as early as the Middle Ages, according to records that mention manufacturing facilities situated outside of the city walls from 1294 (Krischel 2002, p. 103). In that year, Venetian magistracies had forbidden the synthesis of mercury sulphide within the city walls, as there was an awareness of the toxicity of mercury fumes along with a danger of fire in the vicinity of the production centres. Archival documents mention one exception, that in 1523 the manufacturer of cinnabar *Francesco Negro 'dai Cenabrii'* was allowed to open a workshop at least a half-mile away from the living area (Krischel 2002, p. 103).

Mercury sulphide could be produced by either artists or colour sellers, but Cennino Cennini, in his Book of art (*Il libro dell' arte*, late fourteenth century), suggests it is not worth

making mercury sulphide in your own studio, as it is a complex process that requires a distillation kettle. Cennini considered it easier and more affordable to purchase it in a pharmacy shop. Based on Cennini's words, it is possible to assume that at the end of the Middle Ages, it was easy to access mercury sulphide, as it was both locally produced and available (Cennini, 2007, p. 53). He also points out how the pigment should be bought as a lump, because when it is purchased ground, it could have been adulterated with minium or ground brick. Harley (2011, pp. 126-127) reports how recipes of making mercury sulphide vary only in the percentages of mercury and sulphur, and Merrifield delivers different recipes of how to process mercury sulphide, which has to be taken with caution as it is a nineteenth century translation of the historical sources (1967, pp. 676, 678, 704-706).

The seventeenth century English sources provide additional evidence to understand the mercury sulphide manufacturing process. While describing the production process, Harley (2011, pp. 127-128) mentions how seventeenth century manufacturing of vermilion required spherical glass vessels called cucurbit, which could be purchased in glass workshops. The description of cucurbit is similar to the ceramic pots required for extraction of mercury described by Gregorius Agricola in *De Re Metallica* (1556). It was necessary to ensure the pots were in a good condition, and made of the best clay, otherwise, Agricola states 'the quicksilver flies out in the fumes' (Hoover & Hoover 1950, pp. 427-428).

Further, Harley (2001, p. 127) describes how, when mercury and sulphur were heated, the new compound was sublimated, then crystalized and attached to the inner surface of the cucurbit. It required close attention of the manufacturer to observe the manufacturing process and take care that the top of the vessel was not sealed by condensed mercury sulphide. At the end of manufacture, the mould was broken, so the cinnabar made in the form of a cake could be taken out.

9.3.3.5. Trading with mercury sulphide

Venice had access to the cinnabar deposits of Idria in Slovenia since the mines were discovered in 1493 (Leskovac 2008). Still, Venice was synthesizing mercury sulphide and it was one of the products well-known to be exported to the Eastern Mediterranean. Venice was also exporting regionally; mercury sulphide was exported to Firenze, Ferrara, Ancona, and Rome (Krischel 2002, p. 103).

Although the Venetians did synthetically produce cinnabar, it is interesting to note that there are archival evidence of the importation of mercury sulphide to Venice in the second half

of the sixteenth century. The amount of mercury sulphide being used by the artists and artisans seems to indicate that local production was insufficient to fulfil the significant demand related to painting, both for artwork and for objects of daily use. It is known that in 1569 the Venetian Senate allowed import from abroad. It is attested that in this period Venetian colour seller Mattheo dei colori offered cinnabar from Spain (Matthew & Berrie 2010, p. 248). In the transition to the seventeenth century cinnabar started to be imported from the provinces of the northern Alps, especially Nuremberg (Krischel 2002, p. 103).

It is not known if Venetian painters were using imported natural cinnabar or if they used synthesized cinnabar only (Krischel 2002, p. 103). Regardless, mercury sulphide was common in the inventories of Venetian colour sellers. Two colour sellers, Zuan di Nicolo dai colori and Marco da Corphu, established a partnership in 1550 for the export of mercury sulphide and other substances (Appendix 7). Additionally, mercury sulphide was attested in Benedetti's shop from 1594 in two forms – as ground (*masenado*) and burnt (*brusado*) (Krischel 2002, p. 104). Regarding international export based on Tenenti (1959), information is scarce in comparison to shipment of, for example, cerussite or mercury. Mercury sulphide is mentioned only once, as a part of a shipment in nave *Falcon Bianco* from 1609 (82 / 993, Appendix 8).

9.3.3.6. Discussion

Finally, as with most of the other colouring materials from the Gnalić shipwreck, there is a complete absence of studies about the manufacture of Venetian mercury sulphide, while the regional and international trade is known only from sporadic mentions in the historical sources. Based on the bell-shaped form of type A, it is possible to suggest to name it vermilion, as it quite obviously was synthesized according to the manufacture process of heating mercury and sulphur. The layers visible in cross-section of the bell can be explained by the condensation of mercury sulphide on the inner walls of a bell-shaped ceramic pot, perhaps something similar to the pot described by Agricola (1950, pp. 427-428) or the glass cucurbit described in the historical source consulted by Harley (2001, p. 127). The ribbed outer surface of the type A bell-shaped ingots suggests that the mould was made of pottery, because the ribbed surface as seen in Fig. 9-29. appears only on the inner side of pottery vessels. The existence of the channel passing through the bell, with a rounded opening at the top, corresponds to the production process described by Harley (2001, p. 217) saying how the mouth of the manufacture vessel should be monitored to prevent the mercury sulphide from condensing and sealing the vessel. With respect to the abovementioned process, such a channel and its associated opening were

required to release extra fumes during sublimation, otherwise the mould would be broken from the build-up of pressure.

The shape and the structure of the lumped mercury sulphide, type B, does not give enough information to suggest if it is of natural or synthetic origin. However, a research methodology to differentiate synthesized and natural mercury sulphide has been developed by Gettens, Feller & Chase (1993, p. 159), thus in the future characterization analyses and microscopic observations of the shape of particles in type B lumps will provide precise answers.

It was assumed by previous researchers that the mercury sulphide, type A bell-shaped artefacts were a product of Venetian manufacturers because at this exact time the mercury sulphide produced in Venetian workshops had the shape of a bell, in Italian called *pane di cenaprio* (Petricioli 1981, p. 44). This hypothesis still needs to be supported by both historical resource research and characterization analyses. Although it is known that Venice had active production of mercury sulphide during the Middle Ages and in the first part of the sixteenth century, there is not enough evidence for the second half of the sixteenth century. This could be due to the lack of research on archival documents, but it is also possible that Venetian manufacturers were no longer active. The Venetian Senate did allow the import of mercury sulphide from Spain in 1567 (Matthew, Berrie 2010, p. 247), and *vendecolore* Mattheo dai colori had mercury sulphide from Spain in his inventory at that time. In comparison to cerussite and mercury, there is a lack of information about mercury sulphide in insurance document data of goods exported from Venice from 1592 to 1609 (Tenenti 1959). The absence of mercury sulphide in insurance documents certainly could indicate that mercury sulphide manufacture in Venice had gone into decline in the latter half of the sixteenth century. The question of mercury sulphide manufacture and trade requires additional detailed research of the evidence available in both archaeological finds and historical documents.

9.3.4. Red lead (*minio*)

9.3.4.1. General information

Lead (II, IV) oxide is a bright orange pigment known from both archaeological sites and written sources since Classical Antiquity, today known by common names lead tetraoxide, red lead and minium (Eastaugh et al. 2008, p. 235). During the Middle Ages, minium was often used in monasteries for decoration of manuscripts. In fact, it is believed that the etymology of the word ‘miniature’ originates from the Latin word *miniare*, meaning – to write with minium (Thompson 1956, pp. 101-102). It was also used to paint furniture, with the purpose of both decoration and protection (Krischel 2002, p. 105). It was an indispensable ingredient in making pottery glaze and often an addition in the production of glass (West FitzHugh 1986, pp. 112-113). Nowadays it is accepted to use the term minium in general for lead (II, IV) oxide, while the term ‘red lead’ denotes the synthesized version¹¹⁹ (Eastaugh et al. 2008, p. 270).

Written sources often address how minium was used to adulterate mercury sulphide (for *e.g.* see Cennini 2007, p. 53) and the red lake pigments (West FitzHugh 1986, pp. 122). In the sixteenth century, this pigment was applied to paintings in combination with lead white (Hochmann 2015, p. 176). Krischel (2002, p. 105) states this pigment was more preferred among manuscript illuminators than among the painters. It does not appear commonly on the paintings of the Venetian school, except for Tintoretto, who used it more often.

The properties of minium include good covering abilities and quick drying when applied with oil on canvas. While it is stable in oils, it darkens in watercolours (West FitzHugh 1986, pp. 113, Hochmann 2015, p. 176). While painting it was typically used in small amounts because it was fast drying (Krischel 2002, p. 105). It is incompatible with the pigments containing sulphur: arsenic sulphides, cadmium sulphide, mercury sulphide, and ultramarine (West FitzHugh 1986, p. 118).

9.3.4.2. Archaeological context

At the Gnalić site, red lead has been found in only two lumps (Figs 9-33. and 9-34.). The lumps are irregularly shaped, of average length 9 cm, height 5 cm, and width 6 cm. The average weight of each piece is 800 grams. The packaging method is unknown, since the lumps

¹¹⁹ According to West FitzHugh (1986, p. 107) the term minium is used for the mineral in ancient times, while the term ‘red lead’ is used today. Author has decided to follow the more recent definition given by Eastaugh et al. 2008.

were found in the sediment on the southern part of the site, in the layer together with scattered cones of lead white.

Since the red lead had formed a thick dark grey alteration layer, it is not easy to distinguish it from ballast stones or other accretions at the excavation site. Moreover, during excavations, deep layers of sediment above the wooden ship's hull contained various stones removed to access the ship's hull, some of which may have been unrecognized red lead due to the lack of visibility.



Fig. 9-33. and Fig. 9-34. The broken lump of minium. Right photo has sampling positions labelled. (photos: O. Guillon)

9.3.4.3. The results of the characterization analyses

Application of multispectral imaging made it easier to distinguish the core from alteration layers. The clear differences between the colours of grains helped to choose the appropriate sampling positions.

The sampling was done at the three layers, marked with letters 'A' for the orange/red core, 'B' for the white thick line marking a middle layer (a transition between the reddish core and the black outer layer), and 'C', the outer layer (Fig. 9-34.). Analyses were completed only on the samples A and C; 'A' as the original pigment and 'C' the alteration layer. The results of the XRD analyses helped to distinguish major mineral phases within the samples GN-2017-CM35A and -CM35C.

a) The core (red)

XRD spectrum of CM35A is not attached to zero, leaving the impression that there are amorphous phases which the instrument is not able to recognize. The core of the sample is composed of 40% minium (Pb_3O_4), 34.6% quartz (SiO_2), 16.4% hydrocerussite ($2\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$) and 8.9% plattnerite (PbO_2). Hydrocerussite could be part of the original matrix, or an alteration product, as it has been proved by studies of pigment degradation (Aze et al. 2007, p. 883). The plattnerite is a mineral phase that usually appears in the alteration layers of minium on paintings. The alterations on paintings are known as a ‘darkening’ which appears with natural ageing (West FitzHugh 1986, p. 117; Aze et al. 2007). It has also been attested that minium transforms into plattnerite and cerussite in the presence of salts (Kotulanová et al. 2009, p. 376).

b) Alteration layer (dark grey)

The XRD spectrum of CM35C is interpreted as galena (PbS) and cerussite (PbCO_3). Lead (II, IV) oxide reacts in the presence of sulphur and crates galena. The same reaction as previously reported on lead white cones (section 9.3.1.).

9.3.4.4. Production and processing

The mineral of lead (II, IV) oxide exists in both natural and synthetic forms. Mineral deposits of minium appear in Sweden (Långban), Scotland (Leadhills) and Russia (Altai). It appears in these places as a result of oxidation of lead-based minerals, with the most common example being galena alteration (Bermanec 1999, p. 82). The synthesis of minium could be obtained via two processes. The first is by heating lead carbonate to a temperature between 425 and 480°C. This procedure was first described in Classical Antiquity by Vitruvius. Subsequently, the recipe was mentioned in Middle Age sources. The recipe was still in use in eighteenth century England to synthesize red lead (West FitzHugh 1986, p. 110; 122). The second way to produce minium was by heating lead oxide or litharge. This technique is thought to have been adopted from the Eastern Mediterranean, but it was also commonly used in fifteenth-century Germany (Krischel 2002, p. 105).

Within the shop of de’Bendetti in 1594 existed two types of minium, which can be distinguished according to the production process. If the minium was made by heating litharge,

the title in the inventory was *minio de piombo*. If, on the other hand, the minium was made by heating the basic lead carbonate, it was called *minio de biacha* (Hochmann 2015, p. 176).

9.3.4.5. Trading with minium

Minium was a quite common product in Venetian colour seller shops, as it was present in the inventory of Domenico da Gradignan (1534), as well as in the partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550) with the aim to execute international export (Appendix 7). The workshop of Gradignan della Scala had a permission to ‘heat lead’ (*brusar piombo*), which could be interpreted as a minium manufacture (DeLancey 2017, p. 20). Minium is mentioned as *minio masenado* (ground minium) and as *minio de biacha* (minium from lead white) in Benedetti’s inventory from 1594, and listed as *minio ordinarie* (ordinary minium) in the colouring material shipment in the *nave Zena* going towards Constantinople in 1607 (77 / 868, Appendix 8). These records suggest that minium was readily available in a wide variety of forms.

9.3.4.6. Discussion

There is still not enough historical data to support the study of the production and trade with minium. This pigment was not in large-scale use among painters, but was more commonly used by manuscript illuminators. It is also known that the pigment was used in small amounts as it was fast drying. Perhaps this is the reason why it was not mentioned in large amounts in the insurance documents, and only found in very small amounts in the *Gagliana grossa*. The characterization analyses of the minium sample showed the presence of degradation products. Further analyses should take thin sections of the lump, to verify if the degradation products appear deeper in the core where seawater might have entered by diffusion.

9.3.5. Arsenic sulphide – Realgar (*oropimento rosso*)

As already mentioned in the terminology section 3.3, arsenic sulphides encompass orpiment (As_2S_3) and realgar (AsS), which appear jointly in nature, and they could appear together in late Renaissance Venice inventories of the colour seller shops. The inventory of Domenico da Gardignano from 1534 mentions *oropimento* and *rexegal*, while Jacopo de' Benedetti's inventory from 1594 lists *oropimento* and *oropimento rosso*. However, only realgar has been attested at the Gnalić archaeological site, so this section will focus mostly on realgar and mention orpiment only sporadically.

9.3.5.1. General information

Arsenic sulphides are one of the earliest colouring materials that are known to have been traded. The earliest use of arsenic sulphide is recorded in the sixteenth to eleventh century BC in Egypt, used for painting coffins and stellae (Eastaugh et al. 2008, p. 291). The find of orpiment on the Ulu Burun shipwreck in Turkey from the fourteenth century BC is the earliest attested find at an underwater archaeological site. It was probably used in a mixture with beeswax for writing boards (Bass 1997, p. 159). The trading manual named 'Periplus of the Erythrean Sea' from the first century AD delivers information about trading orpiment and realgar to the ports of India (Casson 1989, pp. 208-209).

Besides decoration, arsenic sulphides were used in cosmetic purposes, especially for the purpose of hair removal when mixed with lye. There was a belief that the arsenic compound would act as a remedy against the plague if it was worn over the heart. It was also believed that the fumes of arsenic could cure asthma, as well as coughs that are a symptom of some diseases. Regardless of the abovementioned advantages, arsenic was considered extremely dangerous and poisonous (Biringuccio 1942, pp. 105-107). Biringuccio (1942, pp. 105-107) states it was corrosive and dangerous, the 'most powerful poison to the life of all things.' When mining arsenic-based ores, the workers had to cover their mouths and noses with a sponge wet with vinegar due to the danger of inhaling the poisonous substance. It was recommended to avoid its use, if not needed.

Arsenic sulphides were commonly used on frescos and oil paintings (Hochmann 2015, p. 178). These intensive colours, which range from yellow to orange and red, were in use since the end of the fifteenth century by masters of the Venetian school, and became signature hues

of the late Renaissance. Orpiment was especially favoured by Tizian, while Veronese combined both orpiment and realgar (Hills 1991; Berrie & Matthew 2005, p. 12).

It is well known that arsenic sulphides are not compatible with copper and lead-based pigment, which was addressed in Medieval historical sources (West-Fitzhugh, 1997, p. 52, Hochmann 2015, p. 189). When in contact with light, realgar can create an alteration in orange colour, in a form of its polymorph pararealgar (Corbeil & Helwig 1995).

9.3.5.2. Archaeological context

At the Gnalić shipwreck, arsenic sulphides were found in the form of powders. As was reported by the first researchers, it was transported in casks. It is not entirely clear from the documentation if there were three or five casks on board. One of the casks had a lid bearing the mark N37 (Appendix 11). One of the entirely preserved arsenic sulphide casks was recovered, restored (Appendix 13), and is today presented in the Regional Museum of Biograd na Moru.

During the excavations from 2012 to 2019, none of the positions described in previous reports displayed preserved barrels; the only evidence found on the site was the intensive yellow colour in the sediment. The cask described at position 5 on Map 1 (Fig. 9-35.) left traces on the hull, while the remains of contents of casks at position 7 on Map 1 were recognized to the south of the ship's pump (Fig. 9-36.). Documentation from 1972 represents how casks filled with yellow colour were preserved in different sections. Two casks positioned south of the red ochre barrels are preserved in vertical section. They had a longitudinal and oval shape with a height of approximately 50 to 60 cm (Fig. 9-37.).¹²⁰ The report describes those casks as 'filled with yellow colour', although it can be clearly seen there are no contents. Author assumes this might have been an arsenic-based colouring material, as one of its main characteristics is solubility in water. The cask represented on the drawing is preserved in horizontal section (Fig. 9-38.). There is not enough data (measurements, photos, and drawing) to state that the two types of casks can be distinguished.

¹²⁰ The measurements are given in comparison with the barrels of red ochre for which the author has taken the measurements *in situ*.

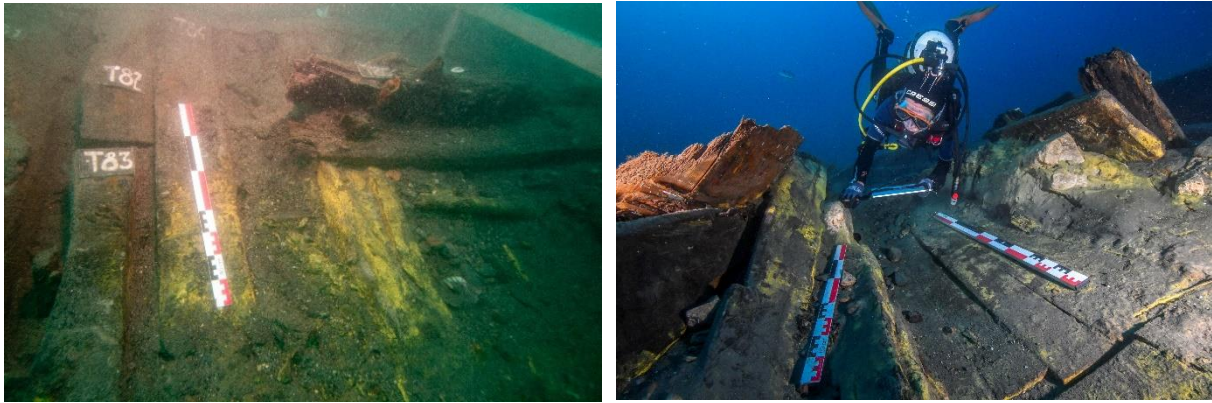


Fig. 9-35. and Fig. 9-36. The traces of the yellow colour at location 5 on Map 1 / left, and location 7 on Map 1 / right (left photo: S. Govorčin; right photo: K. Yamafune).

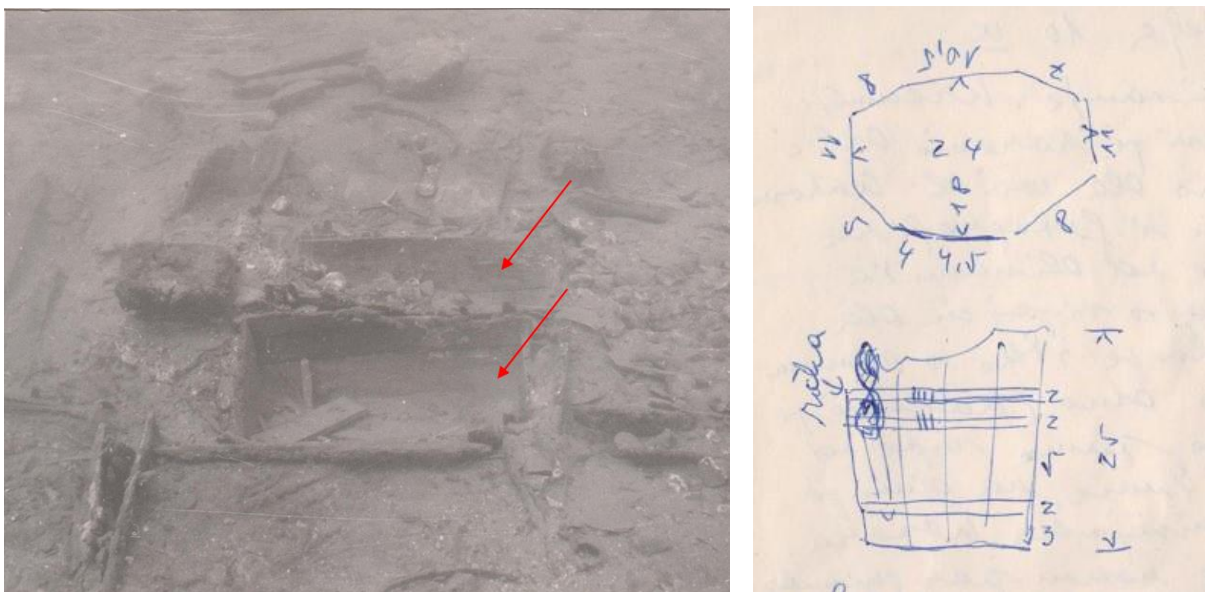


Fig. 9-37. and Fig. 9-38. Casks filled with yellow colour preserved in vertical and horizontal section, recorded during the excavation season of 1972. Left: Location of two longitudinal casks. Notice that there are no contents; Right: Sketch and measurement of the cask containing yellow colour (left: photo inv. no. GN-KOZ-F17b; right: page from the fieldwork diary of Ksenija Radulić, inv. no. GN-KOZ-D166; Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

9.3.5.3. The results of the characterization analyses

The sampling for characterization analyses was done on the solid accumulation of yellow colour and stones to the southwest of the pump's well (GN-2017-CM08) and obtained from the fine sand to the south of the pump's well (GN-2017-CM18). As arsenic sulphides are soluble in water, and no transport container for arsenic sulphide was preserved with its contents, the samples were taken from positions where casks were recorded in earlier excavation seasons. The bright intensive yellow colour remained as a fine-grained powder either on top of the wooden structure or mixed with sediment (Figs 9-38. through 9-41.). Photography under both

visible and ultraviolet light revealed that approximately 10 to 15 percent of the particles fluoresce with intensive yellow colour (Figs 9-40. and 9-41.).

Since most of the arsenic sulphide particles dissolved in the seawater, the chemical component of As was not recognized as a major element in SEM-EDX or XRF analyses. However, the RS both with the near-IR and the green laser showed the peak which corresponds to realgar, α -Arsenic (II) sulphide, As_4S_4 (Bell, Clark & Gibbs 1997, p. 2147). FTIR was not used since arsenic sulphides absorb the infrared region (Vermeulen 2017, p. 141).

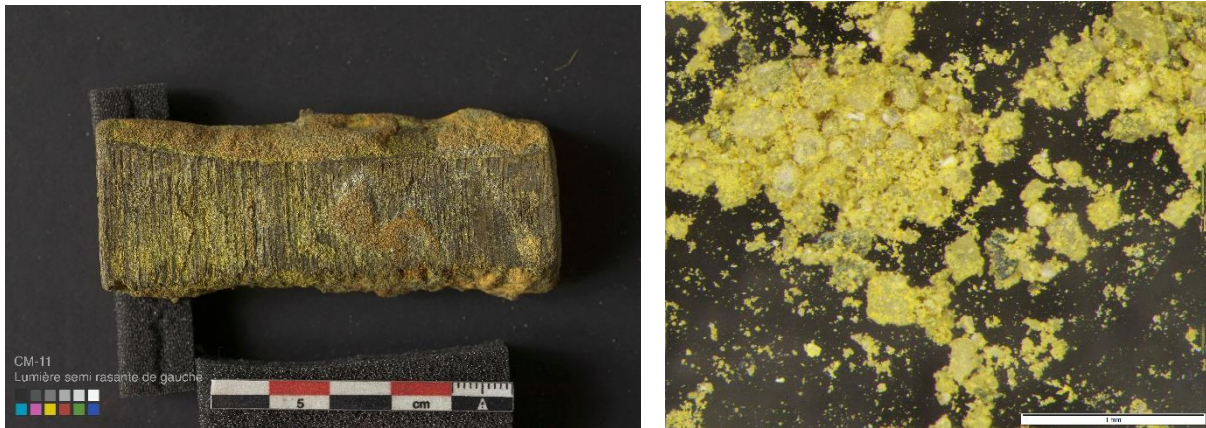


Fig. 9-39. and Fig. 9-40. Left: Accumulation of yellow and orange particles of realgar on the wooden stick, sample GN-2017-CM11. Analysed, but not presented in Appendix 21; Right: Fine-grained realgar on the sand-like particles under binoculars, sample GN-2017-CM08. Results of the analyses in Tab. 9-1. and Appendix 21 (left photo: O. Guillon, right photo: K. Batur).

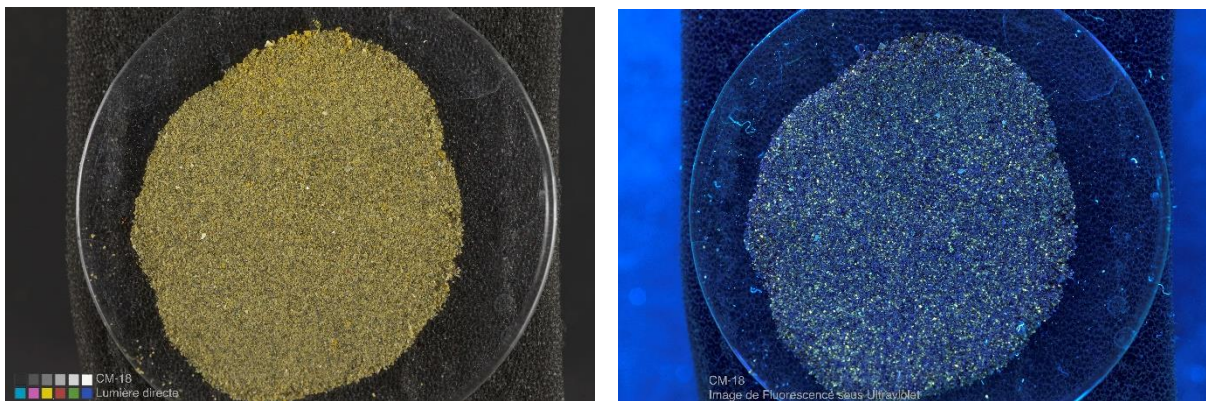


Fig. 9-41. and Fig. 9-42. Realgar recovered with the sediment, sample GN-2017-CM18 (photos: O. Guillon).

9.3.5.4. Production and processing

Arsenic sulphides (orpiment and realgar) are appearing in natural deposits as massive encrustations or in the granular form together with other minerals, such as pararealgar, duranusite, alacranite, dimorphite and uzonite. These are common as sublimes from volcanoes, or they appear very often in association with hot springs (Eastaugh et al. 2008, p. 291). In this section, arsenic oxide (As_2O_3), also known as a white arsenic or arsenious acid (Eastaugh et al. 2008, p. 229), will be mentioned as a substance used in synthesis of orpiment and realgar.

During the sixteenth century, the most exploited natural resources of arsenic-based raw materials were in Felsobanya (Hungary), Allchor (Macedonia), Asia Minor and Central Asia (Lazzarini 1985, p. 136). The material from the natural deposits was refined by a very simple process – by grinding until obtaining a fine powder.

Biringuccio's metallurgy treatises give us the knowledge that from the middle of the sixteenth century, miners recognized the properties of arsenic oxide, as well as both arsenic sulphides – orpiment and realgar.

'They also say, as I told you before, that orpiment and crystalline arsenic are not all of the same nature. And I must say, from all that I have seen or I think I have seen, that their composition is different. For one is clear white or citrine; this indicates that it contains earthiness and wateriness; and the other is of a shining and beautiful golden color and of sulphurous substance as is attested by its yellow color and strong smell.

Both are pulverized and both calcine like antimony, and when they are mixed together through sublimation they make realgar, a thing of the same nature. In the residue of this sublimation, or when they are roasted in some other way, they leave a regulus (of metallic arsenic) very white like silver but more brittle than glass. When arsenic, orpiment and realgar are fused and burned alone they evaporate away in fume' (Biringuccio 1942, p. 107).

However, in addition to natural arsenic sulphide, there was an active manufacture of synthesized orpiment, in Ehrenfriedersdorf, Freiberg, and Reichenstein in eastern Germany, as well as Strassegg, Rotgülden and Walchen in the eastern Alps, Austria (Grundmann 2011, p. 270). In the sixteenth century, the artificial production of orpiment was based on heating or

sublimation of the raw material arsenolite, the so-called 'dry process'¹²¹ (Eastaugh 2008, p. 291, Grundmann et al. 2011, p. 270).¹²² On the other hand, realgar is synthesized by heating orpiment (Eastaugh 2008, p. 325), or it can be made by fusion of sulphur and arsenic, in the presence of carbon (West-Fitzhugh, 1997, p. 55). For this reason, historical sources sometimes mention burnt orpiment (*oropimento arso*) (Grundmann et al. 2011, p. 270).

The Paduan manuscript describes various recipes for the preparation of orpiment of great quality, including how to mix it with other minerals (Merrieffield 1967, pp. 662; 676; 678; 686; 706).

9.3.5.5. Trading with arsenic sulphides

Historical sources report how intensive export of arsenic oxide, orpiment and realgar was executed from the Alps (Styria and Carinthia) to Venice. Artificially produced arsenic-based colouring materials were transported in 200-liter barrels. From the manufacturing centres, arsenic substances were transported in the form of raw glass cake (Fig. 9-46.) or as powder (Fig. 9-43.) (Grundmann et al. 2009, p. 240). The raw glass cakes produced in the abovementioned facilities were probably similar to the preserved pieces of realgar (Fig. 9-42.) originating from the arsenic smelter in Friedberg, Germany (Grundmann & Richter 2008, p. 906).

¹²¹ The second method of manufacture is based on precipitation, the so-called 'wet process', introduced in the nineteenth century.

¹²² Grundmann & Rötter 2007 did experiments using PLM, SEM, XRD and electron beam microprobe, to test whether it is possible to distinguish natural orpiment from orpiment synthesized by the 'dry' and the 'wet' process. The study has shown that is not only possible to clearly distinguish natural from synthetic form, but to conclude if the artificial orpiment is synthesised by 'wet' or 'dry' process. The difference in the production process can be seen with the use of PLM only if the particles exceed the size of 2µm.



Fig. 9-43. 'Realgar, Rotglas' from Muldennütten near Friedberg, Saxony, Germany. Collection of Landesmuseum Joanneum, Graz, Austria (Grundmann & Richter 2008, p. 906).

According to historical sources, the strongest manufacturing centre in the sixteenth century was in Ehrenfriederdsdorf in Saxony (Grundmann et al. 2008, p. 110). From the archaeological point of view, the site of Strassegg, in the vicinity of Graz (Austria), is important as the first researched manufacturing facility for synthesizing arsenic-based colouring materials. The archaeological excavations revealed an area of manufacturing using arsenic-based raw materials, including a sublimation oven, chamber, and elements of a wooden pool for washing the raw materials. This manufacturing centre is well-known for its arsenic-smelting activity. ¹⁴C analyses of charcoal suggested the datation from 1660 to 1960 (Grundmann et al. 2009, pp. 240-242). The finds are including the arsenic oxide and sulphur, but also synthesized glass cakes of orpiment and realgar (Grundmann et al. 2011, p. 270).

In the sixteenth century, arsenic sulphides were sold in different forms. Lazzarini (1985, p. 136) reports arsenic sulphide was sold in the form of powder, contained in a glazed (*invetriata*) jar. *Vendecolore* Jacopo de' Benedetti (1594) had a huge amount of arsenic sulphide-based colouring materials, with amounts of orpiment and realgar exceeding 2000 kg (Krischel 2002, pp. 111-113; Hochmann 2015, p. 187). De' Benedetti sold orpiment and realgar as powder and in lumps, but it is quite interesting to see how he differentiated them according

to their physical properties, such as ground (*masenado*), sieved (*inttcernido*), opaque (*chiaro*), of the middle quality (*mezan*).

According to previously published work (Lazzarini 1985), arsenic sulphides were quite often imported to Venice from the Orient, but they could also be delivered from Germany (Saxony), Austria (Styria and Carinthia), Hungary (Felsobanya), and Macedonia (Allchor). Insurance documents published by Tenenti demonstrate that arsenic-based colouring materials were traded from Venice to the Eastern Mediterranean (2 / 3, 22 / 184, 56 / 608, 70 / 788, Appendix 8).

9.3.5.6. Discussion

During history, orpiment was often used in paintings and confirmed in a greater number of examples than in the case of realgar (West-FitzHugh 1997, p. 66). Venice imported arsenic sulphides from Germany, Austria, and Hungary through land routes, as well as from Asia Minor over maritime routes. The arsenic-based samples analysed for the aim of this dissertation (GN-2017-CM08 and GN-2017-CM18) have been identified as a realgar, although the particles under the microscope seen by Raman vary from bright yellow to an orange and reddish colour. In fact, creation of a yellow-coloured powder of realgar as a result of degradation has been extensively reported. Studies have shown that the transformation to its polymorph – pararealgar – is initiated by the presence of light (Corbeil & Helwig 1995, p. 134).¹²³

It is still possible that orpiment could be present in the cargo of the *Gagliana grossa*, but no sample yet analysed was collected from the right position at the site. Archaeological excavations done at the site of Strassegg, Austria, have defined the appearance of the manufacturing facilities of arsenic-based raw materials, and provided samples of raw glass cake, which are the historical reference of arsenic sulphide manufacture of the region. Should orpiment be detected in the future at the Gnalić site, characterization analyses may be able to compare the sample with the reference samples from Austria. However, there is always a possibility that the crystallization processes of pararealgar in a sea environment, or just solubility of arsenic-based colouring materials itself, caused the loss of the data required for these studies.

¹²³ These authors also suggest the data presented as orpiment in previous research could be confused for realgar.

9.3.6. Stibnite (*antimonio*)

9.3.6.1. General information

In the ancient world, antimony (III) sulphide or stibnite was called *kohl*, and it was used mostly for decorative and ritual purposes. Ground to a fine black powder, it was mixed with gum and applied to eyes with either a finger or a stick. It was so commonly used in Bronze Age Egypt that even cows, before being sacrificed, had eyes painted with *kohl*. Stibnite kept its reputation of remedy even in the Modern period. Nowadays, the females of rural regions of Egypt are still using *kohl* as a beauty treatment and as a remedy, for *e.g.* to relieve eyestrain (Hardy et al. 2006). The term *kohl* was widely accepted, and as time passed became a standard term to describe other fine powders, not only stibnite (Crosland 1962, p. 107).

When used in painting, antimony (III) sulphide or stibnite was finely ground to keep a dark grey colour. It was recognized in numerous examples in the polychrome of Gothic sculpture in Germany, but there are very few early sixteenth-century Northern Italian paintings with attested use of stibnite in the National Gallery of London (Spring, Grout & White 2003, p. 101). With respect to underwater archaeology, ground stibnite mixed with antimony oxide was found on the Kronan Shipwreck, 1676, Sweden (Appendix 5, Lindeke & Ohlson 2018, p. 70; 76).

Artisans in Venice found the compound antimony sulphide indispensable in the production of objects typical for the Venetian markets. The manufacturers in Venice had gained a knowledge of mixing a certain percentage of antimony with other metals to create alloys of improved properties. For example, mixing antimony sulphide into the alloys used to cast church bells improved the quality of the sound. It was also used in the pewter alloys employed to produce household vessels. The use of stibnite is also recorded in mirror production, for both metal and glass mirrors (Biringuccio 1942, p. 92, Kelez 1970).

Antimony sulphide was an indispensable component in pottery production in North Italy. Combined with tin and lead, it was used to produce the yellow glaze *marzacotto* (Piccolpasso 1980, pp. 51, 63), or today's equivalent lead antimonate (Dik et al. 2005, p. 593). While reviewing recipes for the potters' yellow in the sixteenth-century manuscripts, scholars noted that 'antimonio' was often mentioned as a second main ingredient of the glaze. Nevertheless, from title only, in most of the sixteenth-century manuscripts it was not possible to state whether 'antimonio' referred to antimony oxide, antimony sulphide or metallic

antimony (Dik et al. 2005, p. 596). However, it is mostly accepted that ‘antimonio’ referred to antimony sulphide (Agricola 1942, p. 91; Krischel 2002, p. 125).

9.3.6.2. Archaeological context

Since the first Gnalíć excavation campaign of 1967, three lumps of stibnite have been found. All have irregular shape, metallic lustre and bladed crystals.¹²⁴ The lump selected for characterization analyses (GN-2017-CM52) has a length around 7 cm, width of 5 cm, and a weight of 288 g (Figs 9-44. and 9-45.). The specimen was recovered in the stern area in the vicinity of the keel.

It is unknown what type of packaging existed, or where the fragments were originally located on the ship. Since only a small amount has been recovered, it is possible that the pieces were originally located on the upper decks, which had disintegrated and collapsed, so the pieces ended up covered with sediment in the area of the keel.



Fig. 9-44. and Fig. 9-45. Stibnite from the Gnalíć Shipwreck (photo: O. Guillon).

¹²⁴ One piece recovered in a previous excavation campaign was published by Kelez (1970), but its current location is unknown. The Regional Museum of Biograd na Moru does not have it in its possession.

9.3.6.3. The results of the characterization analyses

The microscope observations, XRF and SEM-EDX analyses showing the major presence of antimony (Sb) and sulphur (S) suggested the find might be antimony (III) sulphide (Sb_2S_3), stibnite type. The XRD analyses confirmed its presence.

Other minor phases are present in the XRD pattern, but it was not possible to firmly identify the source. Peaks are positioned at 2θ 3.26, 11.01, 22.62, 26.89, and 31.47. These phases probably contain the elements Si, Al, Fe and possibly Ca, the presence of which could be explained as a result of environment contamination. The changes on the surface layers can be noticed on the multispectral photography. The presence of kermesite ($\text{Sb}_2\text{S}_2\text{O}_2$), valentinite (Sb_2O_3), and calcite (CaCO_3) are also possible, but only in minor amounts.

9.3.6.4. Production and processing

Stibnite can be found in association with quartz, barite, and calcite. Usually, it has a black colour and metallic lustre, but if it has amorphous crystalline structure, the colour of the structure is red (Eastaugh et al. 2008, p. 359).

Biringuccio reports antimony sulphide¹²⁵ originates from Germany (Biringuccio 1942, p. 91). He probably refers to deposits located in the Hartz mountains in Saxony (eastern Germany) or Westphalia in northwestern Germany (Eastaugh et al. 2008, p. 359). Deposits closer to Venice were situated in the region of Siena, in the vicinity of cities Massa and Sovana, and the region Santa Fiore. The number of deposits containing antimony sulphide is even larger. Due to the availability, it does not have high prices (Biringuccio 1942, p. 91-92).

Agricola (2018, p. 428) described the process of making antimony sulphide cakes. The cakes are made by heating metallic ore in ceramic pots and not directly heating inside furnaces. Metallic ore was roasted in a shallow pot covered with an upper pot which had the shape of a bell. When the ore melted, antimony sulphide separated from other materials, and it was poured into the moulds. This process resembles the process of mercury extraction (Fig. 9-47. in section 9.3.7.).

¹²⁵ Smith and Gnudi (1942) discuss the word 'antimony' used by Biringuccio as referring to 'antimony sulphide' in sixteenth-century terminology.

9.3.6.5. Trading with stibnite

Biringuccio reports the antimony is transported in the shape of cakes from Germany to Venice (Biringuccio 1942, p. 92), but further details about the trade with antimony are unknown to author. *Antimonio* appears in the inventory of Jacopo de' Benedetti (1594) but listed as a mineral. There is a complete absence of stibnite (*antimonio*) in the insurance lists published by Tenenti (1959).

9.3.6.6. Discussion

Stibnite (*antimonio*) is recorded in historical sources and quite often mentioned in recipes for glass and pottery production, as an ingredient of the glaze today known under the composition of lead antimonate. Although the historical sources list 'antimonio', according to the description of its use it is clear it refers to the antimony sulphide. Regarding the use of stibnite in art, it was mostly associated with paintings and sculptures which originate in Germany. This is not surprising, as Biringuccio reports that stibnite originated from Germany and was delivered to Venice in cakes. Finding antimony sulphide lumps in the cargo of *Gagliana grossa* together with other colouring materials raises the question whether this was an ingredient for the sixteenth century potter's glaze. Finds of antimony sulphide and antimony oxide within the medical ingredients present on the Kronan ship from Sweden is a reminder that its healing properties should not be overlooked when giving a final interpretation.

9.3.7. Mercury (*mercurio*)

9.3.7.1. General information

Although not a colouring material itself, mercury was included in this dissertation as it imparts to production of the decorative materials. Even though mercury is a hazardous substance, it had wide use in Renaissance everyday life, as a remedy and as a material required in manufactures and arts.

During the sixteenth century, mercury was widely used because of its property to create an amalgam with other metals (Tućan 1957, p. 43). In contact with tin sheets, it created a silvery reflective layer used in the manufacture of mirrors. The technology of blending mercury with tin was known since the end of the thirteenth century, as attested by Giotto's artwork in Santa Maria della Novella in Florence (Berrie 2012, pp. 451-452).

Further, mercury had an indispensable role in gilding and silvering decorative techniques. It has been used for application of precious metals on the surfaces of metal objects. Mercury was applied on the surface of the metal object, and then attaching the decoration of the precious metals created an amalgam. Heating the object would evaporate the mercury and the decoration would remain (Thompson, 1956, p. 193). Mercury was used in large amounts to recover precious metals from ores, so the requirement increased dramatically after the discovery of the New World (Leskovec & Kramberger 2013, p. 5)

Biringuccio (1942, p. 79-85) reports how alchemists appreciated mercury, giving it the role as the base for creation of all other metals. If there was not enough warmth and dryness, mercury will remain in its liquid condition. Otherwise, Biringuccio says, it tends to find cracks in the sealed pottery and fly away.

9.3.7.2. Archaeological context

At the Gnalić shipwreck site, mercury has been found in the liquid state all over the site. The total amount is more than 50 kg, which is equivalent to approximately 4 litres of mercury. Mercury was collected with the help of medical syringes and glass jars. The original method of its packaging is unknown. Having mercury freely running at the site raised the question whether the mercury was an individual cargo item, or perhaps the drops might have separated and fallen from other merchandise present in the hold. The drops of mercury could have also originally

belonged to the reflective surface of mirrors, which were composed of a tin-mercury amalgam (Fig. 9-45.).¹²⁶



Fig. 9-46. Drops of mercury on a mirror from the Gnalić shipwreck (photo: S. Govorčin).

Kelez (1970, p. 42) reported the mercury from the Gnalić site contained 2% of tin in the composition. According to him, the mercury has a high purity, what is a direct evidence that the mercury drops do not originate from mirrors from the ship, but the mercury had been transported as an individual item. Since the ship is positioned on a slope, the largest accumulation of mercury happened at the deepest, southern part of the site. As mercury is heavy by nature, it passed through the sand and was retained against the wooden elements of the ship's hull.

9.3.6.3. The results of the characterization analyses

No characterization analyses were conducted as mercury is a toxic metal. Additionally, no information could be gained.

¹²⁶ Correspondence with the team from the Ruđer Bošković Institute in 2014. Author has no reference to attest whether it is possible for mercury to return to the liquid state from amalgam on mirrors.

9.3.7.4. Production and processing

In nature, mercury appears in the composition of cinnabar ore. In Europe, mercury was extracted from two important deposits: Almadén in Spain and Idria in Slovenia. The tradition of ore recovery in Almadén lasts for at least 2000 years (Leskovec & Kramberger 2013, pp. 5-8), while the deposits in Idria were active from the last decade of the fifteenth century (Zupančič, Žontar & Rozman 1990, p. 18). From archival records related to Idria ore mining, it took around ten days to extract the mercury, starting from heating the ore, cooling melted compounds, extracting the mercury, and finally packaging. The same process was in use in Idria during the period from 1510 to 1652 (Leskovec 2008, p. 4).

The process of recovery of mercury from the ores was described by Biringuccio (1942) and Agricola (2018). There are several processes applied for mercury extraction; for the purpose of this dissertation, the author has chosen two. All of the processes described by Biringuccio (1942) and Agricola (2018) are based on the principle of mercury sublimation and condensation; the difference is only in the set-up of the equipment or instruments.

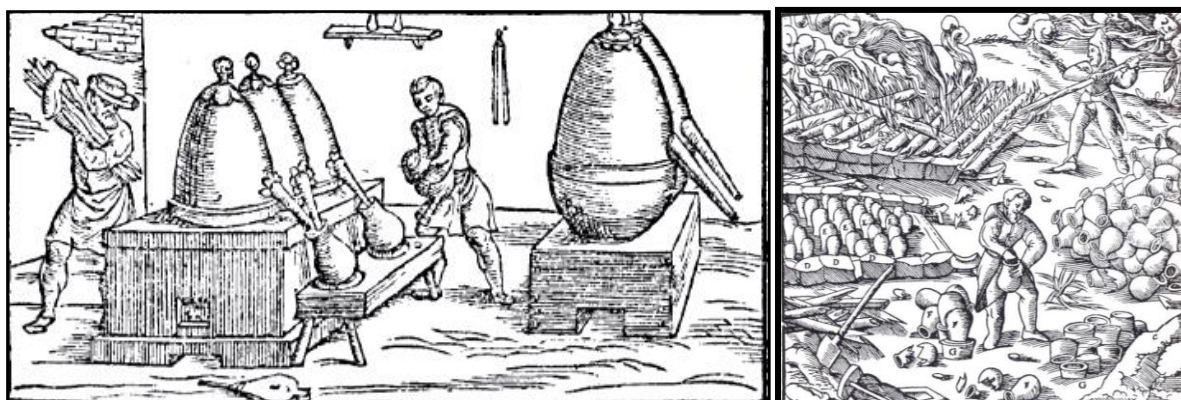


Fig. 9-47. and Fig. 9-48. Examples of mercury extraction: by distillation bell (left, Biringuccio 1942, p. 85) and by heating in the pottery jars (Agricola 2018, p. 427).

Biringuccio (1942, p. 85) describes mercury extraction with the help of the distillation bell (Fig. 9-46.). The ore was positioned in an elevated bell-shaped pot and connected by nozzle to the lower bottle. When the ore was heated, the mercury would evaporate and move through the nozzle to the lower bottle, where it would cool down and transform into liquid state.

Almost two decades later, Agricola (2018, pp. 426-427) reports the procedure of extracting mercury by heating the ore in pottery vessels, which is similar to the purifying of stibnite described in section 9.3.6.4. (Fig. 9-47.). Mercury-rich ore was covered with moss and placed in the shallow pots, being covered by the bell-shaped upper part. The pots were partly

buried in the soil, in order to seal the seam between the pot and the lid, and prevent the loss of mercury by evaporation to the atmosphere. The mercury would sublime from the ore, stick to the inner walls of the pot, condense and fall to the bottom. After cooling off, the liquid mercury would be separated from the remaining soil in the pot.

9.3.7.5. Trading with mercury

Besides mercury, Venetian colour seller shops offered mercury-based substances called *sal ammoniac* and *solimato*. Although their production causes release of extremely dangerous fumes, it is interesting to note that both of them were common due to their utility. *Sal ammoniac* was a mercuric chloride used to cure syphilis and in metallurgy (Krischel 2010, pp. 258-259; Kirby, Nash & Cannon 2010, p. 458). *Solimato* or ammonium chloride has been used in glass production, metal refinement, and manufacture of the green pigment verdigris (Krischel 2010, pp. 258-259, Kirby, Nash & Cannon 2010, p. 457). In the inventory of Jacopo de' Benedetti, mercury appears to be measured in *nozzele*, which refers to drops of the size of a hazelnut (Krischel 2010, pp. 258).

Since the Idria deposits were geographically close to Venice, it is probable that this was the origin of the material. Large international exports reported by Teneti (26 / 209, 31 / 234, 46 / 475, 56 / 608, 69 / 784, 82 / 993, 82 / 993, Appendix 8) of mercury from Venice could be taken as a marker of activity of the deposits in Idria.

9.3.7.6. Discussion

Biringuccio (1942) and Agricola (2018) deliver representational descriptions and graphic illustrations of mercury extraction, but many questions still remain. As with the previously described colouring materials, there are not enough comprehensive historical studies that would determine the most important deposits exploited by the Venetian Republic, or explain how mercury was traded and transported. The source of mercury extraction must have been Idria, but until this hypothesis is attested by historical sources or geological study, it must be taken with reserve.

9.3.8. Red lake pigment (*lacha*)

9.3.8.1. General information

While being unknown in the archaeological field, the term ‘lake pigment’ is familiar to conservators, historians, and art historians who study colouring materials. Similar to dyes, lakes are made of organic materials. The difference is that the lake pigment is precipitated onto a substrate, which is very often a hydrated alumina. The precipitate is composed of organic materials, mostly insects and plants. Lake pigment can be mixed with a binding medium and applied onto various materials, including canvas, walls, and the surfaces of objects. On the other hand, dye, which is without substrate, is soluble in water and cannot be mixed with a binding medium, but it is used for dyeing textiles (Kirby, Bommel & Verhecken 2014, p. 28).

It has been stated by researchers that the red lakes are a by-product of the textile and silk industry. The red lake pigments could be made directly from insects and plants, but due to economical and aesthetic reasons they were usually manufactured by reusing dyed cloth clippings or shearings of dyed silk. This hypothesis was made based on the historical recipes which explain how the textile was dissolved in an alkaline solution and mixed with substrate, in most cases hydrated alumina. The exact colour to be obtained depends a lot on the recipes and the types of the substrate and plants and/or insects used (Kirby, Spring & Huggit 2005; Kirby, van Bommel & Verhecken 2014, p. 32; Kirby 2015, p. 176).

Red lake pigments were widely used in European paintings from the fifteenth to the seventeenth century (Kirby 2015, p. 176). Their use had been attested in wall painting, easel paintings and manuscripts (Andersen 2015, p. 339). The main characteristic of lake pigment is translucence or transparency; it is common to mix this pigment with other organic-based pigments with good covering properties. For *e. g.*, cochineal lake found great use as a cover to vermilion and other lakes (Kirby 2015, p. 176, Andersen 2015, p. 339).

Since the lake pigment balls preserved at the Gnalić shipwreck are made of several sorts of organic components – cochineal, madder and brazilin – this chapter will not give detailed information about the trade of each type individually. In broad view, each of the components has its own story which begins at the place where it was cultivated until it was delivered as a raw material to the dyer’s workshop. Rather, this section will give general information about each of components (cochineal, madder and brazilin) to focus on trade with the colouring material in the second half of the sixteenth-century Venice, which commonly appears under the name *lacha*.

9.3.8.2. Archaeological context

The lake pigment is preserved in the shape of balls, with an approximate diameter of 1.5 cm and an average weight of 1.75 g (Figs 9-49. and 9-50.). Approximately 30 balls were accumulated at the same spot,¹²⁷ in the vicinity of the metal pins, glass beads, small-size metal buckles and the lead seals used to pack the merchandise, in this case probably textiles. The packaging method is unknown, but was probably a textile or leather bag. The balls of red lake pigment were found in the area which is interpreted as the beginning of the upper deck (see numbers 15 and 16 on Maps 5 and 6).



Fig. 9-49. and Fig. 9-50. The balls of red lake pigment (photo: K. Batur).

9.3.8.3. Results of the characterization analyses

Two samples of red lake were analysed with the aim of characterization: one ball was embedded in epoxy resin (GN-2017-CM15), and the second was ground with a pestle into a fine powder (GN-2017-CM16). Both samples were observed under the microscope, revealing heterogenic composition: most of the sample is made of fine-powdered dark purple particles, with inclusions of rounded light-yellow particles and less than 5% of blue and green particles (Figs 9-51. and 9-52.). The UV-photography showed that a large percentage of the sample does not fluoresce (Appendix 21, GN-2017-CM15 and CM16, UV photography). As fluorescence is not a characteristic of brazilin, this particular sample likely did contain brazilin.¹²⁸

¹²⁷ The photo represents only 25; the rest are in fragments or they have been selected for the characterization analyses.

¹²⁸ Personal correspondence with Jo Kirby Atkinson (29 June 2020).

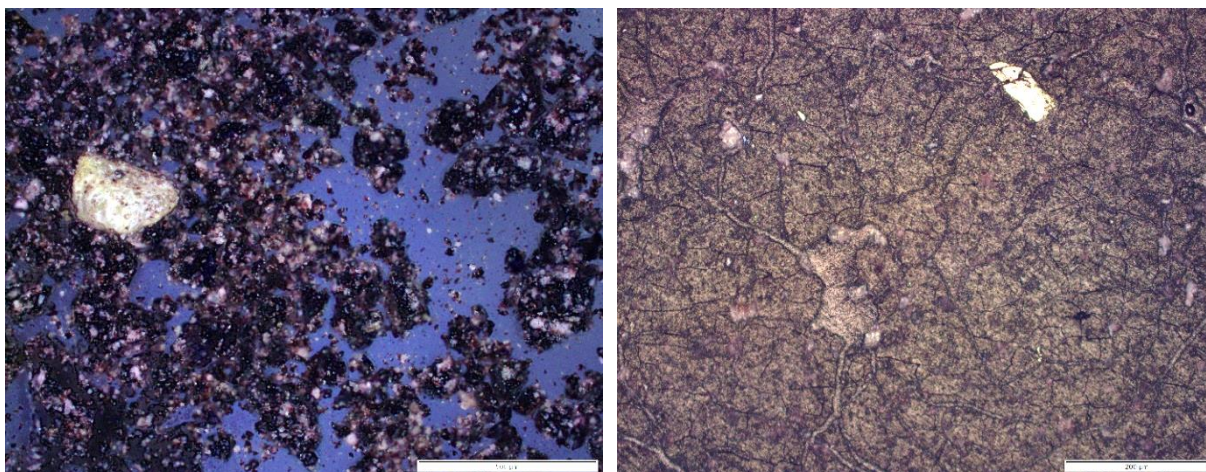


Fig. 9-51. and Fig. 9-52. Heterogeneous composition visible under polarized and analysed light, sample GN-2017-CM16 (left) and visible light, sample GN-2017-CM15 (right) (photos: K. Batur).

A high percentage of light elements detected by XRF (80%) coupled with the existence of nitrogen in the spectra of SEM-EDX was evidence to consider that the sample was organic in nature. The major elements presented by the SEM-EDX are aluminium, silicon and sulphur. Other elements can be detected, such as sodium, magnesium, phosphorous, potassium, and calcium, which is not unusual to find in red lake pigments on paintings. The mentioned elements are found in small amounts (Kirby, Spring & Higgit 2005, p 72). The elements copper and iron are attested in the results of SEM-EDX analyses in both samples (GN-2017-CM15 and -CM16), but other instrumental analyses could not verify to which compounds these chemical elements belong.

XRD analyses were performed on GN-2017-CM16. The XRD pattern is not attached to the zero, which is direct evidence of amorphous phases present in the samples. The noise in the diffractogram is caused by the presence of organic materials. The main phase is identified as alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (80.4%), which is unusual, as alunite is a mineral. It is more common to find alum, which is an astringent salt usually used for dyeing.¹²⁹ There is a possibility the sample contains minor phases - quartz, SiO_2 (12.1%) and calcium sulphate dihydrate – gypsum, $\text{CaH}_4\text{O}_6\text{S}$ (7.5%). It is difficult to attest with certainty as the noise in the pattern prevents recognition of the presence of minor phases. Part of the sample remained unidentified. The XRD pattern contains the peak at theta 7.63 which is not explained.

UHPLC analyses performed on GN-2017-CM16 revealed the sample is composed of mostly brazilin (main phase), with lesser amounts of madder and cochineal (minor phase).

¹²⁹ Personal correspondence with Jo Kirby Atkinson (29 June 2020).

Other, unidentified components are found in traces, and they might be contamination from the site or remnants from the production process.

The results of the FTIR analyses might suggest the presence of wool, since the spectrum resembles the spectrum of wool in the IRUG database (<http://www.irug.org/jcamp-details?id=1671>). The analyses would have to be repeated on several samples to confirm the hypothesis. If the spectrum really represents wool, this would be direct evidence of the production process, obtaining the dye from the clippings of dyed woollen clothes. Another argument for this production process could be the high amounts of sulphur detected by SEM-EDX.¹³⁰

To summarize, the red lake pigment from the Gnalić site is composed of an alunite substrate, with precipitated cochineal, brazilin and madder. There is a possibility of having quartz in the sample, but it is not clear whether it is a result of contamination from the site, or the quartz was a part of the original matrix. The gypsum might be present as a minor phase, in a role of extender.

The existence of green dots (less than 5% in the microscopy sample), attested also by the presence of copper and iron in the results of SEM-EDX, could potentially be evidence of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) or even some other copper-based blue or green coloured mineral, such as malachite $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$ or azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. It is also not excluded that the particles could belong to powdered glass, since this was a common practice of painters in the sixteenth century (Spring 2012).

9.3.8.4. Production and processing

It has been confirmed by studies of the historical recipes from the period of the fourteenth to the seventeenth century that cochineal, madder, and brazilin lake pigments can be made from the clippings of textiles (Kirby, van Bommel & Verhecken 2014, p. 32).

The recipe for preparation of the red lake pigment started with the extraction of the colourant in the solution, from the clipping of clothes. The clippings of clothes are placed in an alkaline solution and continuously heated. Substances such as lye made from wood ash commonly appear in the historical recipes in the role of alkaline solution, sometimes in addition to lime. The solution obtained by extraction of colourants is filtered from the remains of the textiles. Subsequently, a liquid or powdered alum is added to the solution, creating hydrated

¹³⁰ Based on correspondence with Jo Kirby Atkinson (29 June 2020).

aluminium oxide. The latter is the base for the precipitation of organic dyestuff, forming a pigment. Finally, the pigment is filtered and washed, and afterwards formed into cakes – rectangular pieces or balls which were further sold (Kirby, van Bommel & Verhhecken 2014, p. 30).

The results of experiments proved that the colour from the textile was not recycled for economic reasons only. The dye which was extracted from textile and silk clipping had a cleaner composition in comparison to the dye extracted directly from the insects (Kirby 2015, p. 176).

9.3.8.5. Trading with the red lake pigment

Within the history of the use of the dyes made from cochineal insects, it is important to be aware that the quality of colour and the types of the cochineal insects differentiate according to the geographical source. As the sixteenth-century connections allowed leverage of the materials which originated from the New World, the variety of the cochineal used in the European territory grew. Thorough studies were done on the trade with cochineal due to its specific origin, while madder and brazilin were more available throughout Europe. Possible source of alunite, a natural form of alum, is the deposits in Tolfa, near Rome, which had been used widely by Venice from 1462 onwards (Lazzarini 1985, p. 136).

Before the discovery of America, the European world was familiar with the dyes obtained from two sort of insects: kermes (*Kermes vermilio Planchon*), collected in Mediterranean regions of low bushes, as well as the Polish (*Porphyrophora polonica Linnaeus*) and Armenian (*Porphyrophora hamelii Brandt*) scale insects living in the steppes of Eastern Europe and Western Asia. The latter two are more expensive, as the insects provide less colourant, so there is more labour required to collect the insects and exploit the red dye from the tissues. Processing insects resulted in a very low amount of dye, so it was reserved only to paint valuable and rare silks and good-quality wool (Kirby 2015, p. 174).

When the Spanish founded colonies in the New World, Europe was introduced to American cochineal (*Dactylopius coccus Costa*). The large-scale import had an impact on manufacturers, who soon embraced this major development in Europe dyeing industries. American cochineal is made from the scale insect collected from the prickly pear opuntia cactus. The areas from where it was obtained were Mexico and the Peruvian Andes (Kirby 2015, p. 176).

The New World cochineal made from the insect *Dactylopius coccus Costa* was exploited by the Spanish and from the 1520s became commercially available in Europe

(Andersen 2015, p. 339). For *e.g.* the evidence of large exports is based on data in the archival documents related to *Santa María de Yciar*, a Spanish ship sunk along the shore of Padre island, Texas, USA. The ship was transporting barrels and boxes totalling 500 pounds of cochineal in the direction of Europe (Arnold & Weddle 1987, p. 359). However, this large shipment has not been archaeologically attested.

From Seville, cochineal was shipped to Florence, Venice, Antwerp and Rouen. When Spain intensified import from Middle and South America, cochineal became widely accepted throughout Europe and from the 1550s Venice became one of the main consumers of New World cochineal (Kirby 2015, p. 176).

During the sixteenth century, the cochineal pigment was manufactured in different regions, such as Venice, Florence, the Indies, Honduras, Granada, and Madrid. Historical sources often reveal which manufacture centre provided the highest quality cochineal. Other useful information is given by historical sources; the lake was traded in pellets, cakes, tablets, and cylinders, and it was available in three grades of quality – low, ordinary, and fine (Bruquetas & Gómez 2015, pp. 190-192). Cochineal from Venice (Venetian red) was highly appreciated and it obtained the highest prices on the market; for *e.g.* in 1565 the price for one ounce was twenty-two reals, while the red from the West Indies had the value of seven reals only (Bruquetas & Gómez 2015, p. 190).

Both brazilwood (*Caesalpinia brasiliensis*) and madder (*Rubia tinctorum*) were available, cheap, and easy to buy in the colour seller shops. Brazilwood (*verzino*) appears often in the inventory of the colour seller shops, and it was one of the products which Zuan di Nicolo dai colori and Marco da Corphu exported internationally (Appendix 7). In the registers of G. A. Catti and A. Spinelli, it appears in three different forms: as brazilin wood, brazilin lake pigment, and ‘entire brazilin’ (77 / 868, Appendix 8).

Lake pigments also appear in the inventory of Jacopo de’ Benedetti. The variety from dark purple to pink can be noticed, and it was not sold in great amount. In contrast with other materials, next to the lake appeared the abbreviation ‘b^{li}’, so we can assume it was sold in pellets (in Italian possible *balle*, *ballote* and *ballotine*) (Lazzarini 1985, p. 136). However, Hochmann (2015, p. 180) and Krischel (2002, p. 110) suggest that ‘*balla*’ in inventories denotes the type of preparation or storage. The recipe from the Paduan manuscript is given as an example of making the *ballotine* or pellets using brazilwood soaked in lime water and flour (Merrieffield 1967, p. 695).

9.3.8.6. Discussion

The mixture of three types of lake pigment is represented in the balls of lake pigment from the Gnalić shipwreck, with the majority pigment being brazilin, and cochineal and madder in traces. The base is identified as alunite, with potential existence of gypsum as an extender. The lake pigment from the Gnalić shipwreck might be identified as *ballotina di lacha*, appearing in the inventory of Jacopo de' Benedetti from 1594. It is interesting to mention that de' Benedetti's inventory distinguishes four types of the lake pigments, including kermes (*lacha di grana*), cochineal (*lacha di crimese*), brazilin (*lacha de verzino*) and *lacha in balle*, listed separately. Additional evidence for this identification given by Krischel (2002, pp. 110; 131-132) is referring to French written sources, which are naming the pigment as *lacha in palle di Venezia* as equivalent to brazilin. These specimens from the Gnalić site are the only preserved evidence of trade with the lake pigment in its raw form.

It is not unusual to find cochineal mixed with other dyes, as attested on Renaissance paintings. Textile dyeing was done in the tailors' shops, which means that various dyes used to dye textiles could be used to make the pigment (Anderson 2015, p. 359).

Several unidentified components of the pigment indicate that the structure of the sample could be more complex than it seems. Completing characterization analyses in the future will provide answers about the blue / green particles appearing in small amounts as well as confirm these initial analyses results. It is also possible that the XRD pattern did not provide accurate data, since it is unusual to use alunite as a substrate of the lake pigment.¹³¹

9.4. Raw materials and semi-processed products not included in the research

The variety of raw materials and semi-processed products recovered from the Gnalić site, particularly the processed metals of different kinds and forms, testifies to the excellent skills of the Renaissance European manufacturers. Some of the artifacts recovered from the shipwreck are particularly interesting, but they have been excluded from colouring material research. While application of special processes described in coloring materials sections could allow, these artefacts to be used to produce colouring materials, they were more widely used for metal casting. The dissertation is focused mainly on materials that were the most common in the inventories of *vendecolori* and in the painting studio, so all other raw materials and semi-processed products are just briefly presented, according to previously published bibliography.

¹³¹ Personal correspondence with the Jo Kirby Atkinson (29 June 2020).

The raw materials and semi-processed products recovered from the site include several varieties of brass and tin.

The brass cargo came in four different forms: two types of brass sheets, processed in rolls or stacks of medium and low thickness, known as *Bugmessing* (Fig. 9-52.) and *Rollmessing*; brass rods; and brass wire rolled into coils of different sizes (Kelez 1970, p. 41). The markings of the workshop were preserved on the brass sheets: so-called “mirk” which contained an alphabetic and numerical marking, probably to designate the thickness and quality of the brass (Petricioli 1981, p. 43). It is not excluded that the brass sheets or rolls could have been used to make copper-based pigments. When placed in contact with an organic acid, for example vinegar, urine, or wine lees, a copper-based material creates corrosion products. The corrosion could be processed and refined until it took the form of the pigment verdigris (Eastaugh et al. 2008, p. 391).



Fig. 9-53. Brass processed and stacked into sheets (*Bugmessing*). Average length is 73 cm, and width 18 cm (Cassitti 2018, p. 49)

Tin rods (Fig. 9-53) were packed in rectangular wooden boxes, and since the first excavation more than 1000 kilos of tin have been recovered. The average length of a tin rod is 60 cm (Cassitti 2018, p. 49). During the sixteenth century, the largest amounts of tin were imported from the Great Britain to Venice, where it was refined and melted into rod shapes. The final product had the stamp of a Venetian lion, marking the purity and the quality of the product (Kelez 1970, p. 43).

Tin was popular in creating effects of false gilding with the addition of yellow colour and also useful in manufacturing other colours such as mosaic silver and bronze. It was unsuitable as a painting material, so it is not often recorded in the layers of an artwork. In general, it had wide applications in illuminated manuscripts (Eastaugh et al. 2008, pp. 368-

369), and was used in manufacturing pottery glaze and glass production (Berrie & Matthew 2004, p. 214).



Fig. 9-54. A fragment of a tin rod (photo: K. Batur)

10. Final discussion

The Venetian *nave Gagliana grossa* that sunk in vicinity of the Gnalić islet in the middle of the eastern Adriatic coast in November 1583 has become an archaeological site which has brought indispensable data for studies of the trade and relations between Venice and the Ottomans at the dawn of the sixteenth century. Among the cargo, composed of products from prominent European manufactures, including five thousand window panes shipped for the renovation of the palace of sultan Murat III in Constantinople as well as gifts of precious silk textile for the sultan's mother Nūr Bānū, a particularly interesting part is composed of colouring materials. These finds are the only archaeological evidence in existence of the international trade with colouring materials between Venice and Constantinople, which until now was known only from very limited historical documents. The finds present a unique time capsule, allowing physical study and recording of the colouring materials which, regardless of their provenience, were offered in Venice at a particular time and thus become valuable evidence of international export.

To emphasize the value of the find, it must be restated how the fundamental issue in the current state-of-the-art is a lack of historical documents that would allow systematic study of the trade in colouring materials. The remarkable preservation of the colouring materials at the Gnalić site allows recording and comparison with historical documents, delivering new data to facilitate the re-evaluation of hypotheses previously postulated by researchers. In the large scale, these hypotheses are based on questioning Venice's reputation as a centre for colour trade in Europe, revising the list of well-known colouring materials that were manufactured in Venice and had a status of important export products, and understanding the compositions of the colouring materials individually.

Until now, underwater archaeology has not contributed significantly to studies of Renaissance trade with colouring materials due to an almost complete absence of archaeological sites from the Early Modern period.¹³² Information about which colouring materials were offered in sixteenth-century Venice is based on a very limited number of archival documents associated with Venetian colour sellers (*vendecolori*) coupled with the results of characterization analyses of pigments from Renaissance paintings. The state of knowledge of international maritime export is even less well-known; systematic studies cannot be executed

¹³² One potentially interesting site could be the Early Modern shipwreck in Prižba, Korčula island, Croatia mentioned in chapter 2 and Appendix 4. Due to its cargo of arsenic attested at the site, it could possibly be identified as *marciliana Barozza*, which sunk in 1603 near Korčula on her way to Valona (56 / 608, Appendix 8).

as the documents of ships' cargo loaded in the ports, contracts, cargo valuations and port books are scarce or missing for the entire period of the late sixteenth century.

With respect to the above, this dissertation aims to deliver unique information preserved in the archaeological record of the sunken *Gagliana grossa* to supplement historical sources and contribute to the knowledge of international trade and maritime transport of colouring materials. It is focused on recognizing colouring materials which Renaissance society used for different purposes – as pigments on paintings, miniatures and frescos, as medicines or cosmetics, as materials essential in the glass and textile industry, but also for painting objects of everyday use, like furniture, musical instruments, playing cards, or terrazzo floors (Matthew & Berrie 2010; Krischel 2011).

Unused and preserved in the form of manufacturing moulds or as a fine powder, colouring materials were found in the same condition as they were exported from an unknown Venetian manufacturer or colour seller shop. The original packaging in barrels, casks, and boxes, sometimes marked with a monogram or illustrative stamp, has great potential for study. The transport containers and cooperage marks may connect the colouring materials to a specific source, or a particular colour seller. The co-existence of colouring materials with other artefacts of fine manufacture present in the cargo gives an insight into the whole repertoire of objects that were not only present in everyday life in Venice, but appreciated and in high demand in Ottoman society.

Collecting the samples from an underwater archaeological site with respect to archaeological context, then proposing an historical name according to information known from the historical sources as well as experimentally determined chemical composition, proved to be a substantial and sound methodology for colouring material identification. Within the methodology, it was essential to understand the limitations of all three phases – underwater excavations, historical sources, and characterization analyses – and take them in consideration when interpreting the data regarding trade with colouring materials between Venice and Constantinople.

While the *Gagliana grossa's* position at a depth of 26 to 30 metres slowed down the plundering of the site, it also created difficulties when recording colouring materials. Increasing depth lowers the amount of sunlight, resulting in poor perception of colour. Blue and green tones are very difficult to detect, particularly when a potential colouring material is buried in an archaeological layer, or when its original packaging, such as barrel, cask, or box, is missing. Bright yellow is the only highly recognizable hue, when preserved in the sediment or as traces on the ship's hull.

The colouring material cargo from the Gnalić shipwreck probably included a much larger number of items, but unfortunately, those could be lost forever. Since the first excavations were conducted, researchers recorded that the ship was ‘full of mysterious materials’ (section 5.2). The general problem in studies of the artefacts from the Gnalić shipwreck site is the fact that the site was disturbed on multiple occasions during decades of research and exploration. Due to many reasons, we will never be able reconstruct the entire cargo of the colouring materials within the ship. First of all, we have to bear in mind that after the wreck, in December 1583 and January 1584 the shipwreck was salvaged by Greek divers led by Manoli Fregata from Crete. At that time, the personal belongings of the crew, fragile cargo, and other precious items originally loaded onto the (still standing) upper decks were accessible to the divers. The author doubts that raw materials available locally were the items preferred during the recovery, but if there were smaller packages of gold or silver, perhaps intended for decorative purposes, they probably experienced the same destiny as the precious emeralds and jewels loaded by Dutch merchant Guglielmo Helman, which were recovered by divers and returned back to the owner, with compensation of one-third of the total value (Radić Rossi & Nicolardi 2019, p. 143).

Even when the archaeological excavations were officially executed in 1967 and 1968, the use of divers who were never trained in underwater archaeology in many cases resulted in actions not condoned by contemporary methodology. Heavy ship’s equipment such as ship’s guns were pulled through the site, crushing the wood and the artefacts before recovery. Using dredging tools without having the feeling of damaging the artefacts had volatile consequences – many artefacts, especially the ones of smaller size, were dredged together with the sediment, while the integrity of many barrels was disturbed.¹³³ Even if sediments of unusual colours or different morphologies were noticed, they could not be properly analysed, as analytical instruments were not available to the first researchers. Still, the chemical analyses and identifications done by Ivo Kelez (1970) are admirable, since the facilities and equipment available to him were quite modest.

Further, before the official discovery of the shipwreck in September 1967, the site was familiar to foreign divers, some of whom helped themselves to souvenirs and artefacts from the site. This site looting never completely stopped even during and after the official excavation project. Today, many artefacts recovered from the Gnalić shipwreck are not exhibited in the

¹³³ Based on diaries of Ksenija Radulić available in the documents kept in the Ministry of Culture of the Republic of Croatia, Conservation Department in Zadar.

Regional Museum of Biograd na Moru, but are actually part of private collections. Based on photos of artefacts looted from the site and exhibited in diving centres and private apartments in Belgium, we know that many unique artefacts were forever lost to the scientific community (Petricioli 1973).

Regarding recent excavations conducted from 2012 to 2019, it is necessary to point out that the archaeological trenches were opened on the sections previously excavated by researchers in the 1960s and 1970s.¹³⁴ This means that most of the materials, barrels and casks positioned in B17 / B18, C17 / C18 / C19 were already exposed during previous excavations (Maps 5 and 6). By the end of the 2019 excavation season, the excavated area encompassed the aft starboard part of the ship. Should the planned excavation be conducted in the future, the forward starboard section of the ship will be excavated. This part is less disturbed by the previous excavations and the mapping and recording of colouring materials should provide a better picture of the loaded cargo than the one obtained based on excavations to date. The find of one cask filled with lead white ingots on the forward starboard side suggests the beginning of the second barrel area (Map 7).

There are several drawbacks associated with the historical sources studied for this dissertation. First, no systematic research has been done on the manufacturers of colouring materials in Venice, so it is not possible to make comparisons or entirely understand the production processes from which these colouring materials might have originated, including the original sources of the raw materials used in their manufacture. From the aspect of trade, it is unfortunate that the bills of lading or other documents which listed cargo loaded onto the ships are missing. Matthew (2011) points out how those documents, if they existed, would certainly give a complete picture of the amount of goods coming in and out of the city, and enable comprehensive study. However, analyses done on Alberto Tenenti's *Naufraques, corsaires et assurances maritimes à Venise, 1592-1609* demonstrated that colouring materials appeared in maritime insurance documents, and therefore these documents can provide the data of international transport. However, these documents do not have the same value for building a comprehensive picture of trade, as they mark maritime accidents only, not the entire number of ships and their cargo going in and out of port. Other limitations of insurance documents include: sometimes the owners of the goods and their insurers are listed in the document, but the actual list of goods is missing; small, valuable minerals could be smuggled and not listed;

¹³⁴ The progress of the excavations can be followed by maps, which are attached chronologically and marked with numbers from 1 to 7.

some colouring materials can be so cheap that they were not even worth insuring; and finally, the source the author was using represents only two notaries' documents among dozens active in the same period.

Finally, regarding characterization analyses, it is important to be familiar with capabilities and limitation of the instruments, so the interpretation could be justifiable and use the time for the analyses wisely. While several instruments are able to identify one material, as in the case of red ochre identified by XRD, FTIR and RS, others are not so easily detectable. Arsenic sulphide (realgar) was recognized only by the help of RS, while XRD did not recognize it at all due to the small percentage of the material. Arsenic sulphide will also absorb in the infrared region and thus not be appropriate for analyses by FTIR. The components of the red lake pigment (cochineal, madder and brazilin) were recognized only thanks to the access to UHPLC and comprehensive database of organic dyestuff created by the Cultural Heritage Agency of the Netherlands. This is a great example of how access to proper instruments and historical databases created by conservation science experts can ease the process of characterization and identification within archaeological research.

Even though the Gnalić underwater archaeological site is not excavated entirely, but only in the aft part of the starboard side, the remarkable variety and amount of colouring materials recovered from the underwater site are strong evidence of the selection of colouring materials offered in Venice, known as the 'city of colour'. Colouring materials identified during the research include lead white, red ochre, mercury sulphide (bell-shaped presented as type A, and lumps as type B), minium, arsenic sulphides / realgar, stibnite, mercury, and red lake pigment. The ship was also transporting cupreous materials in different shapes, as well as tin rods, which, to some extent, could impart to colouring material production. These raw materials were not included in this study as their use was too wide and they do not appear very often in the sources in the context of colour selling.

While all of these colouring materials are known to have been traded from Venice to the East, they can be separated into three categories:

- colouring materials which were known to be intensively produced in Venice and exported: lead white, minium, mercury sulphide and red lake pigment;
- colouring materials that were common and traded from Venice to the Eastern Mediterranean, even though they were available locally in the Eastern Mediterranean: red ochre and arsenic sulphides;

- colouring materials that also have been discovered on other shipwrecks as a medical supply: antimony sulphide and mercury.

The demand for these materials existed in the East, especially for the ones that Venetian manufacturers were well known for: lead white, mercury sulphide and red lake pigment (Matthew & Berrie 2010). Venice was well known for the strong production of all three and the Gnalić shipwreck is providing a great deal of evidence that strongly supports that statement. Additionally, minium can be included; although not exported in such significant amounts, there is evidence that the Eastern Mediterranean had a certain demand for it, as it was used on Islamic paintings (Berrie 2007).

Lead whites were generally made into conical forms and packed in casks. Casks are preserved on the Gnalić shipwreck site, but mentioned in Tenenti under the term *barili* (Tenenti 1959, p. 74). The average cone size is 2.6 cm diameter at the bottom, 6.3 cm diameter at the top, 5.5 cm height and an average weight of 390 g. More than 1500 kg have been recovered, with wide variation regarding weight and size. The casks were filled with straw to prevent crushing the ingots, and each ingot was probably individually wrapped in leather. Based on analyses of painting material, coupled with historical sources, researchers have previously proposed that the lead white was sold in different varieties and hues (Berrie & Matthew 2011), and that the painters knew how to employ the different varieties of lead white to obtain different effects (Stols-Witlox 2011).

The results of the characterization analyses demonstrate the differences between selected lead white cones: from cerussite only (GN-2017-CM36, -39, Appendix 21 and GN-2018-LW3, additional sample, Appendix 20), to the sample of combined cerussite (65%) and hydrocerussite (35%) (GN-2017-LW2, additional sample, Appendix 20). The presence of calcium has been attested in several samples, but only by SEM-EDX and Raman spectroscopy; it was not recognized by XRD, presumably due to detection limit. The author's suggestion is that the different sizes and weights of the lead white cones, and possibly different packaging as well, might have served to differentiate the lead white according to composition. Another issue that could be contrary to the result is the question whether the existence of hydrocerussite in the lead white cones might have resulted from the conversion of cerussite due to seawater that penetrated through the cracks of the lead white, and not from the original production process. The systematic study of the cones from one or several casks undisturbed by previous excavations has to be completed to understand this problem.

Lead white was manufactured intensively, and some of the Venetian production places are even associated with specific colour seller shops. According to documents, lead white appears under two titles: *sbiacha*, which are probably the flakes or corrosion created in reaction of lead with the vinegar, and *cerussa*, the final product which was made by refining *sbiacha*. The process of synthesizing and refining lead white was well known; Venetians produced lead white of such great quality that it even adopted the name ‘Venetian cerussite’.

Unfortunately, systematic studies of the lead white manufacturers of the second half of the sixteenth century have not been executed. However, there are representatives of manufacturers of lead white / colour sellers that managed to build their wealth based on international exports. The best example is the shop of the family Gradignan della Scala, with the sign of the ladder, which specialized in production of lead-based products which were intensively exported from the second half of the sixteenth century. Some of the Gnalić site casks filled with lead white bore the stamp of ‘the ladder’, but since the Venetian system of marking cooperage is unknown, it is difficult to state without comprehensive historical studies whether those marks can tell us anything.

The ships were transporting large shipments to Alexandria and Constantinople. From what we know based on the insurance documents, the biggest shipments were transported in *saetia Vidala*, with cargo encompassing over 400 casks of lead white going towards Alexandria in 1592 (3 / 10, Appendix 8) and *nave Martinella* with a cargo of 170 casks of lead white going to Constantinople in 1601 (46 / 475, Appendix 8).

Minium or red lead has been preserved in the form of irregular lumps and attested in two examples only. As in the case of lead white, the external surface of the minium lumps were encrusted with an alteration layer, composed of galena. The total amount of recovered minium is 1.6 kg. Minium was present in the inventories of Venetian colour sellers who were active in retail levels of international export. The demand in the East existed, although it never reached the level of request for the lead white (70 / 788, 77 / 868, Appendix 8).

Mercury sulphide was transported in two forms: type-A and type-B. The type-A form was bell-shaped, with height and diameter of 27 cm and a weight from 80 to 100 kg. There were originally 14 type-A bells recovered, a total amount of 1000 kg. The second form, type-B, was in the shape of lumps. The difference between these two forms is unknown – no characterization analyses have been done for comparison purposes. Presumably the different forms represent different amounts that were offered to the customers.

Choosing the proper historical title in the case of mercury sulphide must denote whether the material is of synthetic nature or not. If it is produced artificially, by mixing mercury and sulphur at a high temperature, the product is called vermilion. If it is found as a naturally occurring ore, it is termed cinnabar. This distinction in the terminology used for natural and synthetically prepared mercury sulphide is noticeable beginning in the seventeenth century. Regarding the production or processing technique of the mercury sulphide found at Gnalić, the author can only suggest that the type-A mercury sulphide is of synthetic origin, therefore, it can be called vermilion. This is based not only on the bell shape but also the ‘layering’ present on the surface and the channel visible in the section of the bells. Mercury sulphide often appears in the inventories of the colour sellers, under the titles *cinabro* or *cenaprio*. Cinnabar was a usual item offered in the shops of the *vendecolori* (Appendix 7).

Mercury sulphide was exported internationally, as can be seen from the partnership formed by Zuan di Nicolo dai colori and Marco da Corphu from 1550 (Appendix 7). However, the Venetian Senate allowed the import of mercury sulphide from Spain, as it seems Venice did not manufacture enough mercury sulphide to satisfy demands of the Venetian market. In comparison with other colouring materials mentioned by Teneti (1959), mercury sulphide was exported in small amounts, and it was mentioned only once, transported in nave *Falcon Bianco* in 1609 towards Lisbon (82 / 993, Appendix 8), together with mercury, while the rest of the colouring materials shipment was made of emery and *smaltini*. Based on the large amount of mercury sulphide present in the cargo of the *Gagliana grossa*, trade in this material was clearly strong at the end of the sixteenth century, despite the lack of evidence in historical documentation.

Red lake pigment was one of most popular Venetian pigments. The *Gagliana grossa* was transporting lake in the form of small balls of diameter of 1 to 1.5 cm, composed of alunite substrate, with precipitation of cochineal, the roots of plant madder, and brazilin or redwood. There were around 30 balls of the red lake pigment in the cargo of *Gagliana grossa*. The packaging method is unknown, as the balls were discovered in the part of the ship that would belong to the upper deck, deeply covered in sediment. The balls were found together with pins, small metal elements that resembled buckles, glass beads, and lead seals that were usually placed as a mark during trade with textiles.

Red lake pigments were produced as a by-product of the dyeing industry. They were produced by the process of dissolving cloth clippings in lye and subsequently mixing with alum. All lake pigments were sold in balls, either *ballote* or *ballotine* (Lazzarini 1987, p. 119), which can be associated with the *ballotina di lacha* on the list of goods present in the shop of Jacopo

de'Benedetti from 1594. Merrieffield (1967) reports that 'Venetian lake' is composed of several substances, with the majority being cochineal. Several international shipments mention crimson, which could be equivalent to red dye or red lake pigment (39 / 341, 56 / 608, 77 / 868, 83 / 1017, Appendix 8).

The analyses result of the lake pigment suggest this structure could be much more complex than it seems. Minor traces of indigotin, the main dye present in indigo, were identified, which could be evidence of contamination. Gypsum was possibly used as an extender, while the presence of blueish and greenish dots and associated iron (Fe) and copper (Cu) may indicate the presence of another component, possibly pigment or even glass particles. It is also unusual to have alunite detected in the sample.¹³⁵

Red ochre and arsenic sulphides from Venice were in demand in Constantinople, even though sources of these colouring materials were well known and exploited in Asia Minor (WestHugh 1997, p. 49; Eastaugh et al. 2008, p. 327). This is especially noted in the case of import of arsenic sulphides (Lazzarini 1987, p. 117). It is unknown why the materials originating from Venice were favourable; it could have been due to the special refinement techniques which were well known by Venetian manufacturers, or perhaps it could be the quality of the raw materials. This evidence confirms the statement of Matthew (2011) that, even if the materials were available locally, there was still a great demand for import. The quality of the Venetian processed product was highly appreciated in the East, and perhaps facilities or experts who were capable of processing and refining those pigments were not available. A confirmed explanation for this demand remains unknown to the author; it is possible mineral deposits in Asia Minor were exhausted, so the Islamic world relied on imports from Venice. More likely, this demand was related to the possession of goods that originated from Venice, as it was highly fashionable and a sign of luxury.

Red ochre was transported in six oval barrels from 80 to 90 cm height with lid widths from 60 to 65 cm. Two long barrels, one oval barrel, and two rectangular boxes were also recorded to be filled with the red colour, but never sampled. The pigment is composed of a majority of hematite, along with alunite and quartz, and it was sold as a fine powder.

Lazzarini (1987, p. 119) states that *terra rossa*, material rich in hematite, naturally occurs in the area of Veneto, and it was exploited by Venetians in the sixteenth century. Since the deposits were exhausted in the eighteenth century, it was replaced by a synthetically produced colour which preserved the title Venetian red (Eastaugh et al. 2008, p. 208). With four

¹³⁵ From correspondence with Jo Kirby Atkinson on 29 June 2020.

varieties listed, the inventory of Jacopo de' Benedetti displays the variety of the iron oxide-based pigments offered in Venice at the end of the sixteenth century. It is interesting to see that, even if *terra rossa* was available locally, there was a variety of iron oxide-based pigment available in Venice which originated from the East (*lapis rosso*). Regarding maritime insurance documents, *terra rossa* appears only once, in the abovementioned nave *Zena* (77 / 868, Appendix 8). Even if the local resources suggest exploitation in the region of Veneto, equalizing red ochre with Venetian *terra rossa* would be rushing into unfounded conclusions. The variety of iron oxides listed in de' Benedetti's inventory is clear evidence that any statement about provenience should be taken with caution. The research of deposits in Badia di Calavena in high Illasi Valley and in Monte Lessini, Veneto, Italy done by Cavallo, Riccardi & Zorzin (2015, 2016) gives a potential for future studies by possible comparison of mineralogical data with the samples from the Gnalić shipwreck. Matching of the data would be the first direct evidence Venetians exploited locations explored by the abovementioned authors, and would also confirm that red ochre loaded on *Gagliana grossa* can be identified as Venetian *terra rossa* from either Badia di Calavana or Monte Lessini in Veneto.

At the beginning of the research, the term 'arsenic sulphide-based colouring material' was suggested, to describe yellow, orange, and reddish coloured particles on the ship's hull and in the sediment. Since different hues of the colours were present, it was suggested that both orpiment and realgar were present in the cargo of the *Gagliana grossa*. However, the RS analyses with both green and near infra-red lasers have only confirmed the presence of realgar. The results of the characterization analyses could only define the peaks of realgar and pararealgar, the latter probably existing as an alteration product. The peaks overlap, suggesting that the mineral did not crystalize entirely, and that there were many mineral phases and alteration products present in the sample. According to the early site reports, *Gagliana grossa* transported either three or five casks filled with yellow colour, one of which was recovered and exhibited in the museum along with one lid which bears a mark of the letter N and the number 37. Although only realgar was confirmed in the analyses, it is not excluded that orpiment was also transported as a part of the cargo. There is evidence that orpiment and realgar were often traded together; additional sample analyses may well locate a phase that belongs to orpiment.

The materials were probably transported as a fine powder only, although, according to de' Benedetti's legacy, arsenic sulphides could be present in more varieties (Krischel 2002). Tenenti's register, however, suggests two titles for arsenic-based colouring materials – orpiment and arsenic. For instance, when exporting arsenic-based colouring materials, it was named 'arsenic' and packed in casks (2 / 3, 56 / 608 and 70 / 788, Appendix 8). This could refer

to arsenic oxide used in manufacture of arsenic sulphides. On the other hand, the ship that imported arsenic sulphide from Constantinople and Palermo called it ‘orpiment’ and transported the material in boxes (22 / 184, Appendix 8).

Previous examples present antimony sulphide and mercury as raw products which have to be mixed with other substances in order to be used as painting materials or for various other purposes. For example, antimony sulphide was a major component in brass casting, especially in the production of bells (Kelez 1970). Manufacturers were familiar with the fact that the addition of antimony sulphide improved the quality of the sound (Kelez 1970). Mercury was an important material for mirror production; when placed in contact with tin sheets it created an amalgam, giving a reflective surface to the mirrors. Lastly, since both antimony sulphide and mercury were found on shipwrecks from the Modern Period in the context of pharmaceutical materials (Mary Rose, England, 1545; Kronan, Sweden, 1676; Appendix 5), it is not excluded that some of the materials found at the Gnalić site could be interpreted as medicinal in nature, owned by a travelling surgeon or pharmacist.¹³⁶ Unfortunately, these finds were scattered, and the pestle (Appendix 3) recovered from the Gnalić shipwreck that perhaps could be associated with either medicine or colour preparation was not found in the vicinity of these materials.

Antimony sulphide is a grey coloured mineral with bladed silver texture. Since excavations began in 1967, only three pieces have been found. It is unknown in which transport container those were stored. Antimony sulphide was not common on paintings, but in addition to lead and tin, it was commonly used to prepare the glaze *marzacotto*. Antimony sulphide appears in the list of the goods from de’ Benedetti’s shop with the description ‘mineral’, but it does not appear in maritime insurance documents (Tenenti 1959).

Mercury or quicksilver is present on the site in a liquid state. Its packaging method is unknown, but since 2012 at least 50 kg of liquid mercury have been collected. Unlike materials previously mentioned, it cannot be directly used to impart colour. It was used commonly for the production of synthetic colours, such as mercury sulphide. Mercury also had a wide use in gilding processes, and silvering was impossible without its use (Matthew & Berrie 2010, p. 246). If we consult the documents published by Tenenti, we can see that mercury shipments were often dispatched from the port of Venice (26 / 209, 31 / 234, 46 / 475, 56 / 608, 69 / 784, 82 / 993, Appendix 8).

¹³⁶ It has to be considered that it is unknown whether *Gagliana grossa*, as a merchant ship, had a doctor on board.

Although the cargo of *Gagliana grossa* was loaded in Venice, the question of material provenience should be taken with great caution, as each material individually requires a thorough study. The fact that the cargo was loaded in Venice, which was a prominent trading centre known for its colour seller industry, does not mean all of the cargo originated in Venice. The flow of various raw materials was essential to satisfy not only colour seller demand, but also the glass and dyeing industries, which produced items fundamental to the sixteenth-century Venetian economy. Venetian manufacturers were appreciated for their high expertise and knowledge in processing materials. As stated by Matthew (2011), a wide array of raw materials was imported to Venice, processed, and then exported. The possibility that the cochineal from red lake pigment of the *Gagliana grossa* originated from the Americas adds a great value to this statement. This means that the raw cakes of New World cochineal had to be imported in Spain, then shipped to Venice, where they would be processed and re-exported to the Eastern Mediterranean. Even if Venice was known for the production of the red lake pigment, it is questionable whether the red lake pigment was actually processed in Venice, because it could have been made in for *e.g.* Florence, as mentioned in the shipment of Alvise Gradignan della Scala below.

Another reason why the question of provenience is complex comes from the fact that the colour sellers, who were sometimes involved in international trade, sometimes acted as intermediaries. Their shops could offer materials of foreign origin. If the colour seller was involved in international trade, he could easily make a shipment of materials that were not processed by him, but prepared somewhere else on the Apennine Peninsula or internationally. A great example comes from Alvise Gradignan della Scala, who, together with the lead white products from his own shop, selected the best colouring materials from Italian manufacturers to supply the Spanish royal court with ‘pigments’ in 1572. The dispatch of pigment order listed ‘lead-tin yellow (*giallolino*) from the Venetian island of Murano and red lake from Florence’ (DeLancey 2017, pp. 25-26). The shipment intended for the Spanish royal court could have ended up on the seabed due to maritime accident, and subsequently been discovered by archaeologists 400 years later. Without archival documents to explain the provenience of the shipment, this cargo could face the danger of being interpreted by an archaeologist as products of Venetian manufacturers, which is not entirely true. This example represents how crucial it is to understand historical context, trading mechanisms, and the circulation of raw materials, and to rely on comprehensive historical studies to avoid hasty interpretations of provenience. This is the main reason why this dissertation gives a suggestion, but not the final answer, about the production processes and the provenience of raw materials.

The finds that have been recovered and identified with characterization analyses are all materials that are known to have been traded between Venice and Constantinople, but in the broad picture, between Venice and the East. The fact that a merchant ship ended its trip in Constantinople does not necessarily mean that her cargo was destined to be used there. The cargo could subsequently be transported by caravan routes that were crossing Constantinople, as presented in Appendix 6. The analyses of pigments from Islamic paintings confirmed the presence of lead white, vermilion, red lake, verdigris, orpiment, hematite, realgar, minium, lampblack, powdered silver, and gold (Berrie 2012). Since these materials were used for a much wider scope – painting pottery, various objects for everyday use, walls, and so on – understanding how much the Islamic world used these colouring materials can be improved by consulting these published references. The author does not know the state of research within this field.

Among the abovementioned materials, the presence of verdigris, lampblack, powdered silver, and gold was not detected. It is not known in which shape verdigris was sold, but there is always a possibility that the cupreous rolls within the cargo were intended to be used to create verdigris. If verdigris was ready-to-use, like for instance lead white or minium, it is very likely that the copper on the sheet surface would react in alkaline conditions on the site (Nassau 2001, p. 289), especially in the presence of sulphur. The question is whether this reaction would create an alteration layer, and if the answer would be affirmative, this means verdigris would be difficult to distinguish on the sea bottom at a depth of 26 to 30 meters. Verdigris, or *vert-de-gris* as named in Tenenti (1959), is listed in the colouring material shipments of two ships – *nave Perastana*, sailing in 1605 to Alexandria (70 / 788, Appendix 8) and *nave Zena*, sailing in 1607 to Constantinople (77 / 868, Appendix 8). As the amounts of verdigris listed are of small size, if we consider that they might have been packed in either leather or textile for transport, and the packaging subsequently had disintegrated, it would be very difficult to spot the copper-based pigment in the sediment.

It is also important to mention that in the period considered by Tenenti (1959), the routes to Constantinople could be combined maritime and land routes, as presented in Appendix 6 based on Giuseppe Rossacio *Viaggio da Venetia, a Costantinopoli per mare, e per terra & insieme quello di Terra Santa* from 1598. At the end of the sixteenth century, Venetian loss of its *Stato da Mar* territory caused increased danger in maritime navigation along the old sea route to Constantinople. As a consequence, the ships departing from Venice sometimes sailed in the ‘safe zone’ within the Adriatic, then unloaded their merchandise in Ragusa or Valona for land transport to Constantinople. In this sense, it is possible to consider the shipments of

colouring materials from the unnamed fregata sunk in 1599 (40 / 347, Appendix 8), destined to Ragusa, and *marciliana Barozza* sunk in 1603 (56 / 608, Appendix 8), destined for Valona, as potential shipments to Constantinople.

Looking at the broad picture of all recovered colouring materials, this dissertation questioned whether these colouring materials could originate from the shops owned by colour sellers (*vendecolori*). It must be emphasised that Venice was the first city in Europe that marked the segregation of this profession from the pharmacist (*spezieri*) and the sellers of confectionary (*spezieri di grosso*), where colouring materials were sold before. During the second half of the sixteenth century and the first half of the seventeenth century, the number of shops had grown rapidly. The shops operated on both a retail and wholesale level, while international export was reported only in the cases of creating pacts between two colour sellers. Inventories of the shops owned by colour sellers, when coupled with the Gnalić shipwreck finds, are used to generate an overview of Venetian colour selling materials in the sixteenth century (Appendix 7).

In order to support the hypothesis, maritime insurance documents were consulted, with special focus on the trade with colouring materials (Appendix 8). The author created a review of the colouring materials imported and exported from Venice based on Alberto Tenenti's *Naufraques, corsaires et assurances maritimes à Venise, 1592-1609*. Especially large shipments of colouring materials listed in the insurance documents were selected, so the owners and the insurers of the merchandise can be checked. As a result, two large shipments of colouring materials could be related to families Gradignan della Scala and Bosello. Both family names matched the names of the persons who owned colour seller shops at the end of the sixteenth and the beginning of the seventeenth century. Both families were situated in the *Calla dei Stagneri* in the vicinity of Rialto bridge, and, having a long tradition, built their wealth and reputation on the colour selling business. It is particularly interesting that their mutual wish for improvement of business and wealth resulted in intermarriage between the families. Besides having direct proof that the colouring materials could originate from colour seller shops, the evidence suggests that the large shipments came from influential and wealthy families who could boast of a long tradition of colour selling activity.

The historical value of the Gnalić shipwreck as whole is in the fact that it provides a unique insight into one trading venture between Ottomans and Venetians at the end of the sixteenth century. It is important to consider this in historical context. At this point, the power of Venice is weakened; her loss of main maritime and land possessions resulted in deterioration of safe trading corridors to the East, as well as removing access to natural resources (for *e.g.* grains and raw materials). However, Venice still managed to maintain trading connections,

thanks to the wealth and reputation she had built based on trade with the Eastern Mediterranean in the fifteenth century.

Conflicts and continuously present tensions between Ottomans and Venetians pervaded the sixteenth century. Regardless of frequent conflicts in the sixteenth century, the Venetians kept strong trading relations with the Ottomans. The battle of Lepanto, which happened on 7 October 1571, was the last major conflict of the sixteenth century, but at the same time a turnover in political relations between Venetian and Ottomans resulted with lowered contacts and diplomatic relations. The end of the sixteenth century is a period when the intensity of trade decreased not only due to the decline of shipbuilding and cooling relations with Ottomans, but also due to the appearance of Western maritime powers, as English, Dutch and French fleets began taking over the Mediterranean trading routes.

In the context of the events of the sixteenth century, the *Gagliana grossa* is a not-so-common example of a ship that continued to maintain relations between the Ottomans and Venice, including large trading shipments and diplomatic gifts. This was possible due to the fact that the trade between Venice and Constantinople was executed between family members of the da' Gagliano family – Domenico and Odoardo da Gagliano, whose trading network encompassed merchants of various backgrounds and multicultural profiles (Dursteler 2006; Radić Rossi & Nicolardi 2019). The Ottoman demand for Venetian products in the period of the decline in trade, especially in the case of window panes ordered for Sultan Murat III and the gifts of silks for his mother Nūr Bānū, can be considered as an acknowledgement of the high expertise of Venetian artisans. Even though Venice lost dominance over Mediterranean routes, this shipment proves the reputation for luxury of Venetian products did not lose its shine.

Although there is no information available regarding where these colouring materials were destined or for what purpose they were intended, their existence onboard a Venetian *nave*, which was at the same time shipping valuable cargo to Constantinople, demonstrates that the colouring materials from Venice must have been appreciated. Having the material from the city well-known for trade with colours could be considered as fashionable, and thus favourable among the Islamic world.

It is important to bear in mind that characterizations that lead to identification are just a beginning step to study the objects, as there are more aspects from which these colouring materials can be observed. Firstly, they transmit information left by the society, such as knowledge about technology processing, demand data for certain types of colours, and traces which are the consequence of the formation processes of the archaeological site. When the artifacts are recovered from the site, their shapes, appearance, marks and colours are the result

of numerous factors, such as quality of ore, their production process during manufacture, the act of loading in casks, barrels, chests and then loading into the hold of the ship, and finally the catastrophe of the wreck, when the cargo ended up on the seabed, exposed to the marine environment and in contact with other materials present in the cargo until it was eventually covered with sediment. Further traces on the object will be created depending on the storage conditions after recovery (Artioli & Angelini 2011, p. 850). When characterization analyses are executed, their purpose is not only to identify the material; depending on the type of instrument used, much valuable data may be obtained. If the data is read with respect to the lifetime of the artefact, which means with respect to all intentional and inadvertent human and natural processes, the potential of the data can be fully explored. However, the aim of this study was only to deliver the data about identification of the raw materials, to understand what was packed in the hold and transported. Reconstructing production processes and understanding the creation of alteration layers on objects in a marine environment is, indeed, crucial for the understanding of the nature of the object, but that level of analysis goes far beyond the scope of this work.

The variety of the colouring materials present in the colour seller shops, especially those intended for decorative purposes and listed in thoroughly studied inventory of Jacopo de' Benedetti (Krischel 2002; 2011), is a reminder of how the use of chemicals in Early Modern Venice was very complex and developed within the work of artisans. Many materials of organic origin as well as a wide array of artist materials could be present in the cargo of *Gagliana grossa*, based on insurance documents (Appendix 8) and the abovementioned inventory (Krischel 2010). Previous researchers of Early Modern Sv. Pavao Shipwreck (Beltrame, Gelichi & Miholjek 2014) assumed that organic matter from a shipwreck would very likely be dissolved or disintegrate.

However, the Gnalić shipwreck site proved that colouring materials, mostly metal-based but also organic and composite, can be preserved at underwater archaeological sites. This is shown not only in the excellent preservation of red lake pigments, but also of organic matter – fennel and anise, mentioned in the report from 1972. It has to be taken in consideration that the preservation significantly depends on various factors, such as the depth and nature of the marine environment, as well as the presence of raw metal-based materials (especially lead and tin), which will enhance the preservation of organic matter in the lower layers.

With respect to the above-mentioned preservation, it has been proved by maritime insurance documents that several valuable sites with evidence of colouring material trade at the end of the sixteenth century are still waiting to be discovered in the Adriatic Sea. Before

excavating such projects, the team should apply a sound methodology for recording, while also keeping in mind that some of valuable evidence of colouring materials is ‘masked’ in marine environments during the site formation process, either by the creation of an alteration layer, or through the disintegration of the original packaging. This dissertation provides a full list of the colouring materials, with the addition of artists’ materials, that could be expected on ships that sunk at the end of the sixteenth and the beginning of the seventeenth century (Appendix 8). It is crucial that the team build a knowledge and awareness of the materials that can be spotted, and this can be obtained only by being well informed with the research done on the historical sources.

The potential for future studies is to continue to research each aspect – production, trade, and maritime transport – of colouring materials individually, by matching the results of characterization analyses and historical sources. By executing the characterization analyses, the author also strives to create an official reference collection – in a physical shape and as an online database with published results, to conserve the samples for future studies and make the data available to the public. At the same time, the author will strive to develop a methodology of recording, excavation, sampling and identifying colouring materials at the archaeological site, so that finds that are yet to be discovered contribute to the story about the trade with colouring materials throughout history.

11. Conclusion

The findings provided by this dissertation research contribute to the knowledge of Venetian colour selling industry through three aspects – production, trade and maritime transport. Since the cargo of *Gagliana grossa* was loaded in the port of Venice, the colouring materials assortment presents the variety of materials available for purchase in Venice in 1583, either directly from manufacturers and/or in the colour selling shops. The materials identified in the dissertation include lead white, red ochre, mercury sulphide, minium, arsenic sulphide / realgar, mercury, stibnite and red lake pigment. All of the discovered colouring materials were known to be traded from Venice to the Islamic world (Berrie 2007, Matthew 2011).

The numerous and varied colouring materials were significant part of the cargo of the *Gagliana grossa*. The purposes of the colouring materials are not known; they could have been for routine daily use, or perhaps intended for some special project, such as decoration of the walls of some large property. The final answer will remain unknown.

Each of the materials was identified by characterization analyses, revealing its chemical composition and suggesting an historical title. Subsequently, each material was studied in the framework of trade in the sixteenth century. The discussion following each colouring material section in the same chapter generated new research questions which have to be studied by combining characterization analyses with historical information.

Almost all colouring materials are metal based, so their underwater preservation is not unusual. However, the preservation of red lake pigment, composed of organic precipitates of either madder, brazilin or cochineal onto a base of alunite, as well as finds of anise and fennel mentioned in early excavation reports, demonstrate that preservation of organics at similar sites can be expected. Based on this expectation, the methodological approach in future underwater excavations should be modified with respect to searching for colouring materials of organic nature, in hopes of obtaining additional evidence of trade in organic-based colouring materials.

The colouring materials cargo from *Gagliana grossa* is of great value, as the results of this unique archaeological underwater excavation are used to supplement historical sources. Coupled with the information from the inventories of Venetian colour sellers from the sixteenth century, and with the maritime insurance documents from 1592 until 1609 based on the registers of G. A. Catti and A. Spinelli, the finds from the *Gagliana grossa* provide a great source of information to study the colour selling industry and trading mechanisms of sixteenth-century Venice, known as the ‘city of colour’.

The reputation of Venice as the ‘city of colour’ is based on two factors; firstly, the leverage of various materials from Europe made Venetian markets a trading centre where colouring materials of different origin and quality could be obtained; and secondly, some of the raw materials imported to the city could be processed further in Venetian manufacturing and dyeing facilities, which were known for their excellence in processing and refining. In this dissertation, this hypothesis was well supported by the historical background for lead white production, for which it is possible to say that it was certainly processed by Venetian manufacturers.

Although some studies were done on individuals involved in the lead white trade who were also the owners of lead white manufactures, the same state of the research is not available for the rest of the colouring materials discovered at the Gnalić site. It is largely accepted to say that the mercury sulphide and the red lake pigment were manufactured in Venice, but there is scarce published information about the techniques employed and the manufacturers who actively operated in Venice, especially for the last two decades of the sixteenth century. For red ochre and arsenic sulphide (realgar), even the original source of the raw material is not known. In the case of arsenic sulphide-based colouring materials, it is known that the arsenic sulphides were processed by manufacturers active in sixteenth-century localities in contemporary Germany and Austria. However, it is unknown whether these materials required some sort of additional processing when delivered to Venice. There is also a lack of studies with respect to antimony sulphide, mercury and red lead.

Upon completion of the ship’s hull studies, it will be possible to picture *Gagliana grossa* as a merchant ship with rounded shape and large tonnage, known as a *nave*. According to the list of cargoes delivered by Tenenti (Appendix 8), large shipments of colouring materials were often dispatched by *nave*. *Gagliana grossa* had a tonnage of 1200 *botti veneziane*, which is approximately equivalent to 700 tons in contemporary measurements. While this tonnage somewhat exceeds the standard tonnage of typical contemporary Venetian ships, *Gagliana grossa* could be taken as a representative of the Venetian *nave*, to date the only sixteenth-century ship archaeologically investigated that is known to have been built in Venice, and known to have departed Venice on its ultimate, tragic voyage.

Another reason why the *Gagliana grossa* adds significant value to colouring material historical studies is the fact that it provides direct and unique evidence of the shapes, amounts, and packaging methods for colouring materials traded from Venice to the Ottoman Empire. A special emphasis in this dissertation is given to relations between Venice and the Ottomans, questioning the meaning of the *Gagliana grossa*’s last venture with respect to the intensity of

Venetian contacts with the Ottomans. An overview of the historical situation attested how their unusual relationship of collaboration and conflict did not impact the global picture of Venetian trade with the Eastern Mediterranean until the last decades of the sixteenth century. Ultimately, the reputation of Venice waned, and it could not be maintained on the basis of the glory built in the fifteenth century. Additionally, Venetian shipbuilding went into decline due to several reasons, including a timber shortage. At the same time, English, Dutch and French naval fleets began taking over the trading posts in the Mediterranean (Tenenti 1959). While in the fifteenth and the first part of the sixteenth centuries Venice had an absolute monopoly over the maritime routes, allowing only Venetian ships to operate from the ports, eventually even foreign ships were allowed to enter Venetian ports. *Gagliana grossa* presents one of the attempts to maintain trading and diplomatic relations during a period when Venice was repressed.

All things considered, the most important contribution of the dissertation is that the unique archaeological evidence of Venetian trade with colouring materials from the archaeological site of *Gagliana grossa* has been brought to the public. Its precise dating to late 1583 provides specific archaeological material data, which, in comparison with characterization studies and historical sources, has a great potential to fill gaps in colouring material studies.

The background story of the *Gagliana grossa* based on archival documents includes many characters and displays the ship's dynamic life. The ship has changed roles and owners, being first Venetian, used in a conflict against Ottomans, and ultimately ended up being in Ottoman ownership. A decade later it served again as a connection between the Venetians and the Ottomans through the trading bonds of the da' Gagliano family. This rapid change of identity and malleability based on participating in significant historical events is characteristic for the Early Modern society, and it is fascinating how the ship can be used to depict these changeable relations. Even in this period when the Venetian reputation as a strong trading maritime power was in decline, the existence of a large shipment of colouring materials of various composition and quality is undisputable evidence of how the demand of the Eastern world could still be satisfied by Venetian manufacturers' goods delivered into Venice.

Finally, colouring materials on the shipwreck have a great potential to be studied from the perspective of archaeology, historical sources and characterization analyses. In the future, the author will strive to realize the potential of the studies, and improve the methodology of colouring materials research, both underwater and in the laboratory, to contribute to the colouring materials studies of the sixteenth century.

LIST OF ABBREVIATIONS

Institutions

ASV	<i>Archivio di Stato di Venezia (ASVe)</i> , the State Archives of Venice
CICRP	Interdisciplinary Centre for the Conservation of Cultural Heritage (<i>Centre Interdisciplinaire de Conservation et de Restauration du Patrimoine</i>)
RCE	Cultural Heritage Agency of Netherlands (Dutch <i>Rijksdienst voor het Cultureel Erfgoed</i>)
UVA	University of Amsterdam
VU	Vrije University

Characterization analyses

FTIR	Fourier-Transform Infrared Spectroscopy
UHPLC	Ultrahigh Pressure Liquid Chromatography
LE	Light elements (elements which are not recognized by X-Ray Fluorescence Spectroscopy)
OM	Optical microscopy
RS	Raman Spectroscopy
SEM-EDX	Scanning Electron Microscopy – Energy Dispersive X-Rays
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy

Latin abbreviations

q.	from deceased (lat. <i>quondam</i>)
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Abstract

PRODUCTION, TRADE AND MARITIME TRANSPORT OF COLOURING MATERIALS BASED ON EARLY MODERN GNALIĆ SHIPWRECK FINDS

Keywords: Gnalić; shipwreck; colouring materials; Renaissance; *Gagliana grossa*;

In late October 1583, the merchant ship *Gagliana grossa* headed from Venice loaded with cargo of various provenance. A large part of the cargo consisted of colouring materials intended for the markets of the Eastern Mediterranean. Instead of reaching its destination, the ship sank in Northern Dalmatia, at the southern entrance to the Pašman channel in the vicinity of the city of Biograd na Moru. Archaeological excavations conducted in several phases from 1967 to 2018 yielded thousands of artefacts, giving scholars an opportunity to study the material culture of the late 16th century. Although all recovered objects have historical importance and can be studied from different aspects, the colouring materials recovered from the cargo are unique and particularly interesting finds. These are the first direct archaeological evidence of Venetian international trade in colouring materials.

Venice was a central hub, where the products of different European regions, the Eastern Mediterranean and even America were imported; highly experienced Venetian manufacturers and colour sellers processed the products and made colouring materials appreciated by artisans, artists and merchants. To date, the knowledge of the trade in colouring materials has been entirely based on studies of archival documents; unfortunately, records which testify to international trade with colouring materials, especially Venetian trade with the Eastern Mediterranean, are scarce. On the other hand, existing inventories of colour seller shops provide insight into available materials; from them we can learn which materials were in demand. Combining this historical data with the archaeological finds from the Gnalić shipwreck site gives us a glimpse into which materials available in Venice were also in demand in the Eastern Mediterranean in the late 16th century.

In order to investigate the trading of colouring materials in the Late Renaissance based on the Gnalić shipwreck finds, this dissertation objective is to merge archaeological data, historical data and the data from the characterization analyses (XRF, XRD, SEM-EDX, RS, FTIR, UHPLC). All things considered, the dissertation provides new knowledge about Renaissance-era colouring materials obtained from a uniquely preserved site.

Sažetak

PROIZVODNJA, TRGOVINA I POMORSKI PRIJEVOZ SIROVINA ZA PROIZVODNJU BOJA NA PRIMJERU NOVOVJEKOVNOG BRODOLOMA KOD GNALIĆA

Ključne riječi: Gnalić; brodolom; sirovine za izradu boje; renesansa; *Gagliana grossa*;

Arheološko nalazište broda potonulog kod otočića Gnalića na ulazu u Pašmanski kanal jedno je od najpoznatijih europskih i svjetskih lokaliteta. Očuvanost jedinstvene građe arheološkog nalazišta omogućuje proučavanje plovidbe, brodogradnje i međunarodne trgovine Venecije na zalasku renesanse.

U kasnu jesen 1583, trgovački brod *Gagliana grossa* isplovio je iz Venecije natovaren raznovrsnom robom, s ciljem dostizanja luke Carigrada. Teret broda su činili mahom cijenjeni proizvodi europskih radionica, poput mjedenih svijećnjaka, široke ponude staklenih predmeta, sitnih predmeta za svakodnevnu upotrebu te tekstila. Među trgovačkim teretom je ukrcana i velika količina sirovina za izradu boje. Pronalazak sirovina u svojoj originalnoj ambalaži osobito je značajan budući da je moguće vizualizirati izgled sirovina i njihov način transporta, što je do sada bilo poznato samo temelju podataka iz pisanih povijesnih izvora.

Potonuli brod nalazi se na jugoistočnoj padini otočića Gnalića na dubini od 26 do 30 metra. Premda je istraživan u kampanjama 1967., 1968., 1972., 1973. i 1996. godine, sustavno se istražuje tek od 2012. godine u sklopu projekta *Brodolom kod Gnalića – ogledalo renesansnog svijeta* pod vodstvom Irene Radić Rossi s Odjela za arheologiju Sveučilišta u Zadru. Istraživanja povijesnih dokumenata u Državnom arhivu u Veneciji, koja se odvijaju paralelno s podvodnim istraživanjima, otkrila su niz detalja o životnom vijeku broda *Lazzara*, *Moceniga* i *Bassadona*, nakon promjene vlasnika poznatog kao *Gagliana grossa*. Arhivski dokumenti su iznijeli na vidjelo podatke o posljednjem trgovačkom pothvatu broda, ali i niz informacija o posadi, teretu, životu kapetana, brodskog pisara i posljednjeg vlasnika.

Cilj doktorske disertacije je dokumentirati, istražiti i proučiti sirovine za proizvodnju boje koje su činile dio tereta potonulog broda. Doktorska disertacija prikuplja rezultate arheoloških istraživanja, rezultate karakterizacije materijala provedene putem kemijskih analiza, te podatke iz sekundarnih povijesnih izvora, s ciljem boljeg razumijevanja proizvodnje, trgovine i pomorskog transporta ovog osebujnog tereta. Sirovine za proizvodnju boja se zatim kritički obrađuju u okviru mediteranskog kulturno-povijesnog i gospodarskog konteksta 16. stoljeća.

Od samih početaka istraživanja tijekom 60-ih i 70-ih godina, na lokalitetu je zabilježena zamjetna količina sirovina i poluproizvoda upakiranih u drvene bačve i kutije. Nalazi sirovina po prvi put su objavljeni 1970. godine u radu *O sirovinama*, autora Ive Keleza, u publikaciji *Vrulje 1: Glasilo Narodnog Muzeja u Zadru*. Iako je riječ o jedinstvenom arheološkom nalazu materijala za bojanje sačuvanog u količinama namijenjenim velikom tržištu, nitko u znanstvenim krugovima nije se detaljnije posvetio ovoj tematici.

Interes za ovom vrstom nalaza ponovo je iskazan tek tijekom podvodnih istraživanja u razdoblju od 2012. do 2014. godine kada su se pod sedimentom počeli nazirati obrisi bačvi ispunjenih nepoznatim sadržajem. Preliminarne analize prikupljenih uzoraka provedene su na Odsjeku za geologiju Prirodoslovno-matematičkog fakulteta Sveučilišta u Zagrebu. Radi potrebe istraživanja i izrade doktorske disertacije, ispitivanje sastava uzoraka materijala nastavljeno je u 2018. godini u Interdisciplinarnom centru za konzervaciju i restauraciju kulturne baštine (CICRP) u Marseilleu, u Francuskoj, te u 2019. godini u laboratoriju Ateliergebouw u Amsterdamu, u Nizozemskoj.

U prostoru broskog potpalublja najbrojnije su bačve visine do 50 cm, ispunjene koničnim čunjicima olovnog bjelila (olovni karbonat, ceruzit, ponekad u kombinaciji s bazičnim olovnim karbonatom, hidroceruzitom). Područjem bačava dominira sedam primjeraka duljine oko jedan metar, od kojih je šest ispunjeno crvenim okerom, tj. mješavinom hematita, kvarca i alunita. Ostali materijali za bojanje pronađeni su izvan originalne transportne ambalaže u različitim dijelovima potpalublja. Osim olovnog bjelila i crvenog okera, potvrđeno je postojanje boje cinobera (živinog sulfida, odnosno vermilion, te moguće cinabarita), minija (olovnog II, IV oksida ili crvenog olova), orealgara i pararealgara (sirovina na bazi arsenovih sulfida), stibnita ili blistavca (antimonovog III sulfida), elementarne žive te crvenog lakovnog pigmenta, pripremljenog na bazi alunita, s talogom organske boje izrađene od kukaca košenil (boja karmin), korijena biljke broć (boja kraplak) i brazilskog drva (boja brazilin). Bitno je spomenuti da živa nije izravno korištena kao boja, već je služila za izradu živinog sulfida ili vermilion, te je često korištena za pozlaćivanje ili posrebrjenje predmeta i za izradu ogledala. Prisustvo žive u broskom teretu može biti vezano i uz zalihe broskog liječnika jer je živa služila za liječenje niza bolesti, te je u istom kontekstu potvrđena u teretu ratnih kraljevskih brodova Mary Rose (Engleska) i Kronan (Švedska).

Namjena sirovina pronađenih na brodolomu kod Gnalića nije precizno određena. Prema povijesnim izvorima, poznato je da većina njih nije imala samo funkciju slikarskog pigmenta, već su imale široku primjenu kao kozmetički i medicinski preparati. Neke od navedenih sirovina bile su neizostavni dodatci za proizvodnju stakla i bojanje tekstila. U radu se namjerno

izostavlja termin pigment, s obzirom da bi korištenje termina pigment ograničilo korištenje nalaza isključivo kao slikarskog materijala, eliminirajući ostale upotrebe koje sugeriraju povijesni izvori. Iz istog razloga je izbjegnuto korištenje engleskog termina *pigments*, stoga je u engleskoj verziji korištena inačica koja glasi *colouring materials*.

Metodologija rada dijeli istraživanje na četiri faze: podvodno istraživanje i uzorkovanje, dokumentacija uzoraka, analize karakterizacije i identifikacije, te proučavanje sekundarnih povijesnih izvora. Podvodno istraživanje i uzorkovanje zahtijevalo je detaljnu pripremu u vidu proučavanja dokumentacije sa istraživanja iz 60-ih, 70-ih te 1996, pohranjene u Konzervatorskom odjelu u Zadru, te dokumentacije projekta Brodolom kod Gnalića – Ogledalo renesansnog svijeta. Nadalje, u 2017. godini proveden je detaljan pregled nalazišta tijekom kojeg su zabilježeni najbitniji položaji za uzorkovanje, te su potom isti opisno i fotografski dokumentirani. Zatim je izvršeno uzorkovanje odabranih položaja na nalazištu.

U laboratoriju CICRP je izrađena fotodokumentacija uzorka, uključujući i dokumentaciju pod vidljivim (VIS), ultraljubičastim (UV), infracrvenim (IR) te infracrvenim zračenjem s 'lažnim' bojama (IRfc). Dokumentacija pod različitim zračenjem, tj. valnim duljinama, olakšala je odabir čestica za analize jer su različite boje ukazale na kontaminirane dijelove uzorka. Fotogrametrijsko dokumentiranje izvršeno je samo na uzorcima kojima je bilo važno zabilježiti oblik kalupa, kao što je to slučaj olovnog bjelila. Zapažanja mikroskopom su provedena kako bi se opisala homogenost ili heterogenost uzorka, te oblici, boje i veličine čestica.

Analize karakterizacije su provedene pomoću rendgenske fluorescencijske spektroskopije (XRF); skenirajućeg elektronskog mikroskopa s energodisperzivnim detektorom rendgenskih zraka (SEM-EDX); rendgenske difrakcije na prahu (XRD); infracrvene spektroskopije s Fourierovom transformacijom (FTIR); te Raman spektroskopije (RS). Ukoliko su navedene analize sugerirale postojanje organskih materijala, upotrijebljena je tekućinska kromatografija ultravisoke djelotvornosti (UHPLC). U priložima od broja šest do dvadeset prikazani su rezultati analiza, a diskusija o svakom zasebno može se pronaći u poglavlju broj deset.

U potrazi za povijesnim podacima o načinu proizvodnje, preradi te trgovanju sirovinama, odabrano je nekoliko različitih vrsta sekundarnih izvora: traktati o metalurgiji (Vannoccio Biringuccio, *De la Pirotechnia*; Georgious Agricola, *De Re Metallica*), slikarstvu (Merrifield, 1968), objavljeni inventari mletačkih trgovaca bojama (Matthew 2002; Krischel 2002; Matthew & Berrie 2010), dokumenti o osiguranju na brodovima u razdoblju od 1592. do 1609. godine izdani dvojicom javnih bilježnika G. A. Cattija i A. Spinellija (Tenenti 1959).

Na prijelazu u 16. stoljeće, status Venecije kao trgovačke sile se uvelike mijenja zbog događanja u Sredozemlju te na oceanu. Otkrićem nove pomorske rute prema Indiji preko Rta Dobre Nade, Portugalci su preuzeli vodstvo u trgovini začinima te osigurali ulogu posrednika trgovaca začinima u Zapadnoj Europi. Izgubivši prevlast na tržištima Zapadne Europe, Venecija gubi monopol nad trgovinom začinima. Iako dodatno ugrožena napadima Osmanlija, Venecija ipak uspijeva održati trgovačke veze sa istočnim Mediteranom sve do kraja šesnaestog stoljeća. Tek dolaskom snažnog engleskog, francuskog i nizozemskog brodovlja u posljednjim desetljećima šesnaestog stoljeća, Venecija više ne uspijeva konkurirati na tržištu. Opadanje trgovačkog intenziteta je uzrokovala i nedostupnost drva, što je rezultiralo smanjenom brodograđevnom aktivnošću i smanjenjem broja novoizgrađenih trgovačkih brodova.

Premda je turbulentno šesnaesto stoljeće obilježeno stalnom borbom za prevlast nad mletačkim prekomorskim i kopnenim posjedima, u samom centru Venecije se gubitak moći nije dao naslutiti. Tijekom 16. stoljeća Venecija je slovila kao 'grad boje', što se može protumačiti na dva načina. Vizualni identitet Venecije, raznobojne fasade, te česta upotreba mramora u arhitekturi ostavljali su posjetioce očaranima, kako svjedoče doživljaji pisaca onodobnih priručnika o putovanju. S druge strane, trgovački i proizvodni kapaciteti Venecije pokazuju koliko je 'grad boje' bio zaista opravdan naziv. Osim što se mogla pohvaliti dostupnošću minerala i organskih materijala europskog, istočnjačkog, pa čak i američkog porijekla, mletačke radionice i trgovine su bile poznate po posebnim tehnikama obrade i proizvodnje sirovina za izradu boje. S obzirom na kvalitetu proizvoda, obradu po posebnoj recepturi i raznolikost izbora pri kupnji, ne iznenađuje podatak da je nemali broj trgovaca, majstora i slikara putovao u Veneciju radi opskrbe slikarskim materijalima. Osobito je vrijedno spomenuti trgovce bojama (mlet. *vendecolori*) koji su se kao profesija profilirali krajem 15. stoljeća. Nekoliko očuvanih inventara trgovaca bojama sadržava iznimno vrijedne podatke o ponudi sirovina u Veneciji u 16. stoljeću.

Brodolom kod otočića Gnalića za sada je jedino izravno svjedočanstvo pomorske trgovine sirovinama za izradu boja u razdoblju renesanse. Uzimajući u obzir veliko značenje boja u razvoju renesansne umjetnosti, ali i svakodnevnom životu na svim društvenim razinama, proučavanje materijala za bojanje iz tereta broda potonulog kod Gnalića u kontekstu renesansnih događaja, doprinijelo je poznavanju proizvodnje, trgovine i pomorskog transporta. Pisanjem doktorske disertacije, autorica nastoji upozoriti na postojanje sirovina za izradu boje na nalazištima brodoloma. Doktorska disertacija je skroman doprinos kojim se predlaže prikladna metodologija identifikacije sirovina te se istovremeno upućuje na znanstveni potencijal u okviru proučavanja trgovine sirovinama za izradu boje i slikarskih materijala.

APPENDICES

Appendix 1: Sunken ships with the cargo of colouring materials

No. ¹³⁷	Shipwreck name, Location	Date	Type of colouring material	Shape and amount of colouring material	The position inside of the ship's hull	The purpose (according to the interpretation of author)	Reference
1	Ulu Burun, near Kaş, Turkey	14 th c. BC	Arsenic sulphide (orpiment)	Stowed in one amphora, together with other artefacts	/	Trading cargo, Supplement to the glass production?	Bass 1986, p. 278
2	Madrague de Giens, Giens peninsula, south of Toulon, France	1 st c. BC (more precisely) 75-60 BC - 50 BC)	Egyptian Blue	Around 60 examples of Egyptian blue lumps were discovered and associated two pieces of lead ingots bearing the traces of sawing and remeltage	/	Painting the ship's hull and refreshing the colour on the hull	Liou, Pomey 1985, pp. 567-568; Gianforta, Pomey 1981, p. 296
3	Planier III, islet of Planier, south of Marseille, France	The first half of the 1 st c. BC	Lead oxide (litharge) in form of tubuli, Egyptian Blue, realgar	Many little fragments of litharge in the shape of a cylinder, hollow inside, 41.5 kg; around 20 lumps of realgar, in irregular form; around 15 lumps of Egyptian blue (blue surface, green core)	/ ¹³⁸	Trading cargo, or intended for use on board	Tchernia 1971, pp. 51-82; Gianforta, Pomey 1981, p. 296

¹³⁷ Number on Fig. 2-4.

¹³⁸ Part of the colouring materials were recovered earlier by divers and taken to Direction des Antiquites, so it is not possible to determine exact location on the ship.

No.	Shipwreck name, Location	Date	Type of colouring material	Shape and amount of colouring material	The position inside of the ship's hull	The purpose (according to the interpretation of author)	Reference
4	Cape Glavat, Mljet island, Croatia	1 st c. AD	Lead oxide (minium), lead sulphide (galena), lead carbonate (cerussite)	Lead oxide packed into ovoid pottery jars, while lead sulphide (?) and lead carbonate (cerussite) were transported as irregular cube shaped ingots	Midship area, hold	Lead oxide and lead carbonate were used for painting sculptures, walls, and possibly ships. Galena was used for the production of lead objects	Radić Rossi 2009, pp. 198-199; Radić Rossi 2012, pp. 18-20
5	Cape Ognina, Sicily, Italy	late 2 nd and early 3 rd c. AD	Blue colour	Several kilos of blue colour, packed into a jar	/	Painting the ship's hull and refreshing the colour on the hull	Frost 1959, p. 10, 11, 27; Tchernia 1971 p. 75; Gianforta, Pomey 1981, p. 296
6	Mellicha Bay, Malta	late 2 nd and early 3 rd c. AD	Egyptian Blue	Egyptian blue was often transported in small containers, which were sometimes made of pewter based on fragments of lead-rich tin alloy recovered and from analogies found in Naples. A common size for these containers was one <i>congius</i> (approximately 3.5 liters)	The cargo was scattered across a rocky seabed. Egyptian blue was recovered from one location inside a rock crevice	Painting the ship's hull and refreshing the colour on the hull	Frost 1969, pp. 11, 13, 25, 38; Tchernia 1971, p. 75; Gianforta, Pomey 1981, p. 296 (mentioned only)

No.	Shipwreck name, Location	Date	Type of colouring material	Shape and amount of colouring material	The position inside of the ship's hull	The purpose (according to the interpretation of author)	Reference
7	Serçe Limanı, Turkey	11 th c. AD	Orpiment (arsenic sulfide)	/	Attested in three main living areas. Positioned in the bow compartment, together with personal possessions of the crew.	<p>Cargo of raw glass is present; orpiment as a supplement to the glass production?</p> <p>Less than 1 kg. Possibly in the function of cosmetic and hygiene supply. This is supported by nearby finds of whetstones and flat stone fragments. As lice were a common issue on ships, arsenic sulphides were used for hair removal</p>	<p>Bass 1984, p. 278</p> <p>Bass et al. 2004, pp. 266, 279-283</p>
8	Unknown shipwreck close to Serçe Limanı, Turkey	Approximately 11 th c. AD	Orpiment (arsenic sulphide)	/	/	Cargo of raw glass is present; orpiment as a supplement to the glass production?	Bass 1984, p. 278

No.	Shipwreck name, Location	Date	Type of colouring material	Shape and amount of colouring material	The position inside of the ship's hull	The purpose (according to the interpretation of author)	Reference
9	Gnalić shipwreck, near Pašman Channel, Croatia	1583	Detailed information in Appendix 10	Detailed information in Appendix 10	Stowed in hold in the aft midship area, except for red lake pigment (on the first deck, stern)	Trading cargo, paint, medicine, medical supply	Batur & Radić Rossi 2019, p. 112
10	<i>La Belle</i> Shipwreck, Matagorda Bay, Texas, USA	1686	Cinnabar, iron oxide, red lead	Around 8 kg	Amidship in the main hold and aft hold	Gift and trade item to the natives upon the arrival to new land	Bruseth et al. 2017, pp. 788-796
11	<i>T'Vliegende Hart</i>, Vlissingen, Netherlands	1735	Lead white;	Lead white lump; paint stone with the traces of vermilion, chalk, massicot and black stone	/	Lead white coupled with bucket, a brush and spatula; paint stone with the traces of vermilion, chalk, massicot and black stone	Horst 2001, pp. 274-276.

No.	Shipwreck name, Location	Date	Type of colouring material	Shape and amount of colouring material	The position inside of the ship's hull	The purpose (according to the interpretation of author)	Reference
12	<i>The Hollandia</i> Shipwreck, Scilly islands, England	1743	Cinnabar / vermilion	7 lumps of cinnabar	/	/	Gawronski et al. 1992, p. 439; Horst 2001, p. 274 (mentioned only)
13	Otočac-Prizba, Korčula island, Croatia	Late 18 th c. AD (?) ¹³⁹	Arsenic sulphide (orpiment?)	Lumps with dimension of 2 or 3 cm	Scattered on the seabed	Trading cargo, painting material	Ministry of Culture of Republic of Croatia 2006; Radić Rossi 2005, pp. 43-45

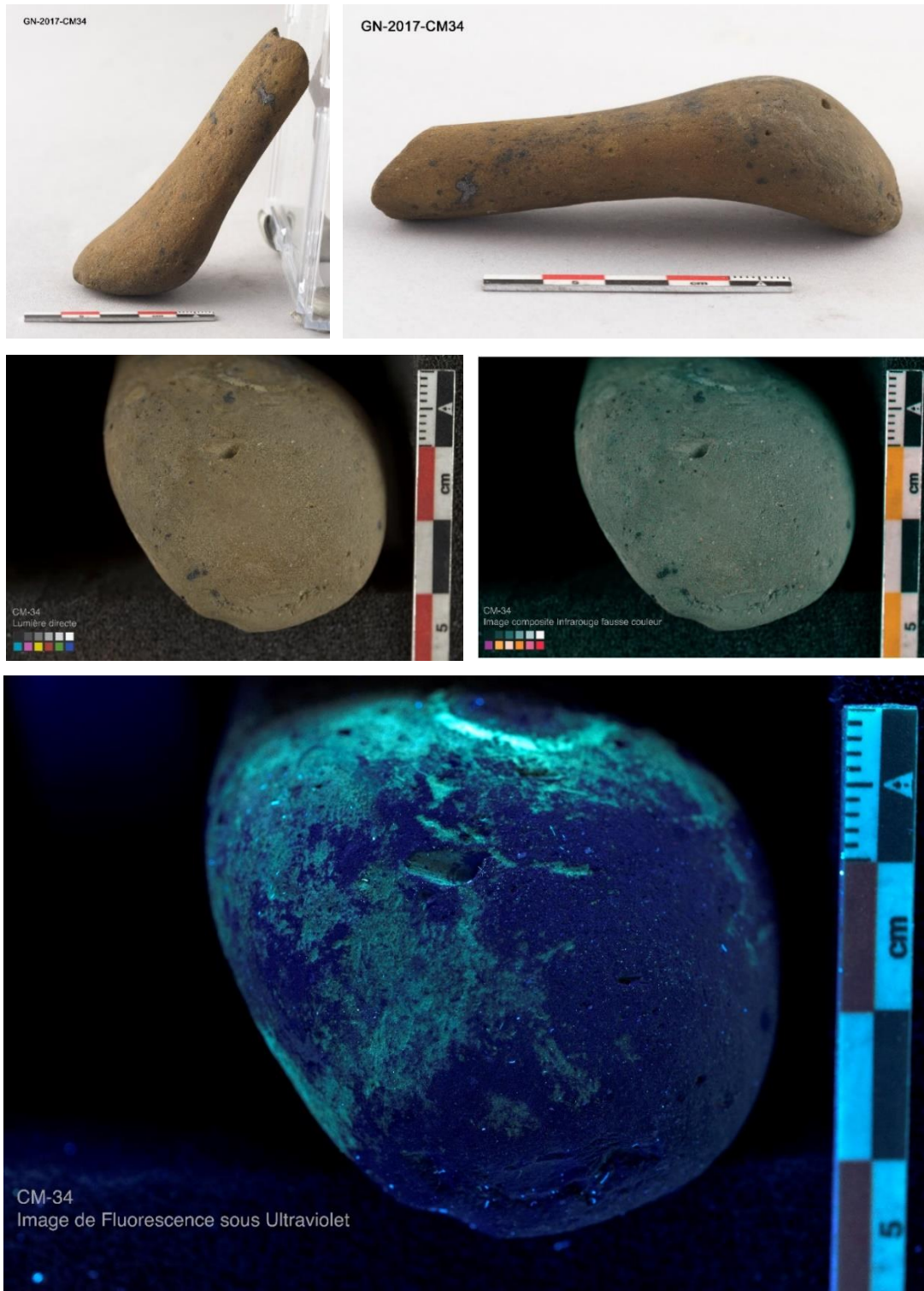
¹³⁹ Date is suggested according to the limited amount of data collected during survey in 2003 and 2006 (Ministry of Culture of Republic of Croatia 2003; 2006).

Appendix 2: Pigments as a decoration on the ship's hull and artists'/painters' tools

Shipwreck name, Location	Date	Object	Pigments identified	The position	The purpose (according to the interpretation of author)	Reference
Gnalić Shipwreck, Pašman Channel, Croatia	1583	Ceramic pestle (height 99 mm, width 35 mm); Appendix 3	None yet, but visible differences in colour under ultraviolet and infrared light	Stern area, hold of the ship (A19.1)	Grinding pigments	Not published
t' Vliegent Hart, Vlissingen, Netherlands	1735	Paint stone (basalt, conical shape, height 157 mm, maximum diameter 110/115 mm, weight 2.5 kg)	Paint stone with traces of vermilion, chalk, massicot and iron oxide	Found at the ship's stern	Paint for the ship	Horst 2001, pp. 274-276
'Roof-tile' wreck, between Texel and Terchelling, Netherlands	1756	Paint stone (conical, diameter 130 mm, height 156 mm)	Red, green, blue	/	Paint for the ship	Horst 2001, pp. 277
Vasa, Stocholm, Swedem	10 August 1628	Sculptures	Yellow and red ochre, red and white lead, smalt, green and blue copper pigments, indigo, orpiment, vermilion, lead-tin yellow gilding, lamp black	Stern and foreship	Decoration of the ship	Tångeberg 2000, p. 149; Hocker 2018, p. 96

Shipwreck name, Location	Date	Object	Pigments identified	The position	The purpose (according to the interpretation of author)	Reference
The Ghost Ship, Gotska Sandön, Sweden	c. 1650	Sculptures	Red and black, further information not available	stern	Decoration of the ship	Eriksson & Rönby 2012, p. 357
VOC Zuiddorp (Zuytdorp), Zuytdorp Cliffs, Western Australia	1702	Sculptures	Lead white, gypsum, possible red lead or hematite	Stern	Decoration of the ship	Van Duivenvoorde et al. 2015, pp. 275, 280
HEIC Hindostan, Wedge Sand, Margate Kent, South-East England	11 January 1803	Paint stone (basalt, cylindrical with smooth bases, diameter 150 nun mm, height 165)	/	/	/	Horst 2001, pp. 277
HEIC Admiral Gardner, Goodwin Sands, South-East England	25 January 1809	Paint stone (basalt, cylindrical with smooth bases, diameter 150 nun mm, 180 mm)	/	/	/	Horst 2001, pp. 277
Diana Shipwreck, Mallaca Strait, Malaysia	1817	Wooden box	Traces of arsenic sulphide (orpiment) (unknown if this was a cargo of colouring material or original paint on the box)	/	/	Horst 2001, pp. 277

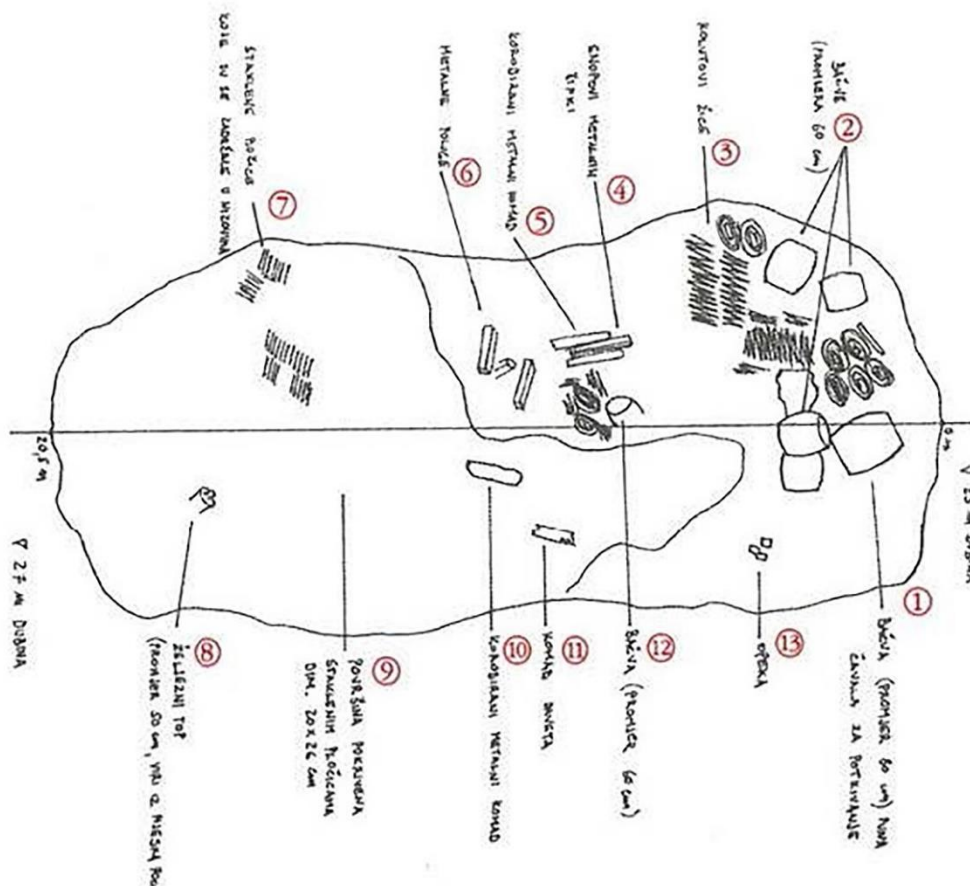
Appendix 3: Pestle from the Gnalić Shipwreck



Pestle from the Gnalić Shipwreck: 1-2 Documentation photos (photos: K. Batur), 3-5 Photography of the bottom taken with the visible, infrared false colour and ultraviolet imaging technique (photos: O. Guillon).

Appendix 4: Otočac shipwreck, Prižba, Korčula island, Croatia

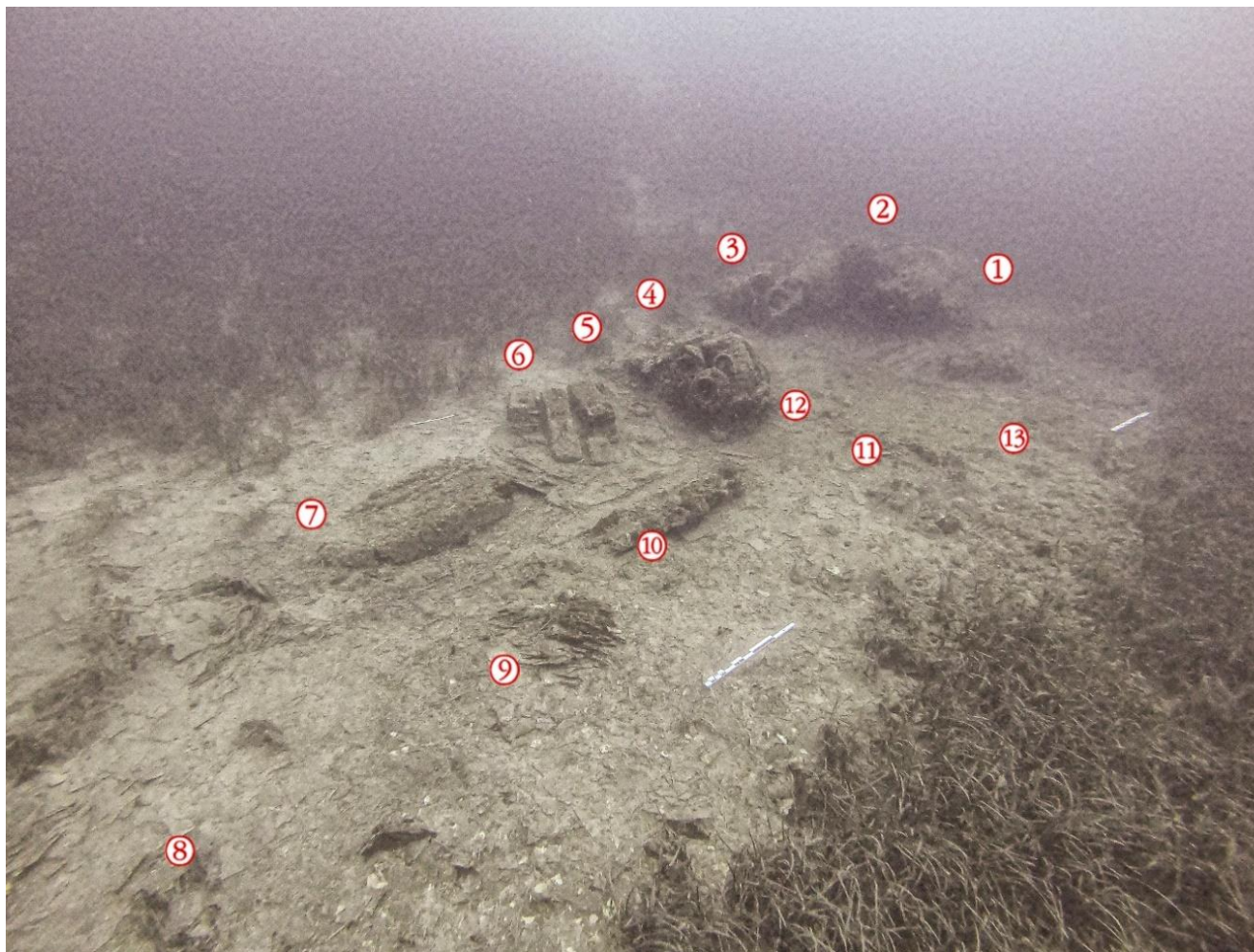
T. I



Modern period Otočac shipwreck, Prižba, Korčula island, Croatia.
Drawing of the situation at the site (from Radić Rossi 2005, p. 44; modified by K. Batur).

Description:

- | | | | |
|----|--|-----|--|
| 1. | Barrel (diameter 80 cm) filled with nails; | 8. | The gun (diameter 50 cm), protruding from the sand; |
| 2. | Barrels (diameter 60 cm); | 9. | The surface covered with rectangular glass sheets (dim. 20 x 26 cm); |
| 3. | Coils of wire; | 10. | Corroded metal fragment; |
| 4. | Bundle of rods; | 11. | Fragment of wood; |
| 5. | Corroded metal fragment; | 12. | Barrel (diameter 60 cm); |
| 6. | Metal bars | 13. | Tiles |
| 7. | Stacked sheets of glass; | | |



Modern period Otočac shipwreck, Prižba, Korčula island, Croatia. Up: Drawing of the situation at the site (from Radić Rossi 2005, p. 44);
Down: Situation on the site in September 2019 (photo: A. Kiss, modified by K. Batur). On the area numbered with 13 are scattered lumps of yellow arsenic sulphide (not marked on the upper site plan from 2005).



Yellow lumps of arsenic sulphide from the Modern period site Otočac Shipwreck, Prižba, Korčula island. Top: Situation at the site during survey in September 2019 (photo: K. Yamafune). Bottom: Sampled yellow lump (photo: A. Kiss).

Appendix 5: The Kronan shipwreck, 1676, Sweden



The Kronan shipwreck, 1676, Sweden: Up: Preserved chest with compartments made to fit glass bottles; Below: Bottles filled with medical content: a) elemental sulphur, b) mixed antimony sulphide and antimony oxide, *lat. Antimonum crudum* (Lindeke & Ohlson 2018, pp. 70; 76).

Appendix 6: The journey from Venice to Constantinople

During the sixteenth century, the seafaring route from Venice to Constantinople was a common trading route connecting Europe with Asia Minor (Fig. 1). The journey started in the Adriatic Sea, or so-called *Golfo di Venetia*, whose well-indented eastern coast with numerous ports and inlets provided safe shelters and conditions favourable for sailing. On the way to Constantinople, the ships followed the coast of Ionian Sea, skirting the promontories south and southeast of the Peloponnesus, then sailing through the islands of the Aegean Sea to finally reach Constantinople.

Venice was the main metropolis of the West, while her counterpart Constantinople, well-known as multicultural and densely populated, enjoyed the reputation of the metropolis of the East. Known as a ‘city of Ottomans’, with the port Galata in its possession, Constantinople attracted many travellers from great distances, driven by business, politics, curiosity, or simply eagerness to visit the capital. Many of the travel books written by Englishmen and Venetians give stirring impressions of the stunning sceneries of the capital, saying it is ‘set in the most beautiful and charming site that man can imagine’, or arouse the feeling (Dursteler 2006, pp. 152-158):

‘I still cannot calm my soul nor my eyes...having fixed [in them] the graciousness of Constantinople, nor can I wait to have the occasion to return and enjoy it; I feel I have died and gone to heaven’.

Besides being praised for its beauty, Constantinople was bustling due to its position as the main port of Asia Minor, the main crossroad of the caravan routes, and the transition port to and from the Black Sea. As Eastern Europe, Asia Minor and Eastern Mediterranean routes met in Constantinople, it provided local markets with a wide array of goods not available in Europe, having the quality or simply the oriental features which made them desirable among European costumers (Lane 1973, pp. 69-70, 129).

Navigational route

To describe the navigational route which the ship *Gagliana grossa* likely followed, the author finds it most appropriate to mention an itinerary from the Early Modern Period, Giuseppe Rosaccio's '*Viaggio da Venezia a Constantinopoli per Mare e per Terra*'. This itinerary was selected with the aim to explain the trading route, as it is chronologically the closest to the date of the *Gagliana grossa*'s last journey. This small travel book was published in 1598, and it gives a description of all the ports and important landmarks on the way to Constantinople. The publication is enriched with etching illustrations of ports and islands and provides particular information regarding the landscape and landmarks. This level of details yields substantial information for geographers', historians', art historians' and archaeologists' research.

The book begins with travel distances from each port in Venetian miles, starting from Venice, and following the eastern Adriatic coast to the cities of Poreč (*Parenzo*), Zadar (*Zara*), Šibenik (*Sebenico*), Hvar (*Liesina*), Korčula (*Curzola*), Dubrovnik (*Ragusa*), Ulcinj (*Dulcigno*), and Vlora (*Valona*). The book continues the voyage into the Ionian Sea, providing distances to Kerkira (*Corfu*), Paxi (*Paxu*), Fiskardo (*Viscardo*), Kefalonia (*Zalafonia*), Zakynthos (*Zante*), Strofades (*Strivali*)¹⁴⁰, Methoni (*Modon*), and Cape Matapan (*Capo Matapan*). The journey is completed in the Aegean Sea, with distances to Cape Maleas (*Capo Malio*), Kythira (*Cerigo*), Monemvasia (*Maluasia / Montebasia*), Nafplio (*Napoli di Romania / Nauplie*), Cape Skyli (*Capo Schili*), Cape Sounion (*Capo delle Colone*)¹⁴¹, Euboea (*Negroponte*), Skyros (*Sciro*), Lemnos (*Stalimete*), Dardaneli (*Dardanelli*), Gallipoli (*Galipoli*), and finally Constantinople. Rosaccio calculates it takes in total 2239 Venetian miles to reach Constantinople from Venice (Rosaccio 1598, pp. 1-2).

The dynamics of the sailing ventures from Venice were calculated based on the seasonal fairs, but it largely depended on weather conditions; in the winter, there were almost no ships on the navigational routes. The mountain passes through the Alps were not usable, and the ships were endangered due to bad weather conditions that could cause wreckage or breakdown (O'Connell 2017, p. 104). Although these restrictions were sometimes relaxed, inevitably the prohibitions were restored due to an increased number of shipwrecks. When traveling towards

¹⁴⁰ Islands in the coast of Elis in Ionian Sea, southeast of Zakynthos. For the reference, I used the dictionary Anthon 1859, p. 1268.

¹⁴¹ For identifying the promontories Capo Schili and Capo delle Colone, the author used Encyclopedia Metropolitana by eds. Smedeley et al. 1845, p. 725.

the East, it was required to stand with respect and awe towards the sea, to avoid unpredictable and violent situation during the winter months (Braudel 1997, pp. 264-267).

Navigational restrictions and dangers at the sea

In order to avoid sailing in the winter, ships could make only one or two voyages between Venice and Constantinople in a one-year period. If a ship left in the early spring, it could return in the fall; if it departed in the fall, it could not return until the following spring. Merchants required a certain amount of time to sell their cargo in Constantinople, and to acquire new merchandise to ship back to Venice and exchange on the Venetian market (Lane 1973, p. 70). Even during spring and summer, trading overseas always incurred risks during the voyages, which could be manifested in breakdowns, shipwrecks, and even piracy. For this reason, merchants insured their goods with insurance companies, which today provides a valuable reference source of procurement and transport of trading goods (Tenenti 1959).

While non-favourable weather caused misfortunes at sea, safe seafaring and trading were also interrupted by frequent attacks by the corsairs of the Uskoks, starting about 1540 and lasting until the first decades of the seventeenth century. The Uskoks were a population which escaped the incursion of the Ottomans and inhabited the eastern coast of the Adriatic Sea, obtaining necessities for living via raid and plunder (Bracewell 1997, p. 5). In addition to threatening Venetian, Florentine, or Genovese ships at sea, this small, organized group occasionally caused fear for Ottomans living inland.

The description of the Uskoks in most cases depended on the point of the view and nationality of the person recording the observation. Venetian historical sources are full of colourful epithets with negative connotations, often addressing the Uskoks as ‘robbers, a tribe of ruffians, iniquitous rogues’ (Tenenti 1967, pp. 3-9). Legends of brutality and violence within their own society additionally supported their frightening identity.

Inhabiting land in the vicinity of Senj in the northern Adriatic, this group lived in a naturally protected area, surrounded by mountains separating it from the hinterlands, and protected by the sea. Often gusts of the strong northern wind known as the bora prevented ships from mooring in the ports. These natural protections prevented other people from attacking, while the Uskoks conducted their main actions at sea by using their own boats known as *brazzere*, small and fast rowing ships, or more often, used captured ships from previous successful attacks (Tenenti 1967, p. 6).

Traveling by caravans

Besides the sea route, Rosaccio also provides information about the alternative land route to Constantinople, consisting of cities and towns starting from Ragusa (present-day Dubrovnik). Thus, merchants could travel by ship to Ragusa, and then switch to caravan routes from Ragusa to Constantinople. The itinerary for the travellers is based on the land routes which have a long tradition of being used by caravans, so the travellers could find public accommodation lodgings, *caravanserai*, to rest during the long travels (Rosaccio 1598, pp. 1-2, Wimmel 2019, pp. 157-160).

Although the goods from *Gagliana grossa* were destined for Constantinople, it does not necessarily mean that the merchandise would have remained in the city. If not shipped by a specific order, the merchandise could be traded further by land routes with caravans to the eastern Mediterranean, or to southeastern Europe. Therefore, when assessing where the trading goods unloaded in Constantinople were ultimately destined, the role of caravans should not be underestimated.

Traveling by caravans was very common and favourable, as demonstrated by many travel books and reports written during the sixteenth century. Caravans could be composed of several hundreds of people as well as cattle, and some routes extended thousands of kilometres. Constantinople was the crossroads of three main caravan routes; the first was going towards Wallachia and Russia; the second started in the Maghreb, passing through Syria, Palestine, and finally Constantinople, then continuing into southeastern Europe and further to Middle and Northern Europe; the third, however, was the most important. With the tradition dating back to Antiquity and known as *Via militaris*, it started in Constantinople and passed along the route connecting Edrine (Adrianople), Plovdiv, Sofia, Niš, and the valley of the river Morava to Belgrade (Fig. 2). While the *Via militaris* was the main road, it had also two divisions; one directed towards Thessaloniki to the Ionian Sea, and the second followed the shores of the Black Sea (Pavić 2014, p. 47, Wimmel 2019, pp. 154-157).

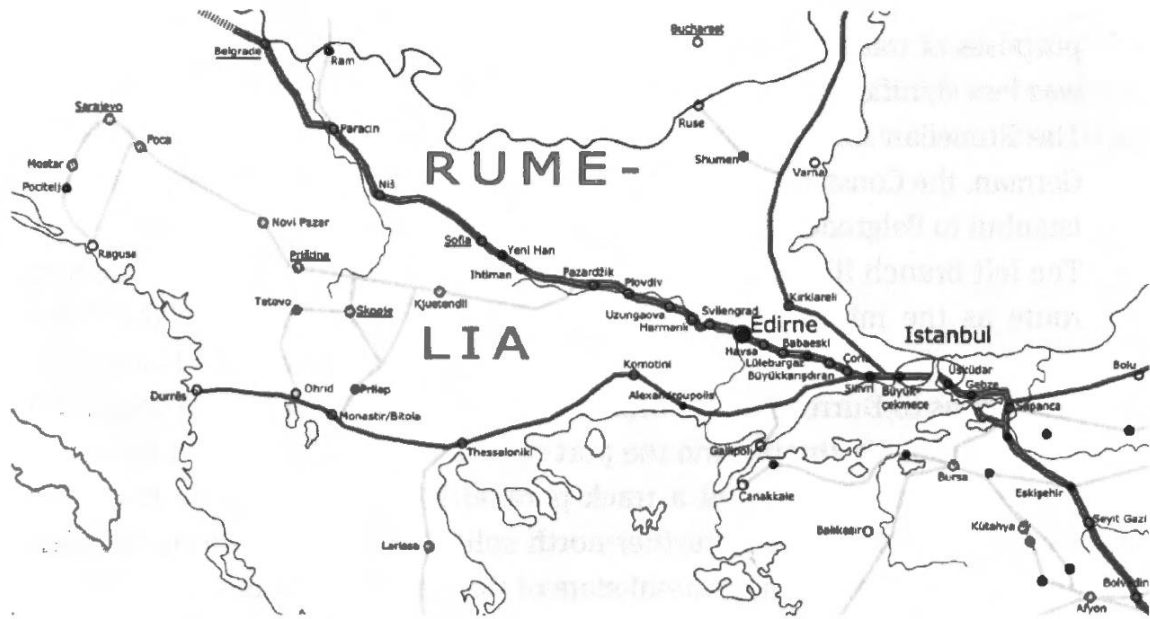


Fig. 2. Caravan routes: *Via militaris*, marked with the thick dark line, passing through Constantinople. Two divisions are marked with the light grey line. Numerous *caravanseraï* are marked with a dot on the lines (Wimmel 2019, p. 155).

Braudel gives an example of a merchant coming from Venice to Constantinople by ship, then shifting to land routes in Constantinople. His long route passed across the Drina River, then the region of Dobruja, ultimately reaching Lviv, Ukraine where he sold his merchandise. When his sales were complete, he used his earned capital to buy new merchandise, and then returned back to Constantinople, where he again sold his goods (Braudel 1997, pp. 211-212).

Appendix 7: Venetian colour sellers and colouring materials selected from inventories

Available evidence of trade with colouring materials in the 16th century	Mattheus q. Joannis a coloribus (1504)	Hieronymo dai Sulimadi (c.1520)	Domenico de Gardignano (1534)	Partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550)	Giovanni Griffalconi (1551)	Matteo dai colori (1556)	Gnalić shipwreck raw (colouring) materials (1583)	Bartholamei a coloribus (1586)	Jacopo de' Benedetti (1594)
LEVEL OF TRADE	RETAIL	WHOLESALE	RETAIL	IT ¹⁴²	WHOLESALE	WHOLESALE	IT	IT	RETAIL
Colouring materials	Lead white	Lead white	<i>Biacha</i>	–	Lead white	–	Lead carbonate and the basic lead carbonate*	–	<i>Biacha</i>
	–	–	<i>Tera rossa</i>	–	–	–	Red ochre	–	<i>Lapis ros[s]o;</i> <i>Terra ros[s]a;</i> <i>Bolo gros[s]o;</i> <i>Terra sigilada</i>
	–	–	<i>Cinabro</i> (vermilion)	Vermilion	–	<i>Cenaprio</i> (vermilion)	Mercury sulphide*	–	<i>Cenaprio</i>
	–	–	<i>Minio</i>	Minium	–	–	Lead (II, IV) oxide	–	<i>Minio</i>

¹⁴² Abbreviation: International trade.

Available evidence of trade with colouring materials in the 16th century	Mattheus q. Joannis a coloribus (1504)	Hieronymo dai Sulimadi (c.1520)	Domenico de Gardignano (1534)	Partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550)	Giovanni Griffalconi (1551)	Matteo dai colori (1556)	Gnalic shipwreck raw (colouring) materials (1583)	Bartholamei a coloribus (1586)	Jacopo de' Benedetti (1594)
LEVEL OF TRADE	RETAIL	WHOLESALE	RETAIL	IT	WHOLESALE	WHOLESALE	IT	IT	RETAIL
Colouring materials	–	–	<i>Rexegal; oropimento</i> (1200 pounds)	–	–	–	Arsenic-based colouring material (realgar and pararealgar)	–	<i>Oropimento rosso; Oropimento comum [sic]m[asena]do; Oropimento intt cernido; Oropimento c[hia]ro; Oropimento mezan)</i>
	–	–	<i>Cremexe</i> (crimson of Old World cochineal); <i>Laca de grana</i> (red lake)	<i>Laca di grana</i> (kermes lake)	–	–	Lake	–	<i>Lacha di grana; Lacha de crimese; Lacha; Lacha de verzin</i>

Available evidence of trade with colouring materials in the 16th century	Mattheus q. Joannis a coloribus (1504)	Hieronymo dai Sulimadi (c.1520)	Domenico de Gardigno (1534)	Partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550)	Giovanni Griffalconi (1551)	Matteo dai colori (1556)	Gnalic shipwreck raw (colouring) materials (1583)	Bartholamei a coloribus (1586)	Jacopo de' Benedetti (1594)
LEVEL OF TRADE	RETAIL	WHOLESALE	RETAIL	IT	WHOLESALE	WHOLESALE	IT	IT	RETAIL
Colouring materials	–	Mercury	–	–	–	Mercury	Mercury*	–	Mercury
	Tin	–	–	–	–	–	Tin*	–	–
	–	–	–	–	–	–	Antimony (III) sulphide*	–	<i>Antimonio</i>
	–	–	<i>Verderame</i> (verdigris) 1000 pounds	Verdigris	–	–	–	–	–
	–	<i>Solimado</i> (mercuric chloride)	–	–	–	–	–	–	–
	–	–	<i>Zafara</i> (smalt)	–	–	–	–	–	–

Available evidence of trade with colouring materials in the 16th century	Mattheus q. Joannis a coloribus (1504)	Hieronymo dai Sulimadi (c.1520)	Domenico de Gardignano (1534)	Partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550)	Giovanni Griffalconi (1551)	Matteo dai colori (1556)	Gnalic shipwreck raw (colouring) materials (1583)	Bartholamei a coloribus (1586)	Jacopo de' Benedetti (1594)
LEVEL OF TRADE	RETAIL	WHOLESALE	RETAIL	IT	WHOLESALE	WHOLESALE	IT	IT	RETAIL
Colouring materials	-	<i>Sal nitro</i> (potassium nitrate)	-	-	-	-	-	-	-
	-	-	<i>Verzino</i> (brazilwood)	Brazilwood (the whole wood)	-	-	-	Brazilwood (the whole wood) 12 000 pounds	-
	-	-	<i>Terra nera</i> (black earth)	-	-	-	-	-	-
	-	-	<i>spodo de cane</i> (bone black)	-	-	-	-	-	-
	-	-	<i>Zalolin</i> (lead-tin yellow)	-	-	-	-	-	-
	-	-	<i>Azuro Todesco</i> (German blue)	-	-	-	-	-	-

Available evidence of trade with colouring materials in the 16th century	Mattheus q. Joannis a coloribus (1504)	Hieronymo dai Sulimadi (c.1520)	Domenico de Gardignano (1534)	Partnership between Zuan di Nicolo dai colori and Marco da Corphu (1550)	Giovanni Griffalconi (1551)	Matteo dai colori (1556)	Gnalić shipwreck raw (colouring) materials (1583)	Bartholamei a coloribus (1586)	Jacopo de' Benedetti (1594)
LEVEL OF TRADE	RETAIL	WHOLESALE	RETAIL	IT	WHOLESALE	WHOLESALE	IT	IT	RETAIL
References	Matthew 2002, p. 681	Matthew and Berrie 2010, p. 246	Matthew 2002, p. 681; Matthew and Berrie 2010, p. 247	Matthew and Berrie 2010, p. 247	Matthew 2002, p. 681	Matthew and Berrie 2010, p. 246	Kelez 1970, pp. 40–45*; fieldwork documentation 2013–2018	Matthew and Berrie 2010, p. 247	Krischel 2002, pp. 93–158

* The material identified in the late 1960s and published by Kelez in 1970

Appendix 8: Colouring materials in the register of insurance documents of G. A. Catti and A. Spinelli

The aim of this database is to extract information about colouring materials based on the register of notaries G. A. Catti and A. Spinelli. Their register contains a wealth of information about the goods traded to and from the port of Venice in the period from 1592 to 1609. Before explaining the organization of the database, it is necessary to explain which criteria were used to select colouring materials among all cargo presented in the documents issued by notaries. There are various cargo items presented in the insurance document of each of 1021 ships in total, so it was required to make a selection of the items that could be attributed to colouring materials.

Prior to composing the database, the author consulted the glossary of terms from the translation of treatises published by M. Merrieffield (1967), data withdrawn from inventories and contracts of colour sellers (*vendecolori*), the glossary of artists' materials (Kirby, Nash & Cannon 2010), and the pigment compendium (Eastaugh et al. 2008). When reading the list of the cargo items according to documents of G. A. Catti and A. Spinelli, the items which the author assumed could be used as colouring materials were compared with items listed in the abovementioned sources. If a cargo item found its match in one of these references, it was included in this database. The explanations are given in the first table. Unknown terms are translated with the help of the dictionary of Venetian dialect (Boerio 1856).

The items were sorted into three categories:

- 1) Colouring materials (CM). As discussed in chapter 3, colouring materials could be used as pigments, medicines, cosmetics, and as substances required to obtain colour in glass or dye textiles, as suggested by historical sources.
- 2) Artists' materials and tools (AM). This category includes all materials that could be found in artists' studios, such as varnish, resin, canvas, as well as substances which were used to produce colouring materials, like acid, alkaline and other solutions.
- 3) Boxes of various merchandise, various groceries, boxes of drugs, etc. (without abbreviations and not listed in definitions). As discussed in chapter 8, these packages could contain small amounts of colouring material cargo.

The list could be much larger. Some raw materials were intentionally omitted, such as copper, brass and tin, as their use was too wide (see section 9.4). The same applies to cargo items which could potentially be colouring and artists' materials, such as oil, pitch, wax (white, yellow, processed), vinegar and charcoal, or objects such as goose feathers or ink which were easy to acquire. Their use is also too wide and they do not originate from specialized workshop, but could easily be made everywhere.

Explanation of each colouring material and artist material individually was given by combining glossary (Kirby, Nash & Cannon 2010) and a dictionary (Eastaugh et al. 2008).

Cargo item	Explanation of use
Aloe / CM	a substance that originally derives from plants of the <i>Liliaceae</i> . Even though they originate from Africa, the Arabic peninsula, and Madagascar, they are becoming present in other locations in Asia and the USA. Use: the plant is known for its medical properties; coloured juice from plant can be left to evaporate, and produce yellow powder (Eastaugh et al. 2008, p. 11). There are different colours depending on different species. Use: colouring agent in varnish and glaze (Merrieffield 1967, xii; Eastaugh et al. 2008, p. 11).
Alum / CM	is sulphate-based substance, with the most common appearing alum or potassium alum sulphate. Various types can appear in documents: plume alum (<i>lume di piuma</i>), roche alum (<i>lume di rocca</i>), alum ground with rose water, egg white and sugar (<i>lume zucharina</i>), potassium tartrate (<i>lume di feza</i>). Use: papermaking, tanning leather, dyeing, lake pigments production (Kirby, Nash & Cannon 2010, p. 447).
Amber / AM	yellow, orange, or dark brown fossilized resin. Use: ingredient in varnish (Merrieffield 1967, p. xii; Kirby, Nash & Cannon 2010, p. 447).
Arsenic / CM	explained in section 3.3e and 9.5.
Canvas / AM	is the support for painting, usually made of linen, stretched over a wooden frame (Kirby, Nash & Cannon 2010, p. 449).
Cerussite / CM	explained in section 3.3a and 9.1.
Cinnabar / CM	explained in section 3.3c and 9.3.
Crimson – Carmine / CM	probably refers to different sorts of red lake pigment (Kirby 2015, p. 177). It might be identified with red lake pigment explained in section 3.3h and 9.8. Merrieffield (1967, p. xvi) states in painting treatises it can refer to cinnabar, or white and ochre mixed, and also red lake, but since in registers cinnabar and <i>terra rossa</i> already appear, carmine clearly refers to red lake pigment.

Cargo item	Explanation of use
Curcuma / CM	Also called turmeric (lat. <i>Curcuma longa</i>). Use: medicine, dyeing (Kirby, Nash & Cannon 2010, p. 459).
Emery / CM	granular form of aluminum oxide, corundum α -Al ₂ O ₃ , usually mixed with hematite, magnetite and silica (Eastaugh et al. 2008, p. 138).
Gallnut / CM	is a growth on plants, a consequence of parasite attack. Use: the source for tannin for dyeing, mordanting, tanning leather, and the production of black ink (by adding green vitriol) (Kirby, Nash & Cannon 2010, p. 451).
Grana / CM	refers to Kermes, or scale insect <i>Kermes vermilio</i> (Planchon, 1864). It was used as a crimson dye. The lake pigment could be prepared directly from the insect, but from the fourteenth century it was prepared by reusing clipping of the textiles (<i>lacca di cimatura di grana</i>). Use: pigment, dye (Kirby, Nash & Cannon 2010, p. 453).
Grana from Corfu / CM	see explanation of grana.
Gum / AM	is water-soluble material, made from special trees and plants, for. e.g. cherry and acacia. Use: as an adhesive and a binding medium in watercolour painting and manuscript illumination. There are different types: <i>gum ammoniac</i> , <i>gum anime</i> , <i>gum Arabic</i> , <i>gum benzoin</i> , <i>gum opoponax</i> , <i>gum sagapen</i> , <i>gum tragacanth</i> (Kirby, Nash & Cannon 2010, p. 452).
Indigo; Indigo <i>lauro</i> ; Indigo bagadet / CM	is a deep-blue insoluble dye, made from the indigo plant, or woad. There are various type of indigo (Kirby, Nash & Cannon 2010, p. 452), but in registers, only three are mentioned: regular, <i>lauro</i> (processed?) and <i>bagadet</i> . ‘Bagadet’ probably refers to place of production (Baghdad) according to Eastaugh et al. (2008, p. 200) and Kirby, Nash & Cannon (2010, p. 452), while Merrieffield (1967, xxii) states ‘bagadel’, ‘bagadon’ and others variation refer to indigo made of indigo plant.

Cargo item	Explanation of use
Mercury / CM	explained in section 3.3g and 9.7.
Minium / CM	explained in section 3.3d and 9.4.
Orpiment / CM	explained in section 3.3e and 9.5.
Refined sulphur / CM	is yellow and solid matter. Elementary sulphur is usually extracted from volcanic environments. Use: heated with mercury to produce vermilion; also a main ingredient of gunpowder (Kirby, Nash & Cannon 2010, p. 458). Merrieffield (1967, p. xxxi) mentions <i>sulphur vivum</i> , or impure Sulphur, which is opposite of refined mentioned in Tenenti (1959, p. 177).
Saffron / CM	colouring material obtained from dried stigmas of saffron crocus. Use: cooking, dye, golden-yellow pigment in manuscripts (Kirby, Nash & Cannon 2010, p. 457; Merrieffield 1967, p. xxviii).
Sal ammoniac (sel amoniac) / AM	is ammonium chloride originating from volcanic regions. Use: flux in glass production, purification of precious metals, production of copper-based blue pigments, as mentioned in medieval recipes (Kirby, Nash & Cannon 2010, p. 457).
Smaltino / CM	or frit, is a blue pigment. It is produced by mixing siliceous materials with copper and other metallic salts at a high temperature and grinding after it is cooled down (Merrieffield 1967, p. xix).
Solimato / AM	crystalline salt known as a mercuric sublimate or mercuric chloride. Use: to cure syphilis, metallurgy (Kirby, Nash & Cannon 2010, p. 458).
<i>Terra bianca</i> / CM (?)	unknown. Possibly chalk.

Cargo item	Explanation of use
<i>Terra ghetta</i> / CM	a synonym for litharge (Merrieffield 1967, p. xxii). Orange-yellow mineral, a by-product of the process of cupellation, which is extraction of silver from the natural ore (Eastaugh et al. 2008, p. 247). Use: used for preparation of drying oil, not recommended as a pigment (Kirby, Nash & Cannon 2010, p. 454).
<i>Terra rossa</i> / CM	explained in section 3.3b and 9.2.
Turpentine / AM	a product of distillation of pine resin, resulting as a solid residue (Kirby, Nash & Cannon 2010, p. 459). Use: ingredient in varnish and refining of lapis lazuli mineral (Merrieffield 1967, p. xxxii). Venetian turpentine refers to semi-liquid resin obtained from the larch. Besides use as a varnish, it was used in medicine (Kirby, Nash & Cannon 2010, p. 459).
Varnish / AM	is a transparent and protective coating used on paintings, furniture, musical instruments, etc. (Kirby, Nash & Cannon 2010, p. 459).
Verdigris (vert-de-gris) / CM	is a blue-green pigment produced by reaction of vinegar and copper (Kirby, Nash & Cannon 2010, p. 460)
Verzin; Verzino wood; Verzin lake; Verzin intero / CM	refers to brazilwood. Explained in section 3.3h and 9.8. Use: dye, lake pigment production with addition of alum substrate lake (Kirby, Nash & Cannon 2010, p. 449). Different types of verzin, verzino are mentioned in Tenenti (1959). Author's assumption is that different variants probably refer to raw material (verzinwood, verzin intero), dye (verzin), and lake pigment (verzin lake).
Vitriol / CM	hydrated copper and iron salt of sulphuric acid. Blue vitriol was copper (II) sulphate; green vitriol was ferrous sulphate and white vitriol zinc sulphate. Use: to produce pigment and ink (Kirby, Nash & Cannon 2010, p. 460).

Explanation of other columns:

Number / number given by Tenenti - provisional number to mark the number of the cargo item / number given in the book of the maritime accidents Tenenti (1959). Bold numbers are marking shipwrecks in the Adriatic.

Type of the ship - *galion, saetia, marciliana, nave, galera, orca, fregata, barca, berton*.¹⁴³

Year – the year when the insurance document was issued.

Direction – the final destination of the ship. Sometimes it had an intermediate stop.

Accident at sea – shipwreck or attack of corsairs, and location.¹⁴⁴

Colouring materials, possible artists' materials, and drugs / various groceries / boxes of colours – While listing materials of all three categories of cargo the common measurements were given. These are: *collo, miaro, botta, barilieto, balla, cantar, zurli, fagotto, scafazzi, sonde, rotoli, caratelli*. Only *libra* is translated to 'pound'.¹⁴⁵

¹⁴³ Tenenti has given the definitions (1959, p. 68), but it requires research of up-to-date bibliography to define the ship types, which goes beyond the scope of the research.

¹⁴⁴ For locations in category 'Direction' and 'Accident at sea', see detail map in Tenenti 1959, Pl. VIII. If there are titles that are not on the map due to archaic title, author explained the location in the footnote in the table below.

¹⁴⁵ The data about measurements will neither be explained nor used in the final interpretation, as studying the amounts and making comparisons goes beyond the scope of the research.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
1592									
1 / 1	<i>Rizzardi et Vidali</i>	galion	1592	to Constantinople, intermediate stop in Candia	shipwreck near Cefalonia	/	liquid varnish (1 cask = 150 pounds)	drugs (3 boxes); various groceries (2 boxes); various merchandise (1 box)	pp. 71, 72
2 / 3	<i>Salvaressa</i>	saetia	1592	to Messina	shipwreck near Lissa (cro. Vis)	vitriol (11 casks = 600 pounds); cerussite (5 casks); arsenic (2 casks = 1000 pounds) sulimadi ¹⁴⁶	turpentine (6 casks)	/	p. 74
3 / 10	<i>Vidala</i>	saetia	1592	from Alexandria	shipwreck in Porto Muneghe ¹⁴⁷	cerussite (400 casks)	/	small box of merchandise	pp. 78, 79
4 / 11	/	marciliana	1592	from Lecce	shipwreck near Brindisi	grana (2 <i>colli</i>); grana (1 <i>collo</i>)	/	/	p. 80

¹⁴⁶ Equivalent to *solimato*.

¹⁴⁷ Porto Muneghe is positioned on the island of Veli Lošinj.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
5 / 14	<i>Moceniga</i>	nave	1592	to Candia (Crete)	shipwreck near Modon	/	/	small box of various groceries	p. 81
6 / 18	/	saetia	1592	from Kalamata and Vitolo	attacked by Uskoks	2 pieces of verzin (brazilin?) (106 pounds)	/	/	p. 82
7 / 28	<i>Sumachiaou Santa Maria de Scoppo</i>	nave	1592	to London	captured in Spain	/	/	drugs (17 <i>colli</i>)	p. 86
1593									
8 / 41	<i>Thebaldo</i>	galion	1593	from Syria	shipwreck in waters of Arcadia (Morea)	indigo (2 boxes); indigo (1 box for 400 ducats); indigo (2 boxes); gallnut (130 ducats per <i>miaro</i>)	/	/	pp. 92, 93, 96
1594									
9 / 87	<i>Martinenga</i>	galion	1594	from Constantinople	shipwreck near Constantinople	indigo (2 boxes)	/	/	p. 117
10 / 88	<i>Canevala</i>	nave	1594	from Sicily	shipwreck near Curzola (cro. Korčula)	indigo (1 box)	/	/	p. 121

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
11 / 90	<i>Balbiana</i>	nave	1594	from Syria	shipwreck near Cyprus	indigo (1 box); indigo (2 boxes); gallnut (24 <i>colli</i>)	/	/	pp. 121, 122
12 / 98	<i>Donna della concettione</i>	nave	1594	to Lisbon	/	saffron (1 cask)	/	/	p. 127
13 / 112	/	saetia	1594	to Naples	/	turpentine (10 casks)	/	colours (3 boxes)	p. 131
14 / 117	/	galion	1594	to Cefalonia	attacked by Ottomans	/	canvas (1 <i>balla</i> = 1006 <i>braccia</i>); canvas for 150 ducats; canvas (2 <i>balle</i> = 1247 <i>braccie</i>)	/	p. 131
15 / 134	<i>Reniera</i>	nave	1594	from Syria	shipwreck in Venice	indigo (2 boxes)	/	/	p. 136
1595									
16 / 139	<i>Pegolota</i>	nave	1595	from Syria	shipwreck near Syracuse	gallnut (10 <i>colli</i>); indigo	/	/	pp. 139, 141
17 / 148	<i>Cigala or Nostra Donna dell'Istria</i>	nave or galion	1595	from Foglie and Scio (Chios)	shipwreck near Ancona	<i>terra ghetta</i> (?) (8 <i>cantara</i> , 28 ducats for <i>miaro</i>)	/	/	p. 145

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
18 / 163	<i>Orlando il Grande</i>	nave	1595	to Amsterdam and Middelbourg	shipwreck in waters of Sicily	/	/	drugs (6 <i>botte</i>)	p. 150
19 / 166	<i>Maniceli</i>	galion	1595	to Palermo	captured by corsairs in Sicily	/	/	drugs (2 boxes, 2 <i>bariletti</i> , 1 <i>balla</i>)	p. 153
20 / 173	/	galion	1595	from Constantinople	/	alum (422 <i>cantara</i>)	/	/	p. 159
21 / 178	<i>Martinenga</i>	nave or saitia	1595	to Corfu	shipwreck in Lodrin gulf ¹⁴⁸	/	/	various merchandise (2 boxes)	p. 163
22 / 184	<i>Patron Vincenzo Ulladi</i>	nave	1595	from Constantinople	immobilized at the island of Mezo, Ragusa (cro. Dubrovnik)	orpiment	/	/	p. 168
23 / 189	<i>Rheniera</i>	nave	1595	from Tripoli, Syria	/	gallnut (10 <i>colli</i>)	/	/	p. 171
24 / 193	<i>Poma</i>	maciliana	1595	from Lecce	shipwreck near Curzola (cro. Korčula)	saffron	/	/	p. 171
1596									
25 / 204	<i>Utria Alamana</i>	orca	1596	/	captured in Malaga by Spanish	refined sulphur (2000 <i>cantara</i>)	/	/	p. 177

¹⁴⁸ Near Durrës.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
26 / 209	/	saetia or galion	1596	to Messina	captured by Ottoman corsairs near Cotrone	cerussite mercury	/	/	pp. 179, 180
27 / 218	<i>Paradiso</i>	nave	1596	to Amsterdam	captured by Spanish armada in Messina	vitriol (1 box)	/	/	p. 187
28 / 220	<i>Pisana et Mazza</i>	nave	1596	from Corfu	captured by Spanish fleet	grana from Corfu (500 pounds <i>alla sotile</i> for 900 ducats)	/	/	p. 187
29 / 223	<i>Cavalier del mare</i>	nave	1596	to London	/	/	/	drugs (1 barrel)	p. 189
30 / 229	<i>Santa maria della neve et san Nicolo or Liona (Ragusan)</i>	nave	1596	from Smyrna	declared as incapable to sail at Ragusa (cro. Dubrovnik)	alum (120 <i>cantara</i>)	/	/	p. 193
1597									
31 / 234	<i>Cordes</i>	marciliana	1597	to Crete	captured by Ottoman corsairs	mercury (7 boxes)	/	/	p. 197

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
32 / 237	<i>Rigola</i>	marciliana	1597	from Corfu	shipwreck near Curzola (cro. Korčula)	grana (2 colli)	/	/	p. 198
33 / 243	<i>Tegiachin</i>	galion	1597	from Liesena (cro. Hvar)	captured by Uskoks	grana (1 collo)	/	/	p. 200
1598									
34 / 294	<i>Maurizza</i>	nave	1598	from Ragusa	/	grana (1 collo)	/	/	p. 220
35 / 295	<i>Colombo</i>	galion	1598	to Malta	shipwreck near Reggio	grana (1 collo)	/	/	p. 224
36 / 303	<i>Liona</i>	nave	1598	to Palermo	shipwreck near Palermo	turpentine (4 boxes)	/	/	p. 224
1599									
37 / 329	<i>Martinenga</i>	nave	1599	from Smyrna	shipwreck near Zara (cro. Zadar)	gallnut (11 cantara); gallnut (50 cantara)	/	drugs (small packages)	pp. 235, 236

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
38 / 334	<i>Esperienza</i>	orca	1599	from Lisbon	captured and taken to England	verzil ¹⁴⁹ (brazilin?) wood (200 <i>cantara</i>)	/	/	p. 239
39 / 341	<i>Speranza</i>	nave	1599	from England	/	crimson (4 casks);	/	/	p. 241
40 / 347	/	fregata	1599	to Ragusa (cro. Dubrovnik)	captured by Uskoks	verzino (brazilin?) wood (4189 pounds)	/	/	p. 243
41 / 379	<i>Agaza</i>	nave	1599	from Constantinople	accident near Zante and Corfu	alum (888 <i>cantara</i>); alum (154 <i>cantara</i>); alum (154 <i>cantara</i>)	/	/	pp. 253, 254
42 / 399	<i>San Giuseppe et San Bonaventura</i>	nave	1600	to Constantinople	captured by Sicilian ship and taken to Messina	cerussite (100 casks)	/	/	p. 261

¹⁴⁹ 'L' at the end of the word is a possible typo.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
1599									
43 / 446	/	marciliana	1600	to Bari	shipwreck near Ancona	/	/	various merchandise (5 boxes)	p. 278
1601									
44 / 454	<i>Pozza</i>	nave	1601	to Cyprus	shipwreck near Istria	cerussite (and nails in small box)	/	/	p. 283
45 / 455	<i>Santa Cattelina</i>	galion	1601	from Cadiz	captured and taken by Barbarians	verzino (brazilin?) wood (244 pieces)	/	/	p. 284
46 / 475	<i>Martinella</i>	nave	1601	to Constantinople	captured by Sicilian ship in Archipel	cerussite (20 casks); cerussite (150 casks); mercury (for 1400 ducats)	/	various merchandise (18 <i>colli</i>); various merchandise (1 box)	pp. 291, 292
47 / 483	/	barca	1601	to Fortore	captured by Turkish corsairs	lapis lazuli, aloe (next to tin for 460 ducats)	/	/	p. 296

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
48 / 486	<i>Nana et Ferra</i>	nave	1601	from Cyprus	shipwreck near Cyprus	indigo (8 boxes)	/	/	p. 297
49 / 514	<i>San Giovanni Battista</i>	berton	1601	to Palermo	captured by Sicilian ship	/	/	merchandise (1 box); various merchandise (32 <i>colli</i>)	pp. 307, 308
1602									
50 / 548	<i>Rosetta</i>	marciliana	1602	to Cefalonia	shipwreck near Lecce	/	/	various merchandise (1 box)	p. 321
51 / 552	<i>Fachinella</i>	marciliana	1602	to Bari	shipwreck near Rodici	cerussite (1 <i>collo</i>); vitriol (2 <i>colli</i>)	/	various merchandise (11 boxes)	p. 323
52 / 555	<i>Canevala</i>	nave	1602	from Tripoli (Syria)	captured by Ottoman corsairs	gallnut (6 <i>colli</i>)	/	/	p. 324
53 / 567	<i>Giustiniana et Benvenuta</i>	nave	1602	coming from Syria	captured by Sicilian ships	indigo (10 boxes); indigo (1 box); indigo (2 <i>zurli</i>);	/	drugs (3 <i>colli</i>)	p. 335

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
54 / 579	<i>Rizzarda</i>	marciliana	1602	coming from Crete	shipwreck near Lecce	gallnut (3 bags)	/	/	p. 341
55 / 596	<i>Manarina</i>	marciliana	1602	from Cefalonia	shipwreck near Augusta	grana (477 pounds)	/	/	p. 348
1603									
56 / 608	<i>Barozza</i>	marciliana	1603	to Valona	shipwreck near Curzola (cro. Korčula)	<i>terra bianca</i> (2 boxes); alum (200 pounds); arsenic (100 pounds); mercury (1 box); sulima ¹⁵⁰ (1 box); crimson (13 pounds); arsenic (100 pounds)	/	/	p. 358
57 / 636	<i>Bersatona</i>	marciliana	1603	from Candia	captured by English corsairs	grana (2 bags)	/	/	p. 372

¹⁵⁰ Equivalent to solimato.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
58 / 639	<i>Marubin</i>	berton	1603	to Alexandria	captured by English corsairs	/	different objects (1 box)	/	p. 374
59 / 643	<i>Buonaventura Giopanditi</i>	nave	1603	from Smyrna	captured by English corsairs	<i>terra ghetas (277 cantara)</i>	/	/	p. 377
60 / 648	<i>Reata et Guidotta</i>	nave	1603	to Constantinople	/	cerussite (20 barrels)	/	/	p. 382
1604									
61 / 683	<i>Beni et rosseti or Rosseta</i>	marciliana	1604	from Lecce	shipwreck near Ancona	saffron	/	/	p. 395
62 / 707	<i>Costantina</i>	marciliana	1604	from Corfu	captured by corsairs	gallnut (1 <i>collo</i>)	/	/	p. 403
63 / 711	<i>Silvestra</i>	nave	1604	to Constantinople	captured by Neapolitan ships	/	/	various merchandise (16 <i>colli</i>)	p. 405

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
64 / 734	<i>Marchesi</i>	galion	1604	to Corfu	Ancona	grana, saffron (next to corduan ¹⁵¹ , <i>schivavine</i> ¹⁵² , silk); gallnut (3 bags)	/	/	pp. 420, 421
1605									
65 / 745	<i>Pigna</i>	nave	1605	from Tripoli (Syria)	captured by Sicilian ships	<i>sel amoniac</i> (2 boxes for 245 ducats)	canvas (next to pieces of artillery, iron, tools)	/	p. 425, 426
66 / 750	<i>Pelestrina</i>	marciliana	1605	from Zante	shipwreck near Cattaro (Kotor)	grane, saffron (next to corduan, silk)	/	/	p. 429
67 / 763	<i>Vidala</i>	nave	1605	from Alexandria	captured by corsairs	indigo (7 <i>zurli</i>); indigo (4 boxes); indigo (2 <i>colli</i>)	/	/	p. 432, 433
68 / 782	<i>Persavale</i>	nave	1605	from Smyrna	shipwreck at Malamocco	<i>terra ghetta</i> (721 <i>cantars</i>); <i>terra ghetta</i> (595 <i>cantara</i> 1/2); gallnut (5 bags); gallnut (10 <i>colli</i>)	/	/	p. 441

¹⁵¹ Plant with medical properties.

¹⁵² Rough, thick woolen cover (Boerio 1856, p. 552).

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
69 / 784	<i>Stella</i>	nave	1605	to Lisbon	captured by Ottoman corsairs	mercury (2845 pounds; 910 ducats 9 gr.)	/	/	p. 442
70 / 788	<i>Perastana</i>	nave	1605	to Alexandria	accident in Alexandria	minium (4 casks); d'or <i>pinente</i> (probably orpiment) (2 boxes); vert-de-gris (and silk <i>de peneli</i> 1 box); cerussite (50 small casks); arsenic (4 casks);	raw amber (786 pounds)	/	pp. 445, 448.
71 / 801	<i>Balba</i>	nave	1605	from Tripoli (Syria)	captured by corsairs	gallnut (next to silk and pepper)	/	/	p. 456
1606									
72 / 808	<i>Albanese</i>	marciliana	1606	from Corfu	shipwreck near Porto Cigala ¹⁵³	saffron, grane (next to silk, wax, <i>schivavine</i>)	/	/	p. 461

¹⁵³ Island of Veli Lošinj.

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
73 / 811	<i>S. Anna</i>	saetia	1606	from Palermo	waters of Tarente	orpiment (6 boxes); curcuma (2 <i>caratelli</i>)	/	/	p. 463
74 / 812	<i>Moresina</i>	nave	1606	from Cyprus	accident near Milo	indigo (27 boxes, 2 <i>scafazzi</i> and 5 <i>sonde</i>); indigo (14 boxes); indigo (2 boxes)	/	/	p. 467
1607									
75 / 846	<i>Rubbi</i>	nave	1607	from Alexandria	captured by corsairs	indigo (1 <i>zurlo</i>); indigo (11 <i>zurli</i> , 1 <i>fagotto</i>); indigo (3 <i>colli</i>); indigo bagadet (2116 <i>rotoli</i>); indigo (1 <i>fagotto</i>); indigo (9 <i>colli</i>); indigo (15 <i>colli</i>); curcuma (420 <i>rotoli</i>); curcuma (4 <i>colli</i>)	/	/	pp. 479, 480, 481

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
76 / 848	<i>Liona</i>	nave	1607	from Syria	captured by fustes in the port of Vatican	indigo <i>lauri</i> ; indigo <i>lauri</i> (2 boxes); indigo (1 package); indigo (2 boxes); indigo (1 box); indigo (4 boxes); indigo (16 <i>scaffacci</i>)	/	/	pp. 482, 483
77 / 868	<i>Zena</i>	nave	1607	to Constantinople	captured by corsairs	<i>verzin</i> (brazilin?); (290 pounds); <i>terra rossa</i> and crimson (2500 ducats); sal ammoniac; vert-de-gris; minium ordinaire; <i>verzin lake</i> ; <i>verzin intero</i>	turpentine	/	p. 496
78 / 877	<i>Rheniera et Soderina</i>	nave	1607	from Syria and Cyprus	captured by two bertoni ships	indigo (26 boxes)	/	/	p. 502
79 / 887	<i>Balbiana</i>	nave	1607	from Alexandria	/	curcuma (2 <i>zembeli</i>)	/	/	p. 506

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
1608									
80 / 905	<i>Cathelana</i>	nave	1608	from Messina	shipwreck at Cesenatico	indigo (2 <i>caratelli</i>); gallnut (1 bag)	/	/	p. 515
1609									
81 / 986	<i>Salvetta</i>	nave	1609	to Syria	Shipwreck near Acri	indigo (1 box); indigo (10 boxes), sal ammoniac (5 <i>colli</i>); indigo <i>lauro</i> (4 caisses); indigo (2 caisses) indigo (5 boxes); indigo (20 boxes); indigo; indigo (next to silk and pillows); gallnut (2 <i>colli</i>)	/	/	pp. 542, 543, 544
82 / 993	<i>Falcon Bianco</i>	nave	1609	to Lisabon	captured by corsairs	emery (10 boxes); smaltini (2 boxes); mercury and cinnabar (1 box)	gum (1 box)	/	p. 549

Number / number given by Tenenti	Ship's name	Type of the ship	Year	Direction	Accident at sea	Colouring materials	Possible artists' materials	Drugs / Various groceries / boxes of colours	Number of page
83 / 1014	<i>San Jacopo</i>	nave	1609	from Alessandretta	/	indigo (2 <i>scaffazzi</i>)	/	/	p. 556
84 / 1017	<i>Reatta</i>	nave	1609	to Syria	shipwreck near Rodici	crimson (1 <i>collo</i> ; 6 ducats for a pound)	canvas (260 <i>braccia</i>); processed amber (130 pounds)	/	p. 558, 559
85 / 1019	<i>Nanti</i>	berton	1609	to Smyrna	shipwreck near Ragusa (cro. Dubrovnik)	/	canvas (240 <i>braccia</i>)	/	p. 560

Appendix 9: Vendecolori active in Venice from the mid-sixteenth to the mid-seventeenth century

The database is based on the list published by Julia De Lancey (2011) in the article ‘In the Streets Where They Sell Colors’: Placing *vendecolori* in the urban fabric of early modern Venice, *Wallraf-Richartz-Jarbuch*, vol. 72, pp. 193-232. The names matching large cargo shipments in Appendix 8 are marked in bold letters.

Shop sign	Year (earliest – latest date)	Names	Pages
<i>The Corone</i>	1594 – mid 17 th c.	Piero q. Domenico Boschetti, Matthio di Zuanne Zucca, Gio. Giacomo Pedrezzoli	pp. 212, 213
<i>The Croci</i>	1598	Zuane Luca Guaroni	pp. 212, 213
<i>Agnus Dei</i>	Early 17 th c.	Zuan M[aria] Guerinoni, Zianne di Ottavian di Moca	pp. 212, 213
<i>Anzolo</i>	1594 (1532?) / at least 1624 if not 1640	Iseppo [q. Carlo] Gagin, Zuanne Battista and Zuanne Piero q. Iseppo Gagin, Margarita widow of Zuane Piero	pp. 212, 213
<i>Aquila</i>	1514 – 1560/c. 1660	Francesco and Nicolo q. Filippo, Piero Leoni	pp. 212, 213

Shop sign	Year (earliest – latest date)	Names	Pages
<i>Calese (Calice)</i>	1602 – mid 17 th c.	Domenico Baldo, Mattio di Lodovico Ferrari	pp. 212, 213
<i>Campana</i>	1594/1699	Alessandro di Mutti, Bettin di Mutti, Piero di Mutti, Vicenzo di Mutti, Zanetto di Mutti, Carlo Castagna	pp. 212, 213
<i>Carro</i>	1604 – 1612 at least	Stefano Albertini, Francesco di Piero di Regli	pp. 212, 213
<i>Chiave</i>	1602 – 1604	Antonio di Andrea della Chiave	pp. 212, 213
<i>Colombina</i>	1594 - 1660	Paolo di Antonio Gratarol, Zuane Maggioni	pp. 212, 213
<i>Corona</i>	1604 – c. 1660	Alvise [di] Vincenzo Bonelli, Zuane Martinelli, Antonio Martinelli	pp. 214, 215

Shop sign	Year (earliest – latest date)	Names	Pages
<i>Croce</i>	c. 1604? – c. 1664	Simon Finorti, Anzolo Monello (Antonio Pedrini)	pp. 214, 215
<i>Fortuna</i>	1551 / c. 1604	Giacomo Ciribelli	pp. 214, 215
<i>Gallion (Galia, Galere)</i>	c. 1604 (?) – c. 1660	Zuan Battista Fanton	pp. 214, 215
<i>Giesù / Jesus (Gesù)</i>	1594 / c. 1672	Anna Venerio, Simon della S. Cadrin, Bernardo Scotti	pp. 214, 215
<i>Madonna (I) (also S. Maria Virgine)</i>	At least 1577 – early 17th c.	Iseppo Bosello, Marco Esperti, Giacomo di Antonio Bosello	pp. 214, 215
<i>Masena</i>	1594 only	Giacomo and Vincenzo di Barolomeo Bonello	pp. 216, 217
<i>Melon</i>	1594 – c. 1672	Mattio Ferrari, Giacinto Este, Milan Milani, Giovani Pietro di Francesco Tirabosco	pp. 216, 217

Shop sign	Year (earliest – latest date)	Names	Pages
<i>Naranza (Arancia)</i>	1594 – 1604	Bartolo & Galo Rizzo, Antonio di Zuan	pp. 216, 217
<i>Pigna</i>	1604	Bartolo Gazan	pp. 216, 217
<i>Rioda (Ruoda)</i>	1604/c. 1672	Zuan Maria Zerbina, Domenico q. Bortolo Baldi, Giacomo Zerbina, Angelo Rossi	pp. 216, 217
<i>S. Antonio</i>	1604 - 1672	Cabriel Cabrieli, Piero Marchesi, Zuanne Barazato	pp. 216, 217
<i>S. Barbara</i>	Later 16 th c.	Anzolo Picenti, Giacomo Cavagnis	pp. 216, 217
<i>S. Caterina</i>	1604 – 1605	Zuan Antonio (Tomio) Giosi	pp. 216, 217
<i>S. Francesco</i>	1594 – late 17 th c.	Comin di Zuan Bonelli, Marco Trussardo	pp. 216, 217

Shop sign	Year (earliest – latest date)	Names	Pages
<i>S. Giustina</i>	1594 / c. 1699	Giacomo Trentin, Zuanne q. Bortolo Simoncini, Maffio Ferrari, Alberto q. Maffio Ferrari	pp. 216, 217
<i>S. Iseppo</i> (?), <i>S. Giuseppe</i>	c. 1604 – 1605	Bartolo di Comin Bonelli	pp. 216, 217
<i>S. Lorenzo</i>	c. 1605 / c. 1699	Sebastian Ucelli/Vicelli, Zacharia Perini	pp. 216, 217
<i>S. Martin</i>	1589 – 1604	Zuan [Antonio] Spinelli, Menego (nephew of Zuan Antonio), Agostin di Zuan Antonio Spinelli, Gratoso q. Antonio Spinelli	pp. 216, 217
<i>S. Nicolo</i>	1567	Piero da l'Oglio, Zuan Ambrogio Perlasca	pp. 216, 217
<i>S. Rocco</i>	1597 – c. 1672	Anzolo Giosi, Zuan di Anzolo Giosi, Paval & Niccolò Marini	pp. 216, 217
<i>S. Zuan Battista</i> (<i>S. Giovanni Battista</i>)	1562	Tomaso q. Bergamin del Mogio	pp. 216, 217

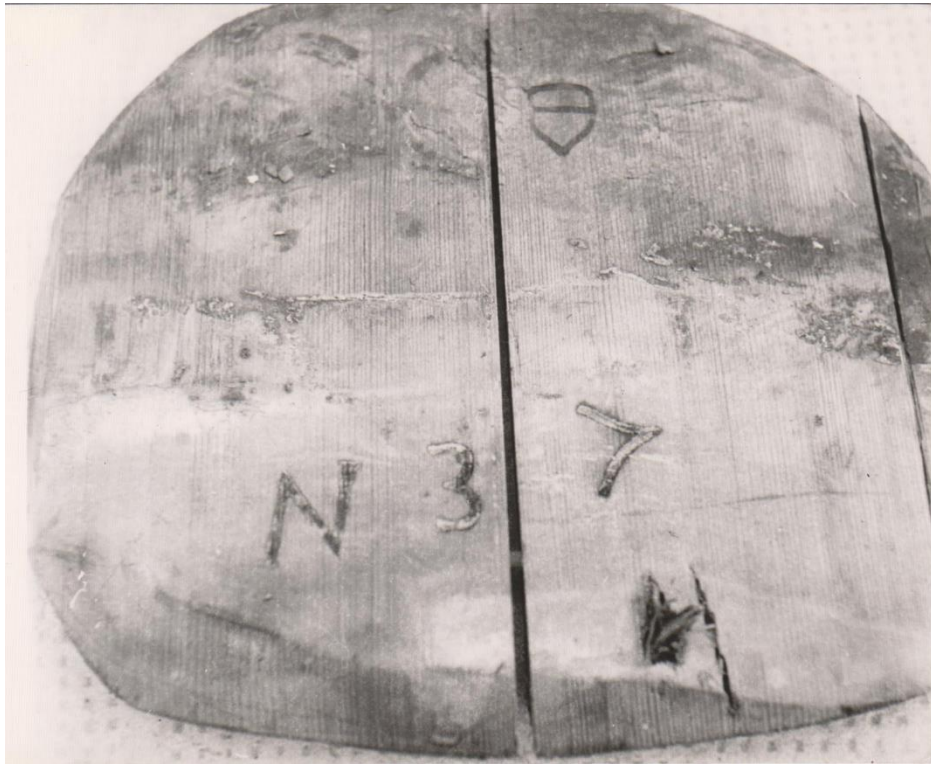
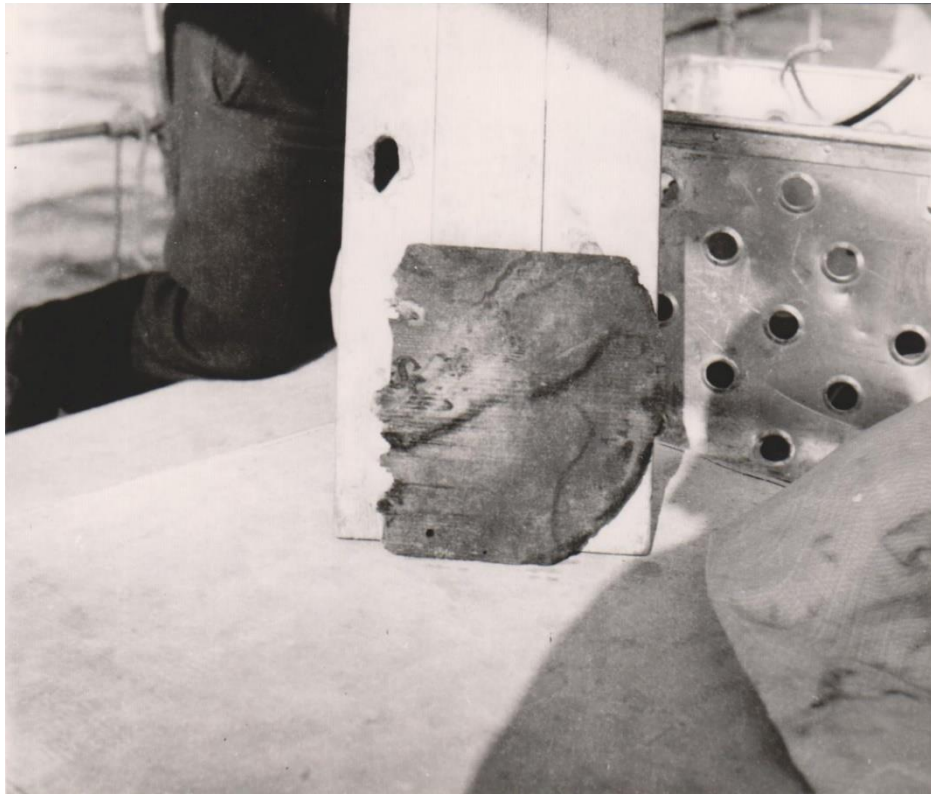
Shop sign	Year (earliest – latest date)	Names	Pages
<i>S. Zuan Evangelista</i>	1562	Zuane Navi[s] (?) ‘alemano’	pp. 216, 217
<i>Scala</i>	1534 - 1664	Domenico q. Gabriele; Alvise & Gabriele q. Domenico; Domenico & Anzolo; Gabriele, Alvise and Francesco q. Anzolo; Alvise q. Francesco; Iseppo Armeno	pp. 216, 217
<i>Serena</i>	1568 / c. 1672	Zuanmaria Zerbina, Marco di Z. Maria Zerbina, Zuanbattista Zerbina, Giacomo Carrara	pp. 216, 217
<i>Simia</i>	1594	Michael Rizzardi	pp. 218, 219
<i>Sol</i>	1567 / c. 1604	Zorzi de Bartholo, Valerio di Mazzi, Francesco di Piero, Domenico Baldo	pp. 218, 219
<i>Stadera</i>	1567	Zuane dai colori	pp. 218, 219

Shop sign	Year (earliest – latest date)	Names	Pages
<i>Stella</i>	1590 – c. 1699	Paolo Bartolotti, Bartolo q. Paolo Bortolotti, Zan Antonio Zinelli	pp. 218, 219
<i>Torre</i>	1594 / c. 1660	Niccolo Bonfadini, Zuane detto Bonfadini Chizzal (?), Andrea Vidali	pp. 218, 219

Appendix 10: Colouring materials from the Gnalić Shipwreck

Gnalić shipwreck raw (colouring) materials	Form	Transport container	Amounts
Lead white	Conical ingot	Casks (height c.43–50 cm; diameter: 30 cm)	Full casks still <i>in situ</i> ; over 1500 kg recovered
Red ochre	Powder	Oval barrels (height 85–125 cm)	63 kg red ochre* per barrel (based on calculations on barrel no. 3); At least six barrels of red ochre were present at the site.
Mercury sulphide	Bell-shaped, possibly vermilion (type A)	Chests (80 × 110 cm)	14 bell-shaped ingots; over 1000 kg total
	Lump (type B)	unknown	26 kg
Minium	Irregular lump	Unknown	c.1.6 kg
Arsenic sulphide-based colouring materials (realgar)	Powder	Two barrels with yellow powder (?) mentioned in the 1972 fieldwork report, three or five in total.	Not possible to calculate; visible staining with some material preserved on the ship's hull and in the sediment
Stibnite	Lump	Unknown	2 pieces; 0.288 kg
Mercury	Liquid pool	Unknown	Over 50 kg
Red lake	Ball	Unknown	Average weight of one ball: 0.00175 kg; total amount (c.30 balls of lake pigment): 0.00555 kg

Appendix 11: Designations on the lid of the casks



Different marks on the casks. Excavation campaign 1972.
(Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

Appendix 12: Designations on the lid of the lead white casks

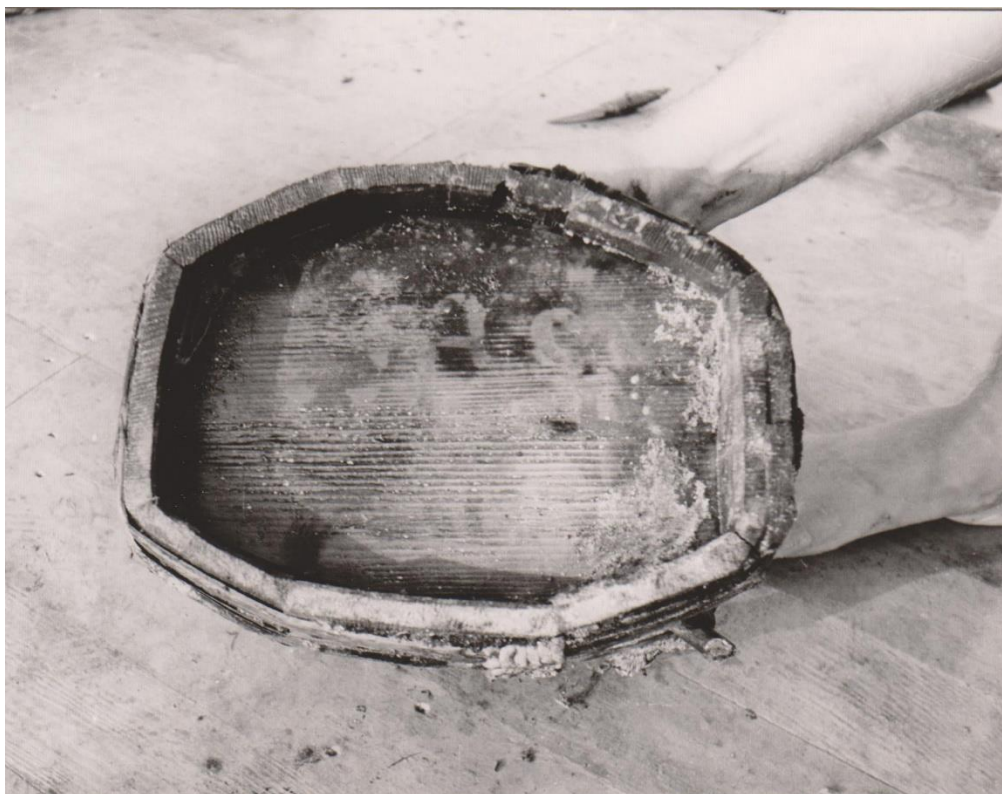


Lids of the casks bearing stamps. Top: monogram composed of G, P and the profile of a head;
Bottom: various marks. Excavation campaign 1972
(Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).



Lids of the casks bearing stamps. Top: monogram composed of S, Z and cross;
Bottom: motif of the ladder in the circle. Excavation campaign 1972
(Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

Appendix 13: Cask filled with yellow colour



Casks filled with yellow colour of unknown composition, excavation campaign 1972. Researchers assumed it was sulphur, although it was very likely arsenic sulphide-based colouring material (Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar).

Appendix 14: Recovery of barrel 3



Recovery of barrel 3 by using carbon fibre support, executed under the direction of Barbara Davide and Marco Ciabattoni from Superior Institute for Conservation and Restoration (ISCR), Rome, Italy (Archive of the project: The Shipwreck of Gnalić – Mirror of Renaissance World, photo: B. Vukičević, CROPIX).

Appendix 15: Cones of the lead white



Gnalić Shipwreck,
Croatia
GN-2017-CM36
5 cm

Lead white ingot, Gnalić shipwreck



Lead white ingot, Gnalić shipwreck



Gnalić Shipwreck,
Croatia
GN-2017-CM40

5 cm

Lead white ingot, Gnalić shipwreck



Lead white ingot, Gnalić shipwreck



Lead white ingot, Gnalić shipwreck

Appendix 16: Wrapping of the lead white cones



Lead white cones with remains of leather-like material and straw (photo: M. Martinčák).

Appendix 17: Mercury sulphide bells



Bells of mercury sulphide, Gnalić Shipwreck. Top: Discovery of the bells in September 1967 (photo: D. Balenović, Archive of Republic of Croatia Ministry of Culture, Conservation Department in Zadar). Bottom: Bells of mercury sulphide in the Regional Museum of Biograd na Moru (photo: N. Čuk).

Appendix 18: Lump of minium



Gnalić Shipwreck,
Croatia
GN-2017-CM35
5 cm

Minium, Gnalić shipwreck

Appendix 19: Colouring materials as a part of the reference collection of the Cultural Heritage Agency of the Netherlands



REPUBLIKA HRVATSKA
MINISTARSTVO KULTURE

Uprava za zaštitu kulturne baštine
Konzervatorski odjel u Zadru

Klasa: 612-08/19-24/3256
Urbroj: 532-04-02-13/5-19-2
Zadar, 08. studenog 2019.

MINISTARSTVO KULTURE
Uprava za zaštitu kulturne baštine
Runjaninova 2
10000 Zagreb

PREDMET: Izdavanje dopuštenja za izvoz / iznošenje predmeta koji nisu kulturna dobra – Katarina Batur, Sveučilište u Zadru, Odjel za arheologiju – izvoz 21 uzorka kamena i sedimenta s ostacima boje s nalazišta brodolom kod otočića Gnalić u Nizozemsku – daje se

Poštovani,

u prilogu vam dostavljamo presliku Potvrde za izvoz / iznošenje predmeta koji nisu kulturna dobra br. 005173.

Potvrđujemo da uzorci kamena i sedimenta s ostacima boje prikupljeni tijekom istraživačkih akcija provedenih tijekom 2017. godine na nalazištu brodolom kod otočića Gnalić, nemaju svojstvo kulturnog dobra te slijedom navedenog ne podliježu zabrani iznošenja iz Republike Hrvatske u Nizozemsku.

Od ukupno 21 uzorka kamena, minerala i sedimenta izdvojeni su ulomci ili po nekoliko grama uzoraka koji će se donirati nizozemskom Ministarstvu kulture (Cultural Heritage Agency of Netherlands) čime će postati dio svjetske kolekcije povijesnih sirovina za izradu boja.

Analiziranje i uzorkovanje materijala izvela je Katarina Batur sa Sveučilišta u Zadru, Odjela za arheologiju, Obala kralja Petra Krešimira IV 2, 23000 Zadar.

S poštovanjem,

PROČELNIK

Igor Miletić, prof.



Dostaviti:

1. Birgit Reissland, Cultural Heritage Agency of Netherlands, Hobbemastraat 22, NL-1071 ZC, Amsterdam, Netherlands
2. Pismohrana, ovdje

Official document for export of the samples issued by Ministry of Culture of Republic of Croatia. The samples used in this dissertation were donated to the reference collection of the Cultural Heritage Agency of the Netherlands.

Appendix 20: Selected lead white from the barrels recovered in 2013 and 2014

Inventory number	Barrel	Position	Weight (g)	Diameter bottom (ø cm)	Diameter top (ø cm)	Height (cm)	SEM / EDX	XRD	Lead isotope analyses	Radiocarbon dating of 13C and 14C
GN-2018-LW1	19	C17	565	3,6	7,1	7,1	x	/	x	x
GN-2018-LW2	17	C17	350	3,2	6	5,6	x	x	x	x
GN-2018-LW3	28	C19	515	3,1	7	6	/	x	x	x
GN-2018-LW4	39	C17	241	2,5	6,1	4,5	/	/	x	x
GN-2018-LW5	15	C17	437	3,9	7,3	5,2	x	/	x	x
GN-2018-LW6	11	B16	228	3,6	5,7	4,4	/	/	/	/
GN-2018-LW7	16	B17	338	2,8	5,9	5,8	/	/	/	/
GN-2018-LW8	42	B19	262	2,9	5,5	4,4	x	/	x	x
GN-2017-CM36	/	D17	576,4	3,6	6,3	7	x	x	x	/

Appendix 21: The database of the colouring materials samples

GNALIĆ SHIPWRECK

GN-2017-CM02

Sample information

Location of sample

Northeastern part of C17.2 / stave of barrel 1

Date of recovery (YYYY-MM-DD)

2017-08-15

Condition upon recovery

Barrel 1 was recovered from underwater site and sampled on board

Sample description

Powder on the wooden fragment

Colour

Red

Storage condition

Kept wet in the plastic bag

Cross / thin section

n/a

Analyses done

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

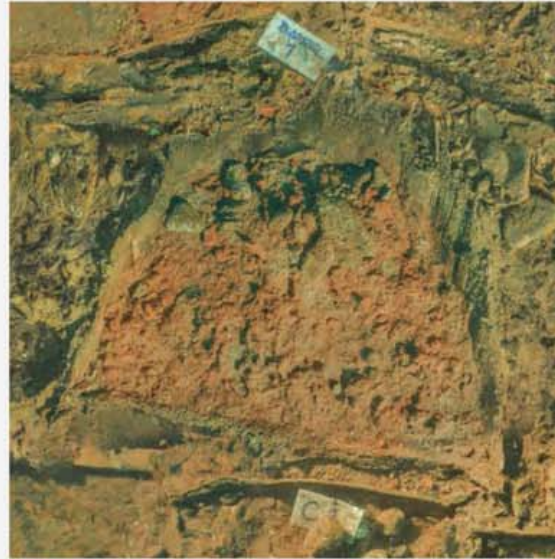
FTIR

RS

UHPLC

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

Notes

/

To conduct in future projects

/

Microscope photo 1



Texture description

Binocular observations:

Fine-grained red powder and white crystals (salt?) on wooden fragment.

Microscope photo 2

Microscope photo 3

GN-2017-CM02

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

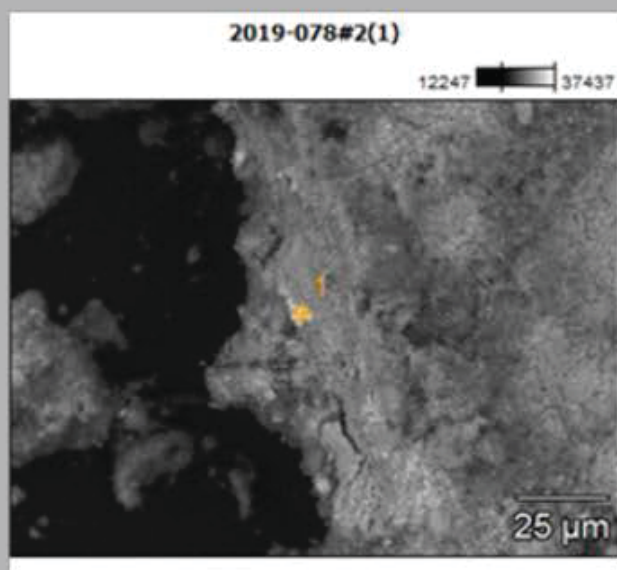
Conclusion

Pt 1: Chemical elements

Magnification: 750

Pt 1: S, C, O, Fe/F, Na, Mg, Al, Si, Pb/S, Cl, K, Ca, Cu□/ O, Al, Pb/S, Fe

Pt 1: BSE image



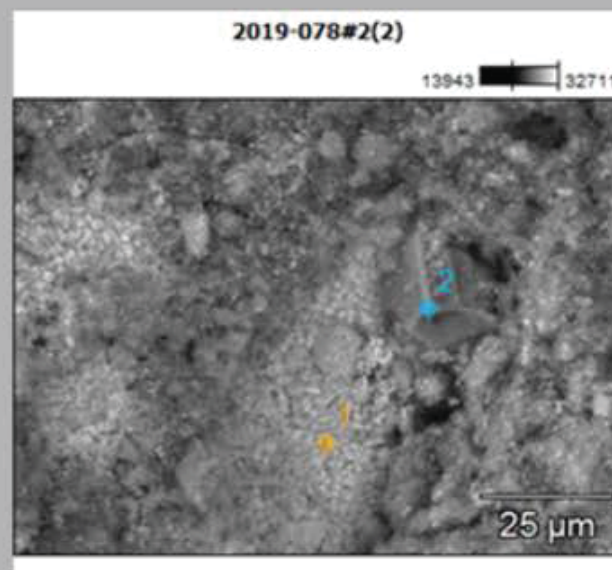
Pt 2: Chemical elements

Magnification: 1100

Pt 2-1: S, C, O, Fe/F, Na, As, Mg, Al, Si, S, K, Ca, As / Fe, S

Pt 2-2: C, O, Na, Mg, Al, Si, P, S, K, Fe / O, Al, S, Fe

Pt 2: BSE image



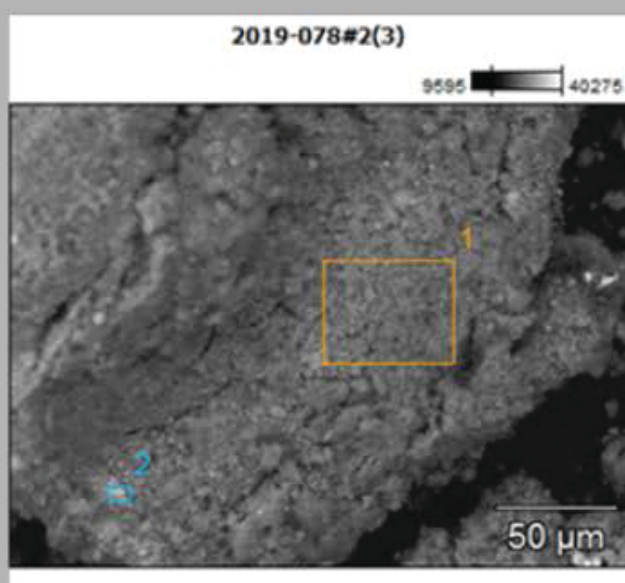
Pt 3: Chemical elements

Magnification: 500

SA 3-1: C, O, Na, Mg, Al, Si, S, Cl, K, Fe / O, Al, Fe

Pt 3-2: C, O, Na, Mg/As, Al, Si, S, K, Ca, Fe, As / O, Al, Fe

Pt 3: BSE image

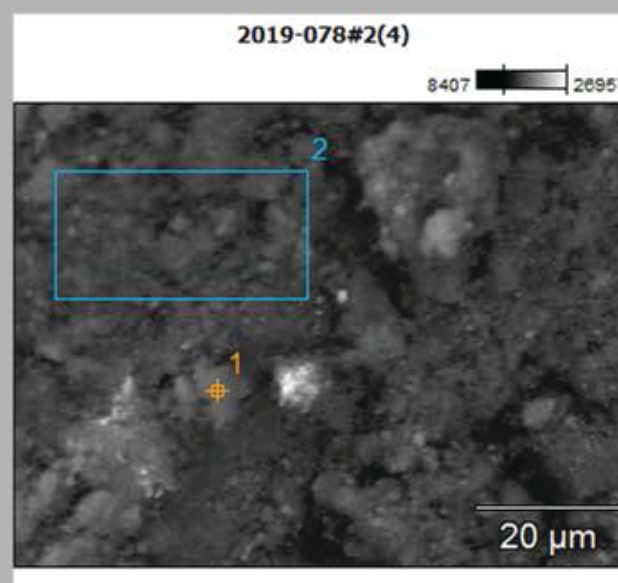


Pt 4: Chemical elements

Pt 4-1: C, O, Fe, Na, Mg, Al, Si, S, K, Fe / O, Al, Fe

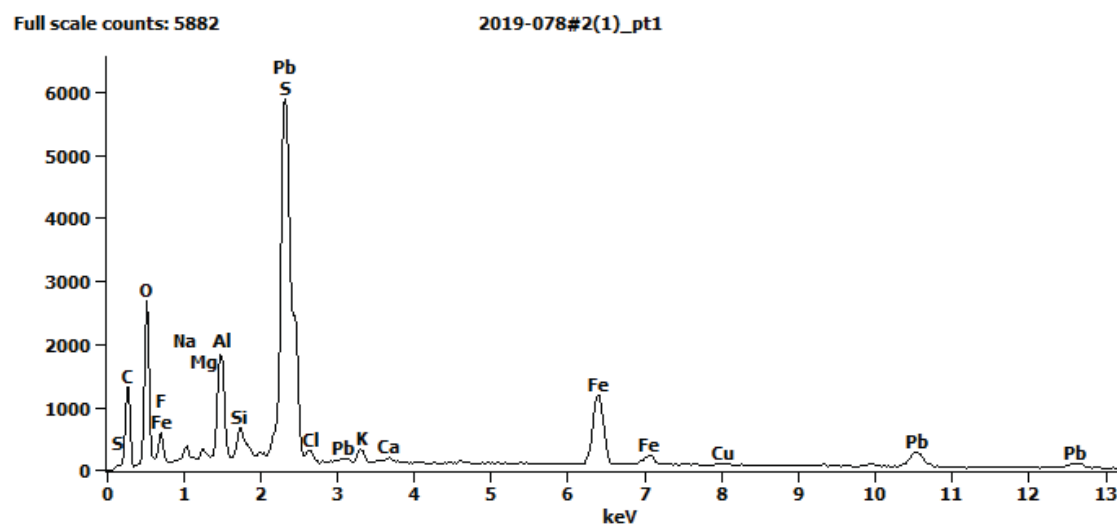
SA 4-2: C, O, Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe / O, Al, Fe

Pt 4: BSE image

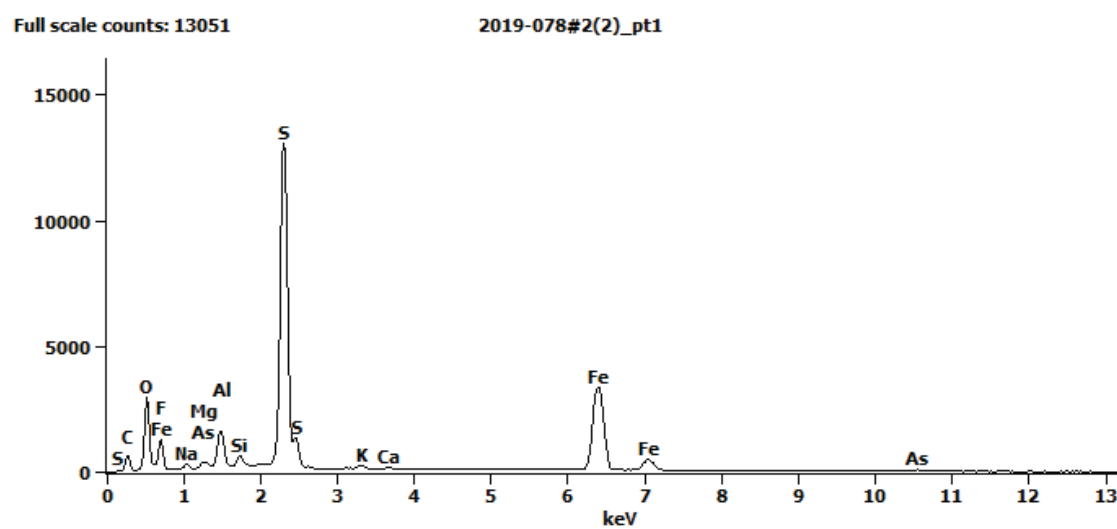


GN-2017-CM02

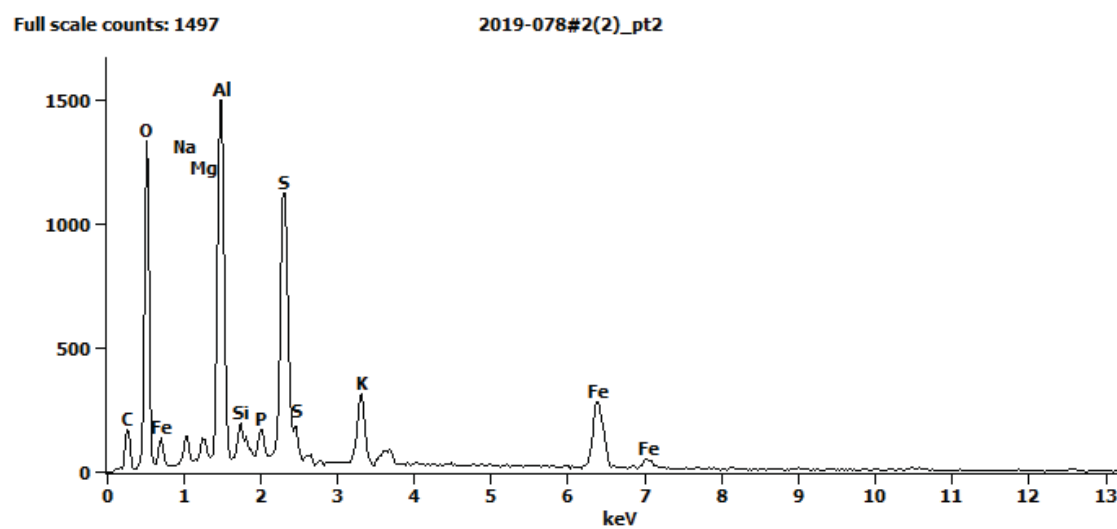
Point 1:



Point 2-1:

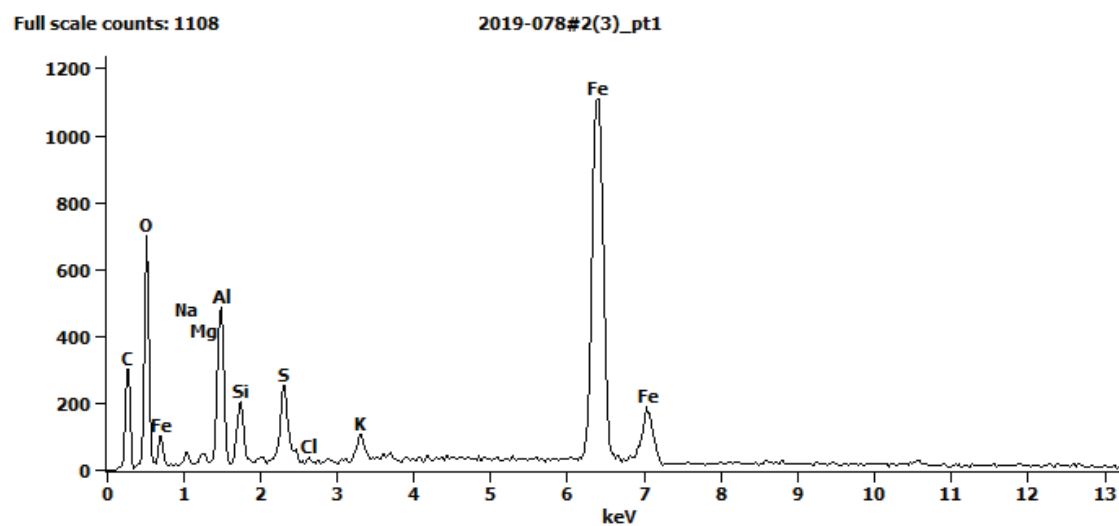


Point 2-2:

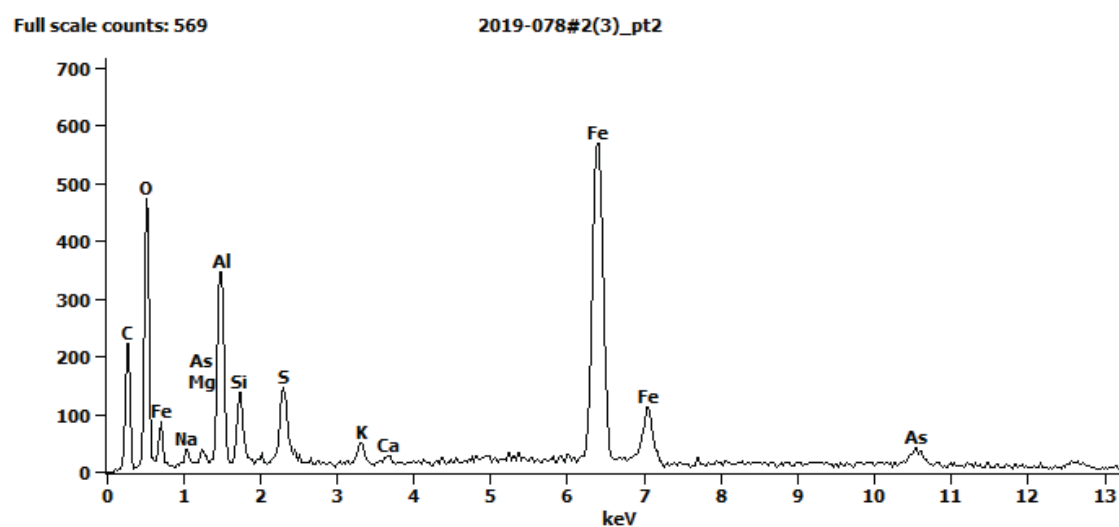


GN-2017-CM02

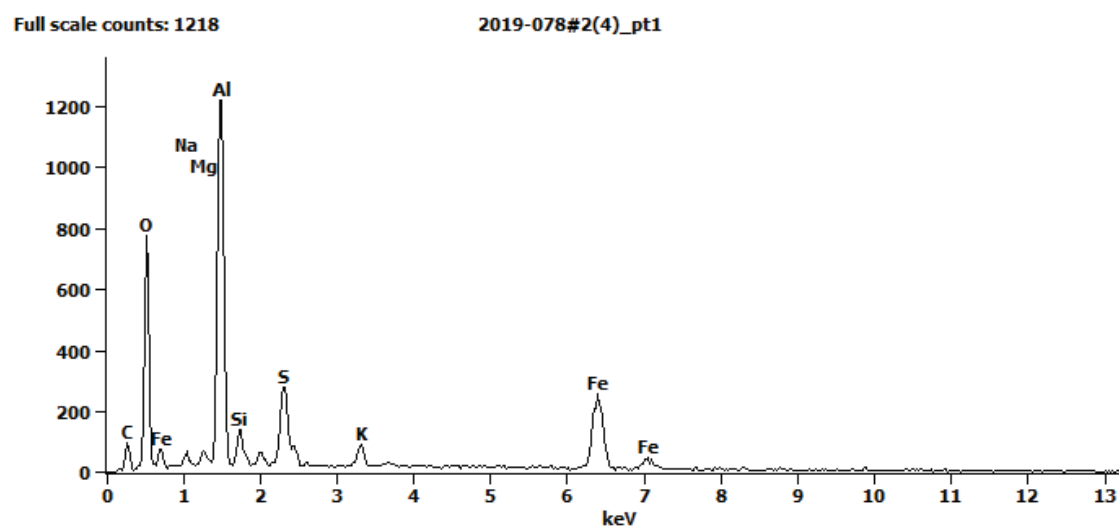
Surface area 3-1:



Point 3-2:



Point 4-1:

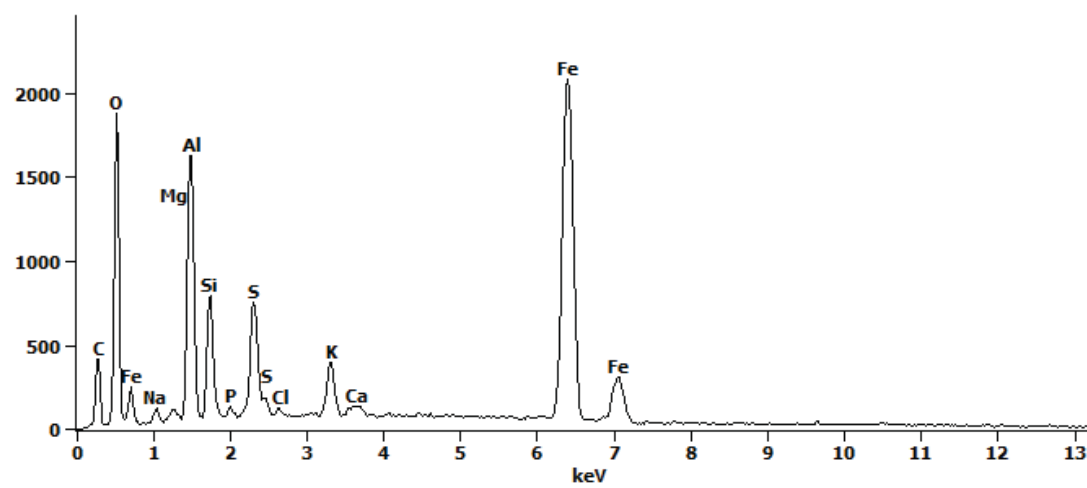


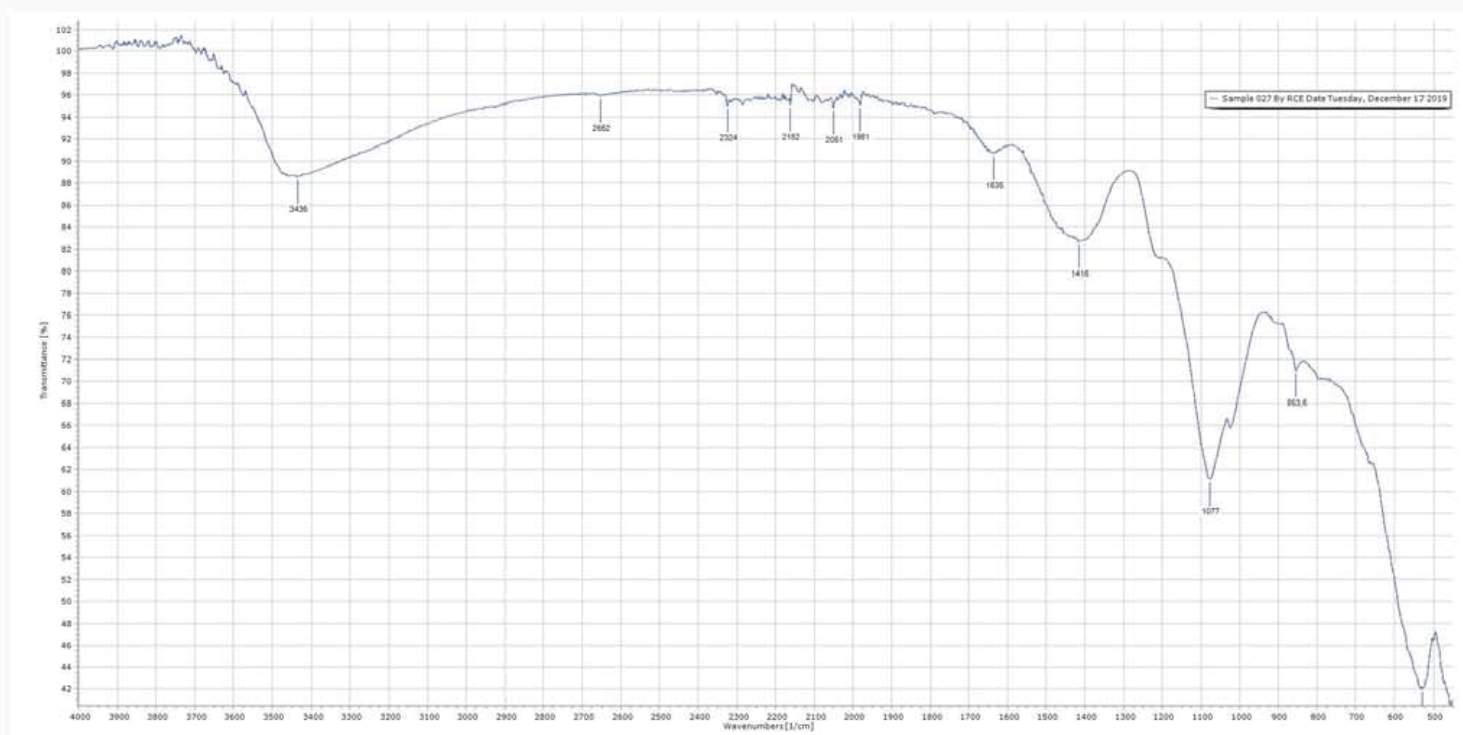
GN-2017-CM02

Surface area 4-2:

Full scale counts: 2079

2019-078#2(4)_pt2





FTIR results

Absorption bands visible: **3436 b**; **1635 w**; 1416 mb; 1077 vsh; 1029 sh; 853,6 wsh; **530 vsh**; **456 vsh**

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: **3000 – 3600 b (3446 peak)**; **1614 w**; **468 vsh**; **538 vsh**;

* Silicon oxide: reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: 1077-1022 sh;

* **853,6 wsh** - calcite (?)

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4.

Corresponding absorption bands: 1030 sh, 795 w, 531 sh, 431 sh;

(b - broad; w - wide; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM02

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

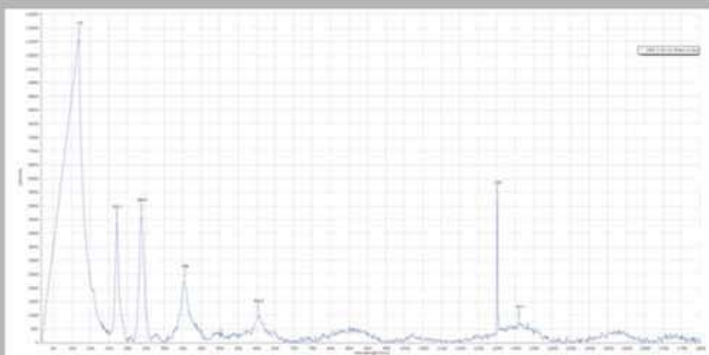
XRD

FTIR

RS

Conclusion

RS spectra 1

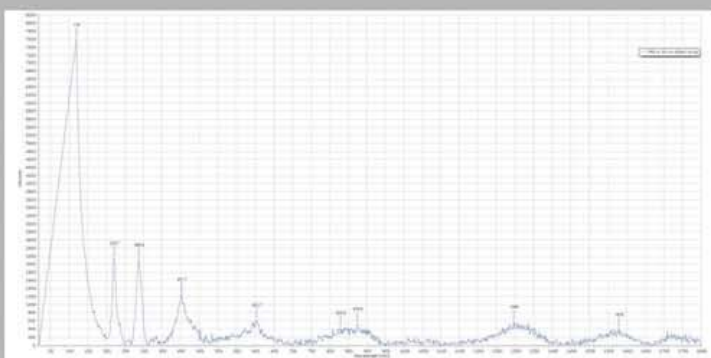


RS results 1

Settings: 30%, 1s, 30 accumulation

Peaks: 119 vs; 222,1 m; 288,8 m; 406 m; 604,3 w;
1251 m; 1311 w;

RS spectra 2

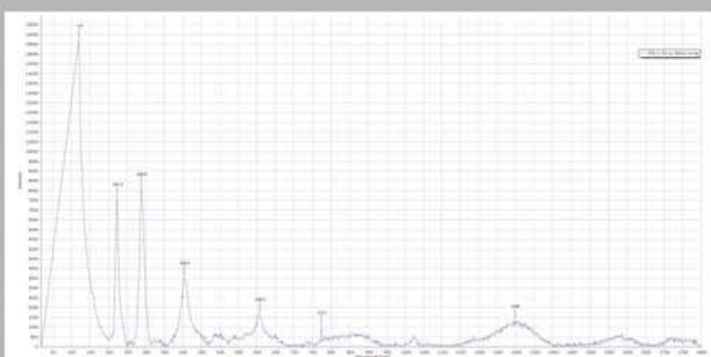


RS results 2

Settings: 30%, 1s, 45 accumulation

Peaks: 119 vs; 220,7 m; 286,9 m; 401,7 m; 603,7
w; 874,9 w; 1296 w; 1336 w; Similar as no. 1,
without 1251.

RS spectra 3



RS results 3

Settings: 30%, 1s, 50 accumulation

Peaks: 119 vs; 222,3 m; 288,6 m; 405,3 m; 606,8
w; 773,7; 1298 w; Similar as no.1, without 1251.

Summary

Corresponds to red ochre - Iron (III) oxide (Fe_2O_3 + clay + silica). Band wavenumbers and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174). intensive peak at 119 nm suggesting the existence of the lead-based component. Reference: lead based pigments from IRUG database.
Wide massive peak from 1200 to 1400 cm^{-1} refers to clay minerals.

GN-2017-CM04

Sample information

Location of sample

Northeastern part of C18 / content of barrel 5

Date of recovery (YYYY-MM-DD)

2017-09-24

Condition upon recovery

Sampled *in situ*

Sample description

Fine powder, with presence of the sand from environment

Colour

Red

Storage condition

Stored in a glass jar which contains seawater

Cross / thin section

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

No

UVL-VIS-IR-IRfc

No

XRF

No

SEM-EDX

Yes

XRD

No

FTIR

Yes

RS

Yes

UHPLC

n/a

Notes

/

To conduct in future projects

/

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

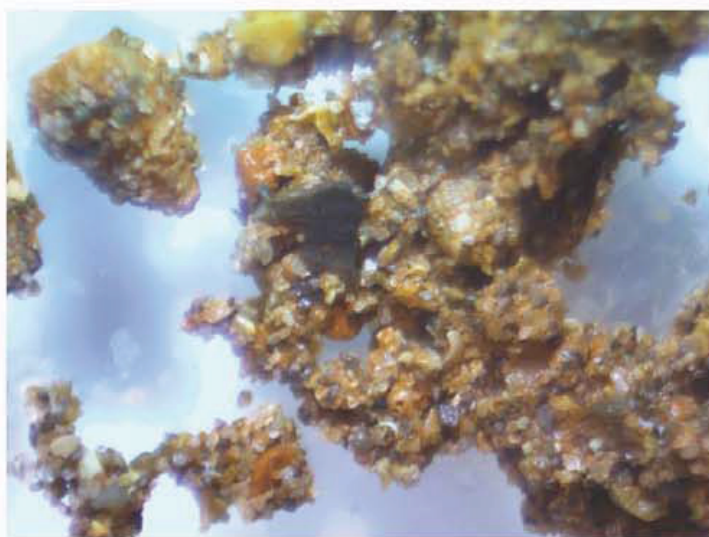
XRD

FTIR

RS

Conclusion

Microscope photo 1



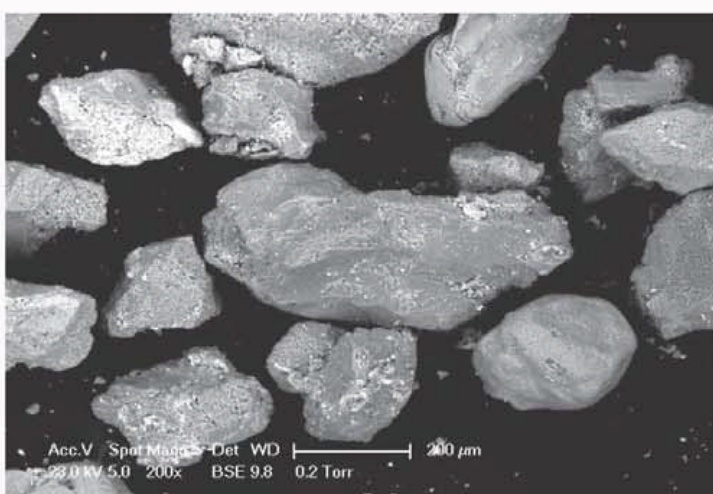
Texture description

Binocular observations:

Colour: heterogenous

Fine grained reddish particle mixed with sand like particles (contamination?).

Microscope photo 2



Microscope photo 3

GN-2017-CM04

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

Conclusion

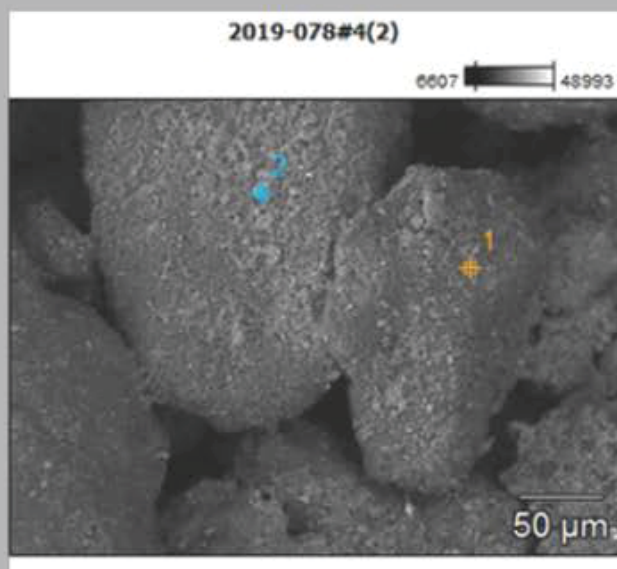
Pt 1: Chemical elements

Magnification: 350

Pt 1-1: C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Fe / **Si, O**

Pt 1-2: C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe / **Fe, O**

Pt 1: BSE image

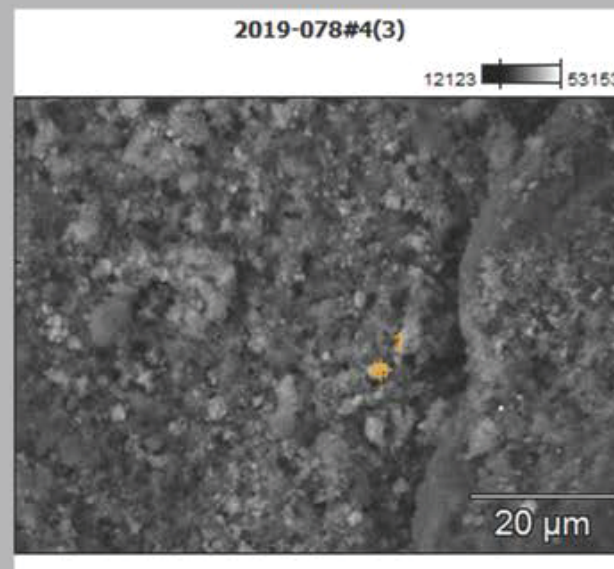


Pt 2: Chemical elements

Magnification: 1500

Pt 2-1: C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ba, Fe / **O, Al, Ca**

Pt 2: BSE image



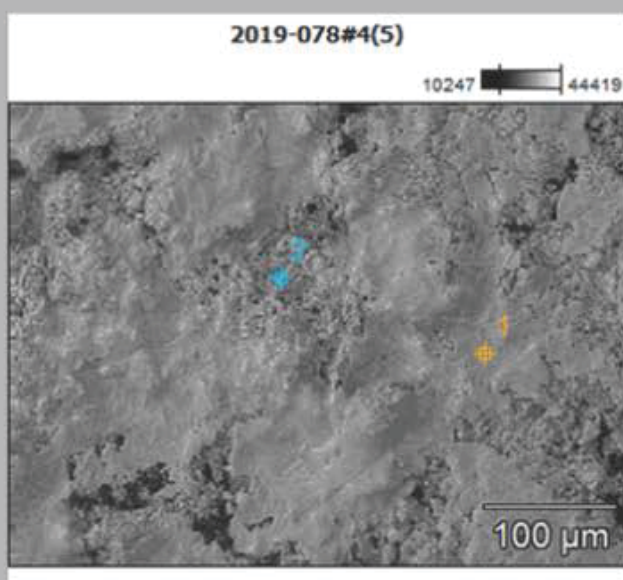
Pt 3: Chemical elements

Magnification: 270

Pt 3-1: C, O, Cl, Na, Mg, Al, Si, S, Cl, Ca, Fe / **Na, Cl**

Pt 3-2: C, O, Cl, Na, Mg, Al, Si, P, S, K, Ca, Fe / **Fe, O, Al, Na, Cl**

Pt 3: BSE image

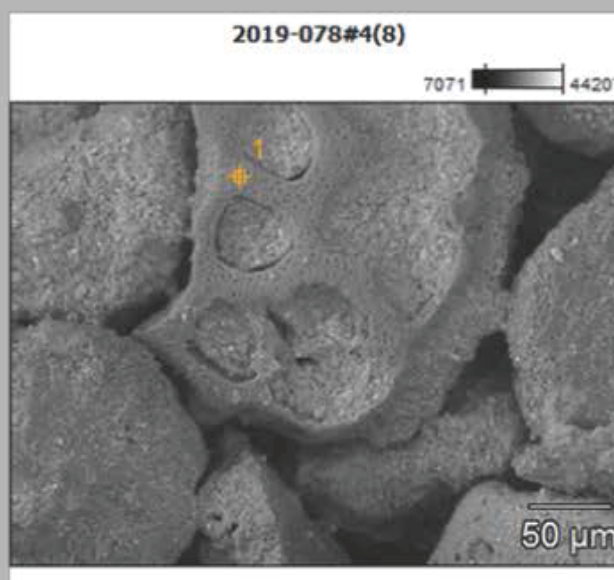


Pt 4: Chemical elements

Magnification: 330

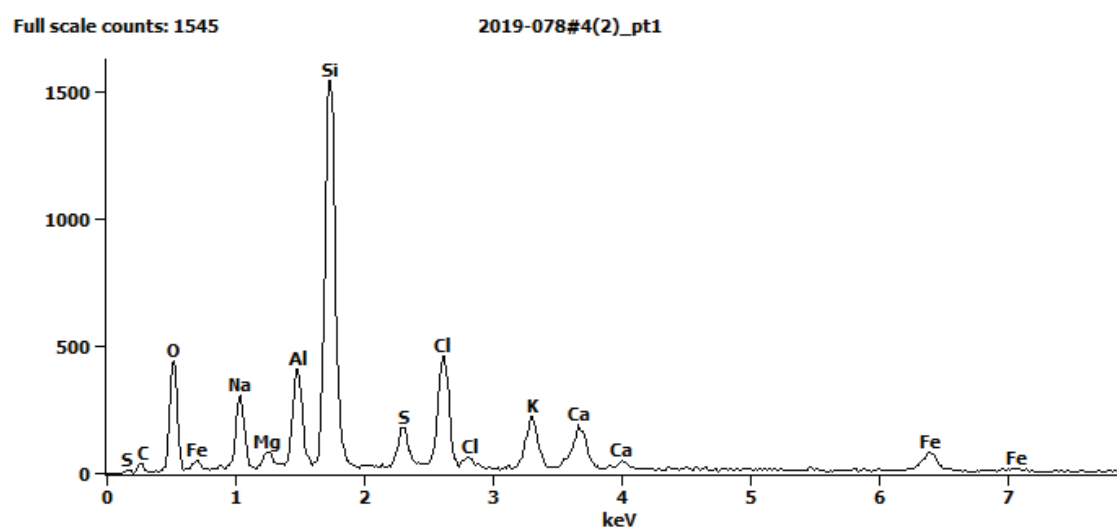
Pt 4-1: C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Fe / **Ca, C, O, Cl**

Pt 4: BSE image

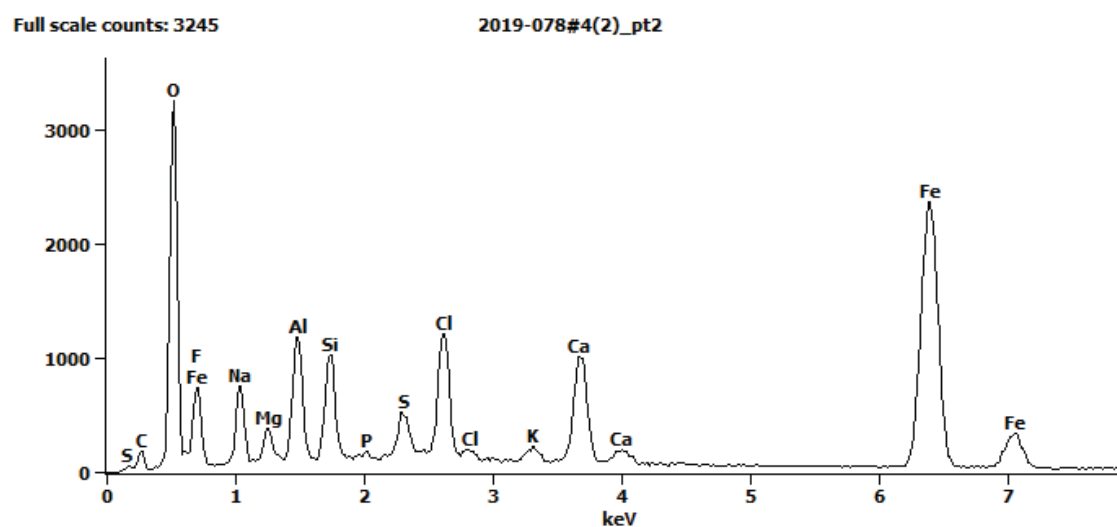


GN-2017-CM04

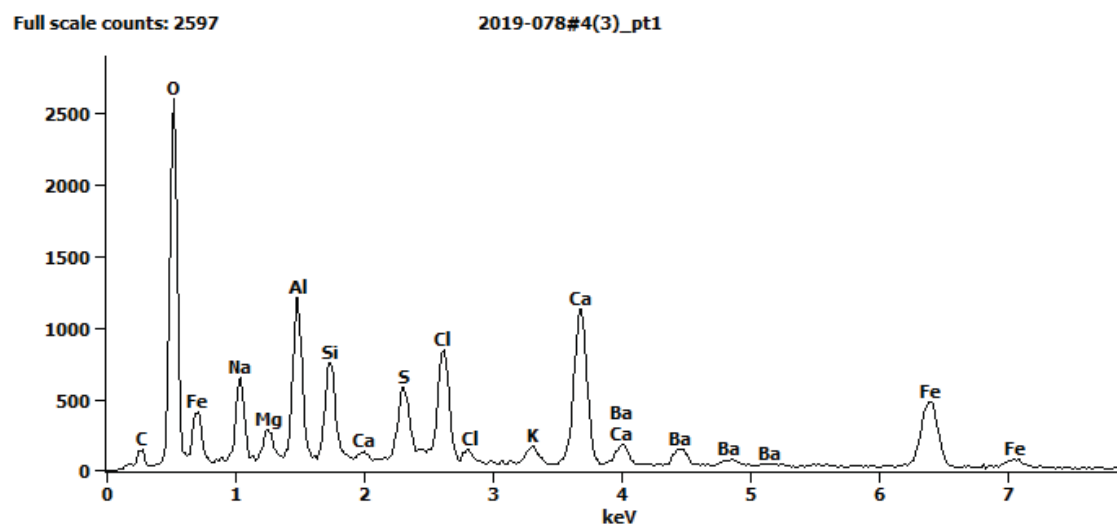
Point 1-1:



Point 1-2:

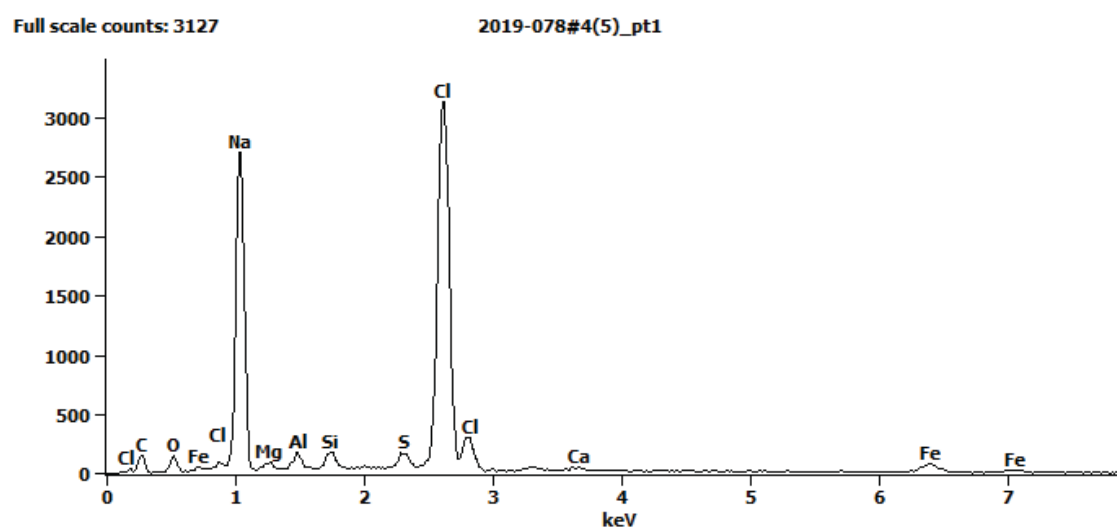


Point 2-1:

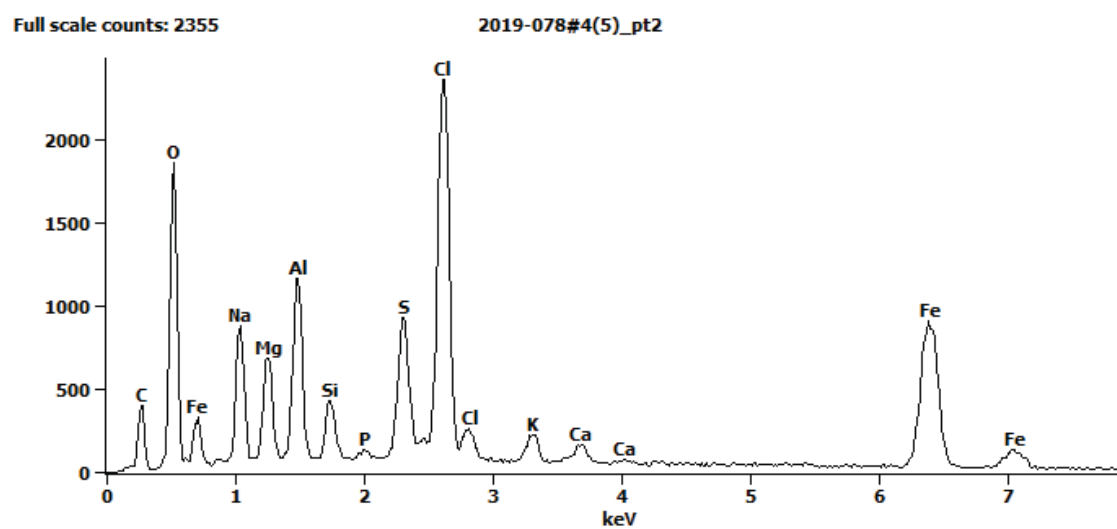


GN-2017-CM04

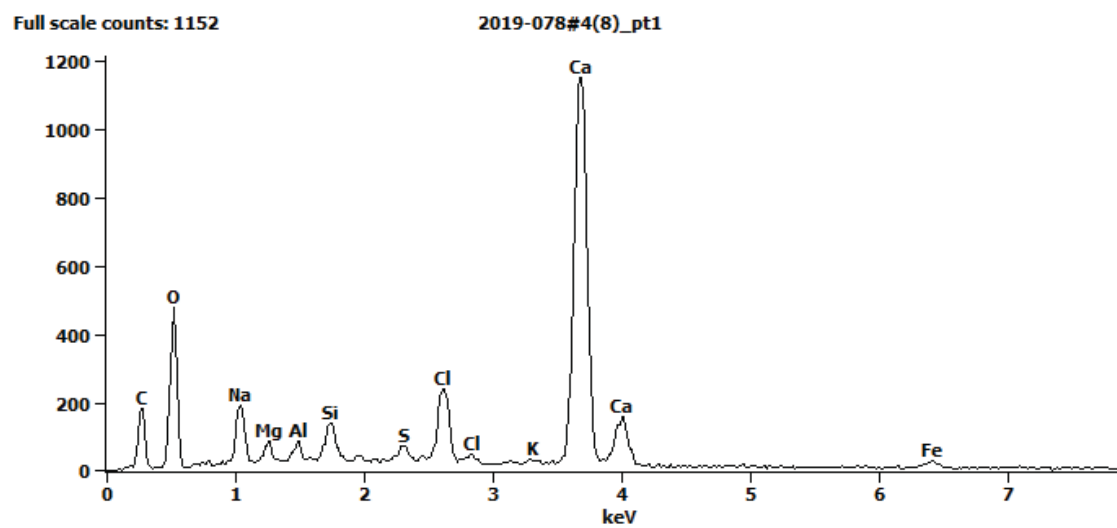
Point 3-1:

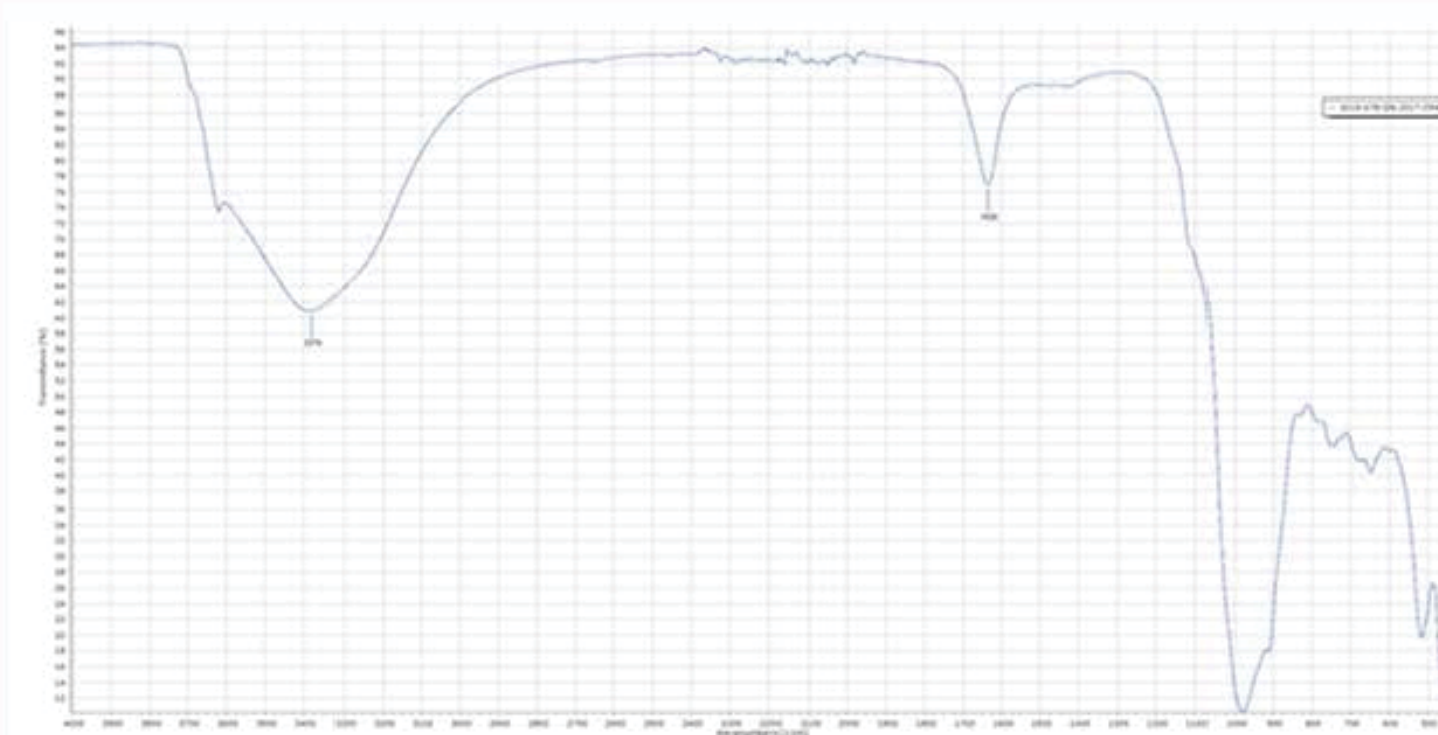


Point 3-2:



Point 4-1:





FTIR results

Absorption bands visible: **3625 msh; 3379 vb; 1635 msh; 979 vsh; 911 msh; 743 w; 674 w; 514 msh.**

* Hematite: reference in IRUG Database, sample number IMP00364 <http://www.irug.org/jcamp-details?id=824>

Corresponding absorption bands: **3600 – 3000 b (3446 peak); 1614 w; 538 vsh; 468 vsh.**

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: 1452 w; 1162 w; 1033 vsh; 920 msh.

* Silicon oxide: reference Reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: 1022-1077 cm⁻¹ (in spectra 1077 vsh; 1029 sh)

* 743 w, 674 w - unknown

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4

Corresponding absorption bands 1030 sh, 795 w, 531 sh, 431 sh)

(b - broad; w - wide; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM04

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

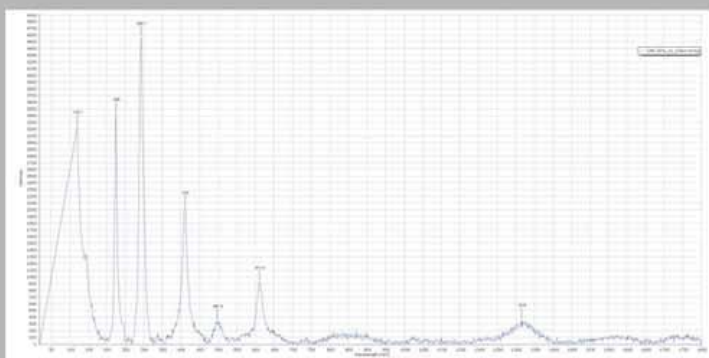
XRD

FTIR

RS

Conclusion

RS spectra 1

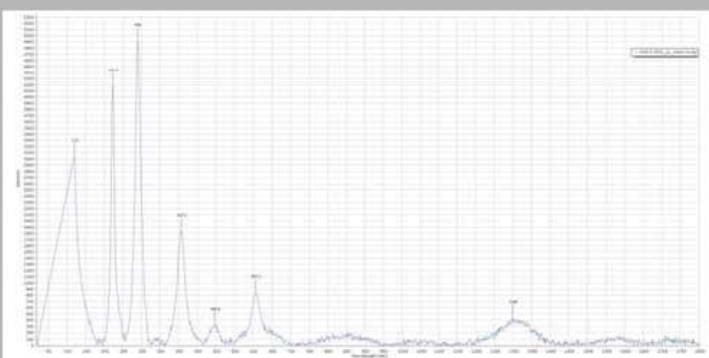


RS results 1

Settings: 30%, 1s, 10 accumulation

Peaks: 119 s; 143 m; 225 s; 245,31 w; 292,1 vs, 410 m; 497,3 w; 611,4 m; 1316 w.

RS spectra 2



RS results 2

Settings: 30%, 1s, 10 accumulation

Peaks: 119 s; 222,7 s; 290 vs; 407,2 m; 495,9 w; 607,2 m; 1299 w.

RS spectra 3

RS results 3

/

Summary

The Raman spectra corresponds to red ochre - Iron (III) oxide chromophore (Fe_2O_3 + clay + silica). Band wavenumbers and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174).

The intensive peak at 119 cm^{-1} , and 143 cm^{-1} in the point one, suggests the existence of the lead-based component. Reference: lead based pigments of IRUG database.

Wide massive peak from 1200 to 1400 cm^{-1} belongs to clay minerals.

GN-2017-CM05

Sample information

Location of sample

Northeastern part of C19 / content of barrel 6

Date of recovery (YYYY-MM-DD)

2017-09-24

Condition upon recovery

Sampled *in situ*

Sample description

Powder of fine consistency

Colour

Red

Storage condition

Stored in a glass jar which contains sea water. Kept in a dark space on a room temperature

Cross / thin section

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

Yes

RS

Yes

UHPLC

n/a

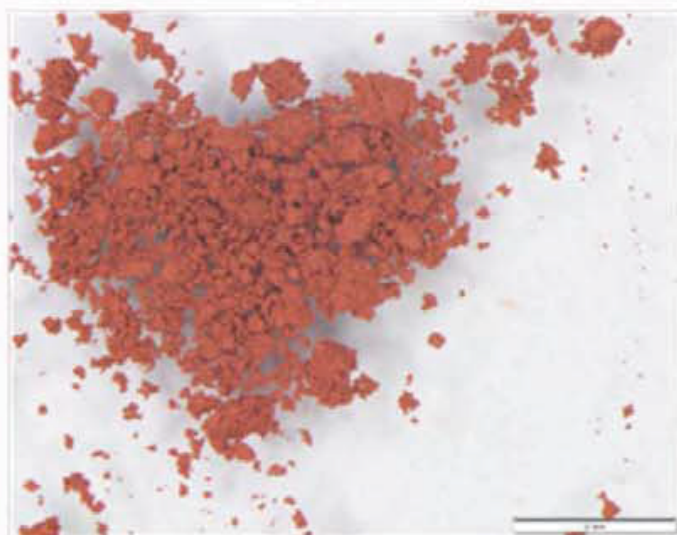
Notes

/

To conduct in future projects

/

Microscope photo 1



Texture description

Colour: homogenous

- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope, UV illumination.

Particles: red particles, not possible to describe size and shape at this scale.

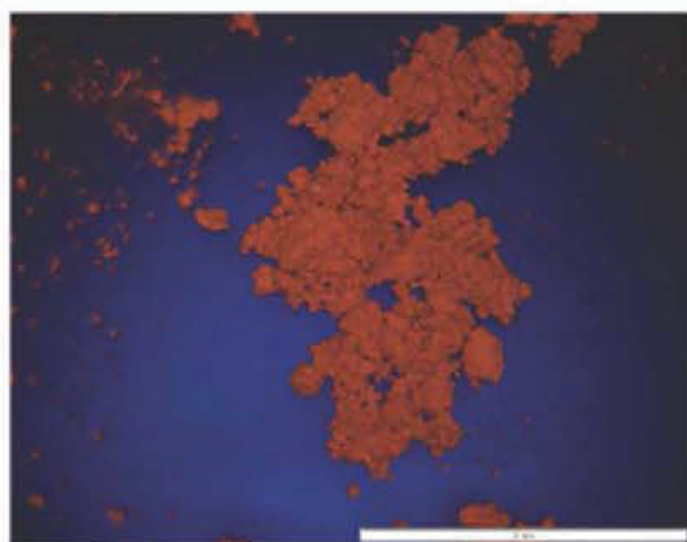
Particles:

- red (various colours and shape) = 70%;
- white particles = 10%.

Microscope photo 2



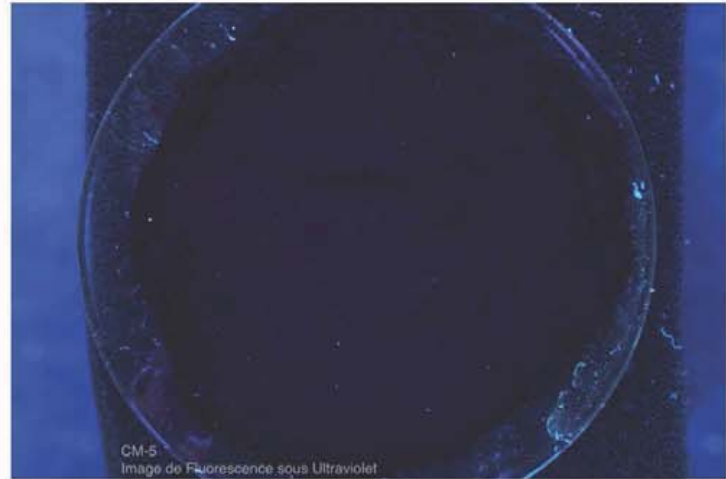
Microscope photo 3



Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



GN-2017-CM05

Microscope

UVL-VIS-IR-IRfc

XRF

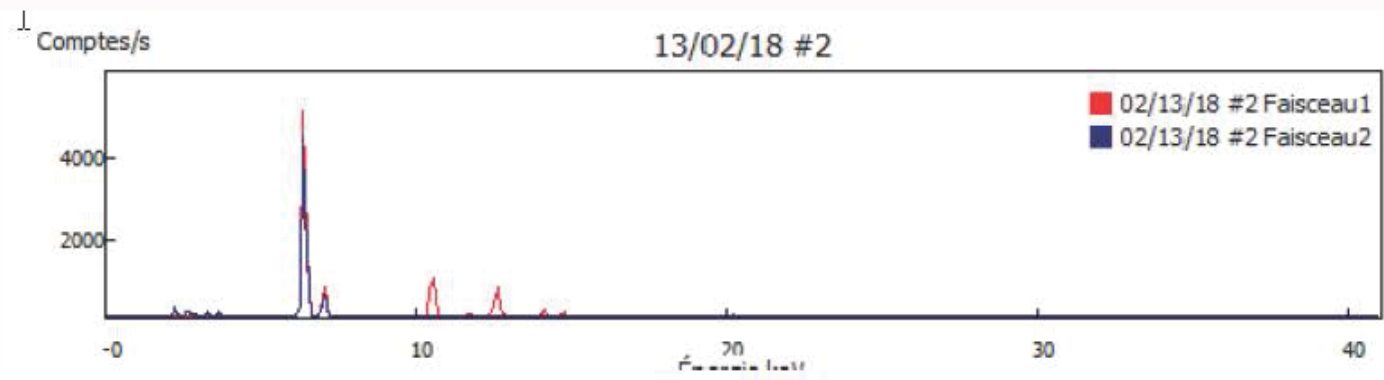
SEM-EDX

XRD

FTIR

RS

Conclusion



Chemical elements

Light Elements (46.27%)
Other: Fe (23.30%), Al (8.37%), S (3.52%), Si (4.52%), Pb (2.43%),
K (1.32%), Ca (0.66%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

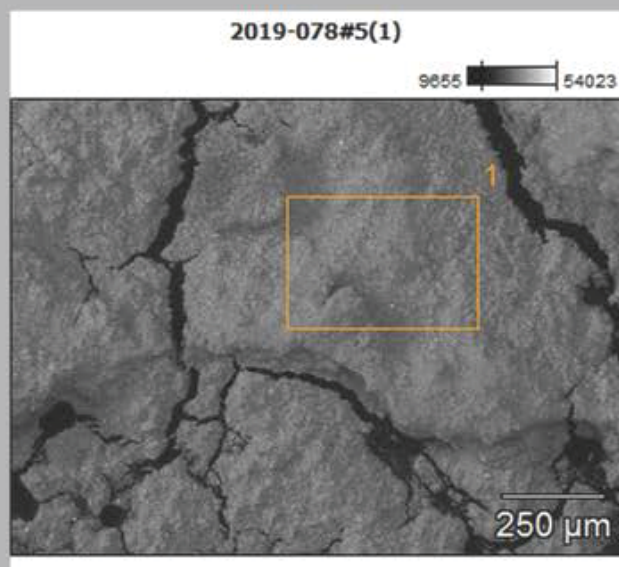
RS

Conclusion

Pt 1: Chemical elements

Magnification: 85

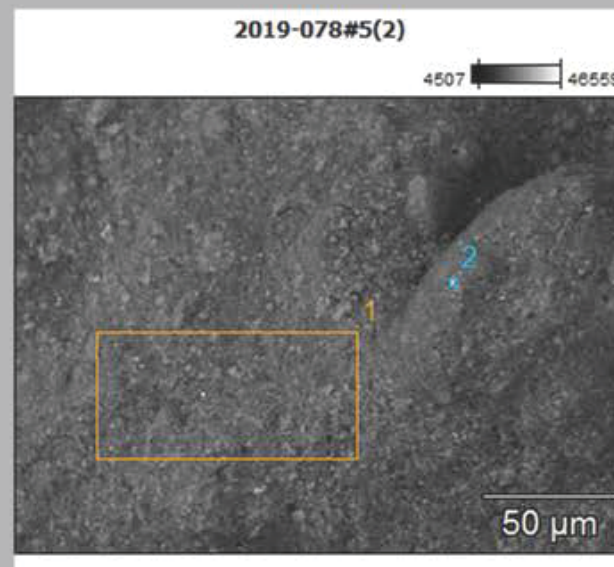
SA 1-1: C, O, F/Fe, Na, Mg/As, Al, Si, P, S, Cl, Ca, Ba, Fe / O, Al, Si, Fe

Pt 1: BSE image**Pt 2: Chemical elements**

Magnification: 550

SA 2-1: S, C, O, F/Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe / O, Al, Si, Fe

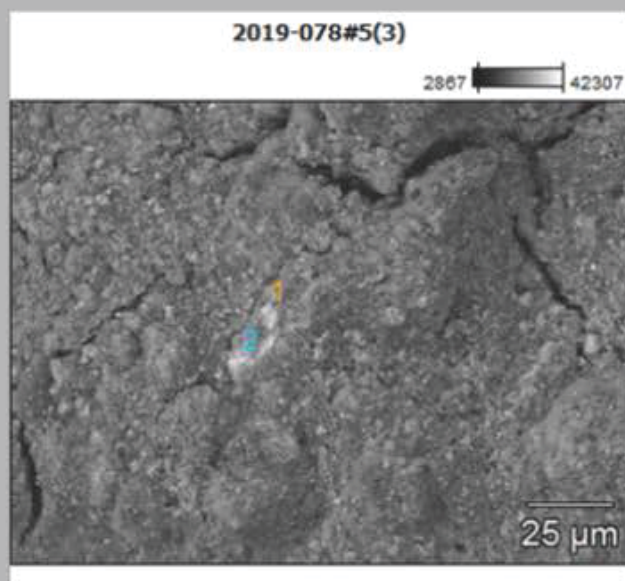
Pt 2-2: C, O, F/Fe, Na, Mg, Al, Si, S, Cl, K, Ca, Fe / O, Al, S, Fe

Pt 2: BSE image**Pt 3: Chemical elements**

Magnification: 700

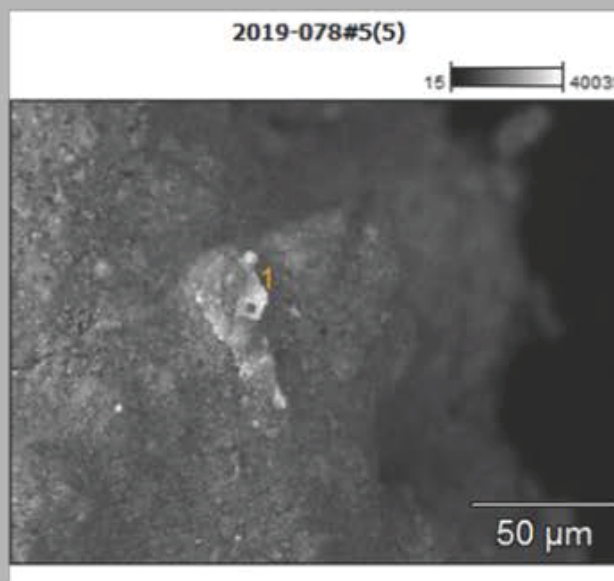
Pt 3-1: C, O, Fe, Na, Mg, Al, Si, S, K, Ba, Fe / O, Al, S, Ba, Fe

Pt 3-2: S, C, O, Na, Mg, Al, Si, S, Cl, K, Ba, Fe / O, Al, S, Ba, Fe

Pt 3: BSE image**Pt 4: Chemical elements**

Magnification: 500

Pt 4: C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ba, Fe / O, Al, Si, Fe

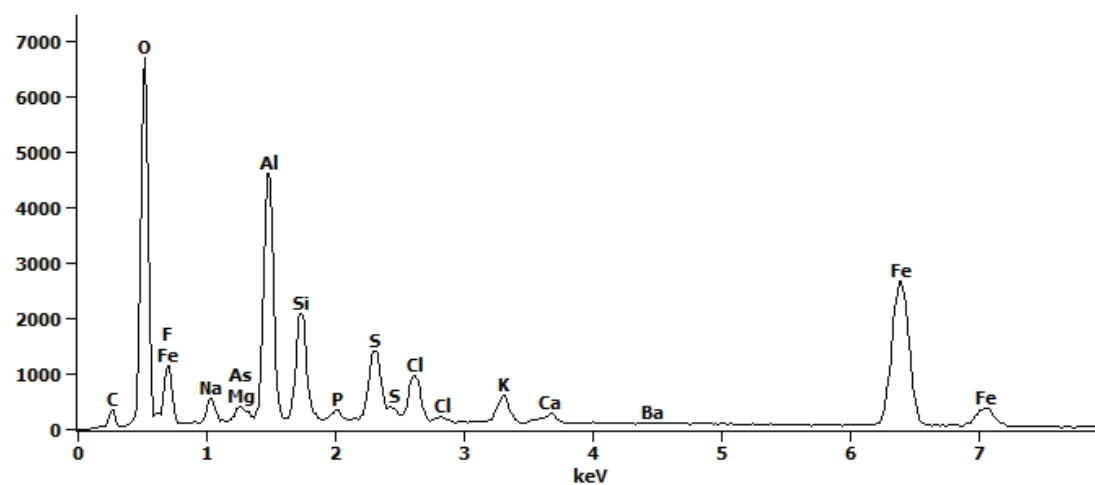
Pt 4: BSE image

GN-2017-CM05

Point 1:

Full scale counts: 6696

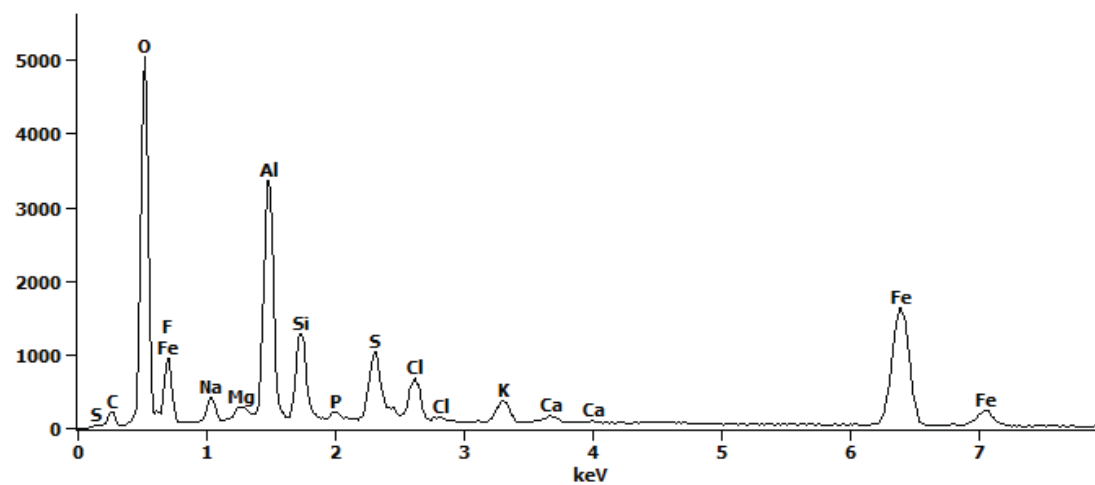
2019-078#5(1)_pt1



Surface area 2-1:

Full scale counts: 5039

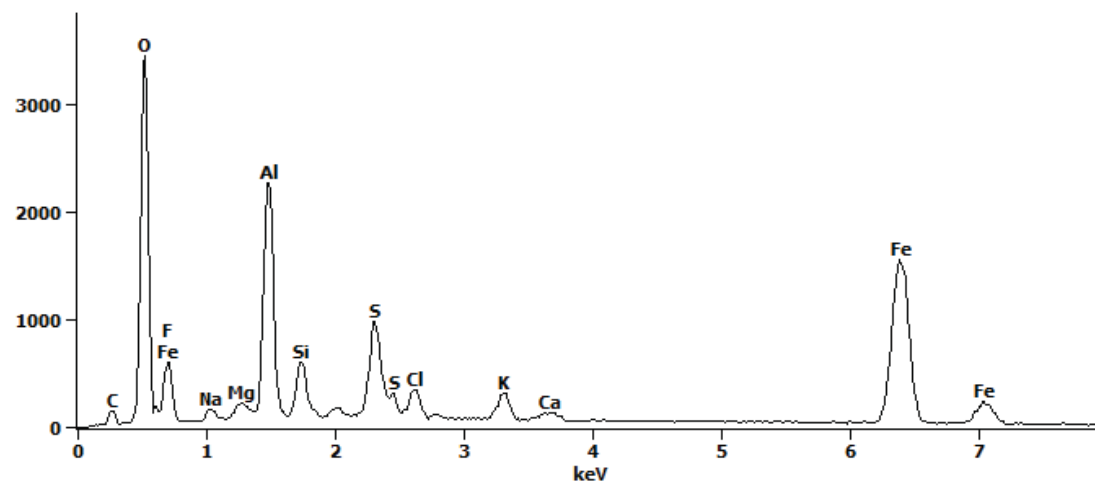
2019-078#5(2)_pt1



Point 2-2:

Full scale counts: 3446

2019-078#5(2)_pt2

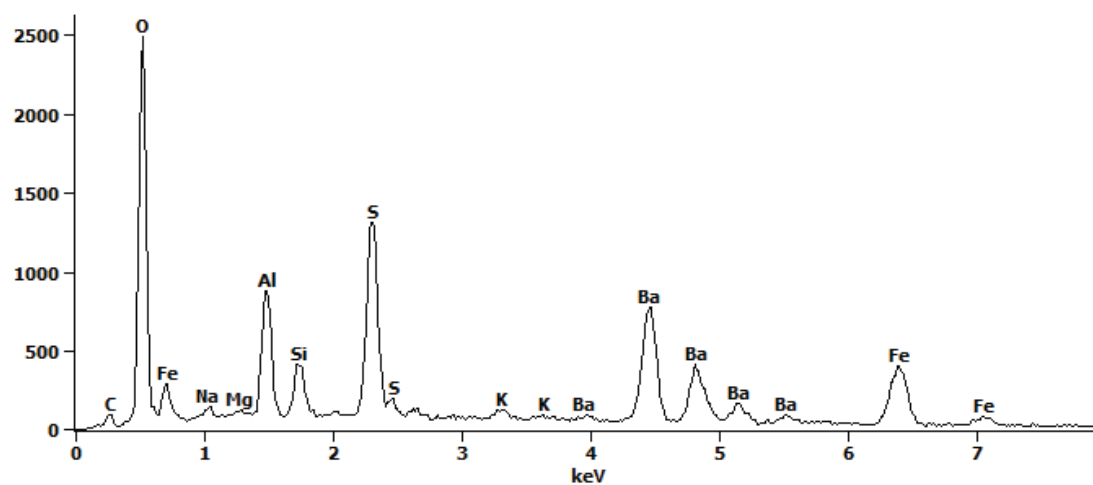


Point 3-1:

GN-2017-CM05

Full scale counts: 2485

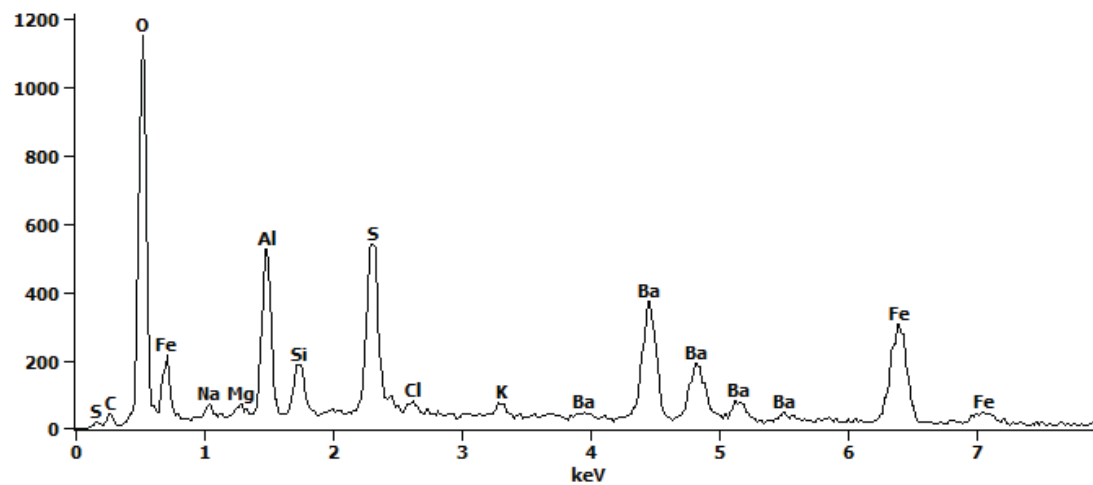
2019-078#5(3)_pt1



Point 3-2:

Full scale counts: 1149

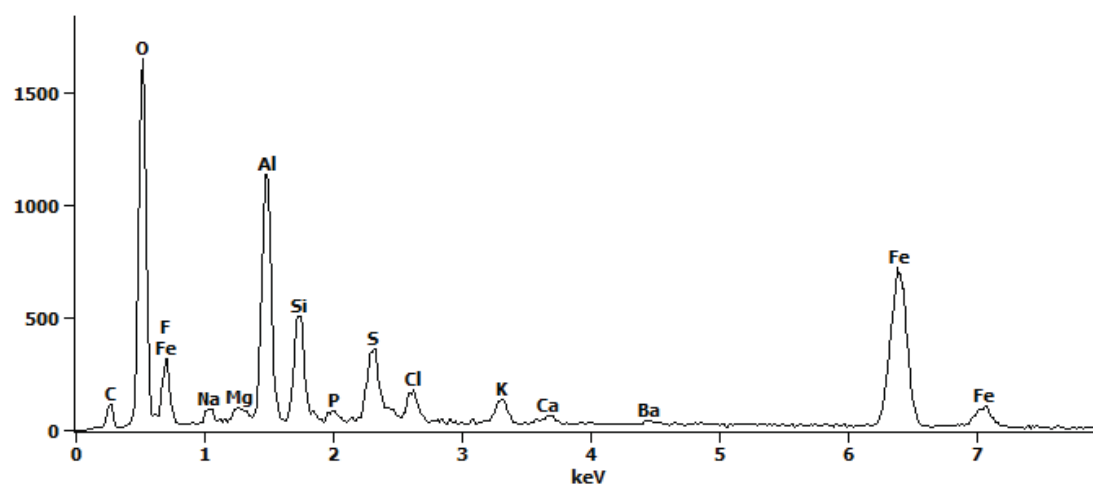
2019-078#5(3)_pt2

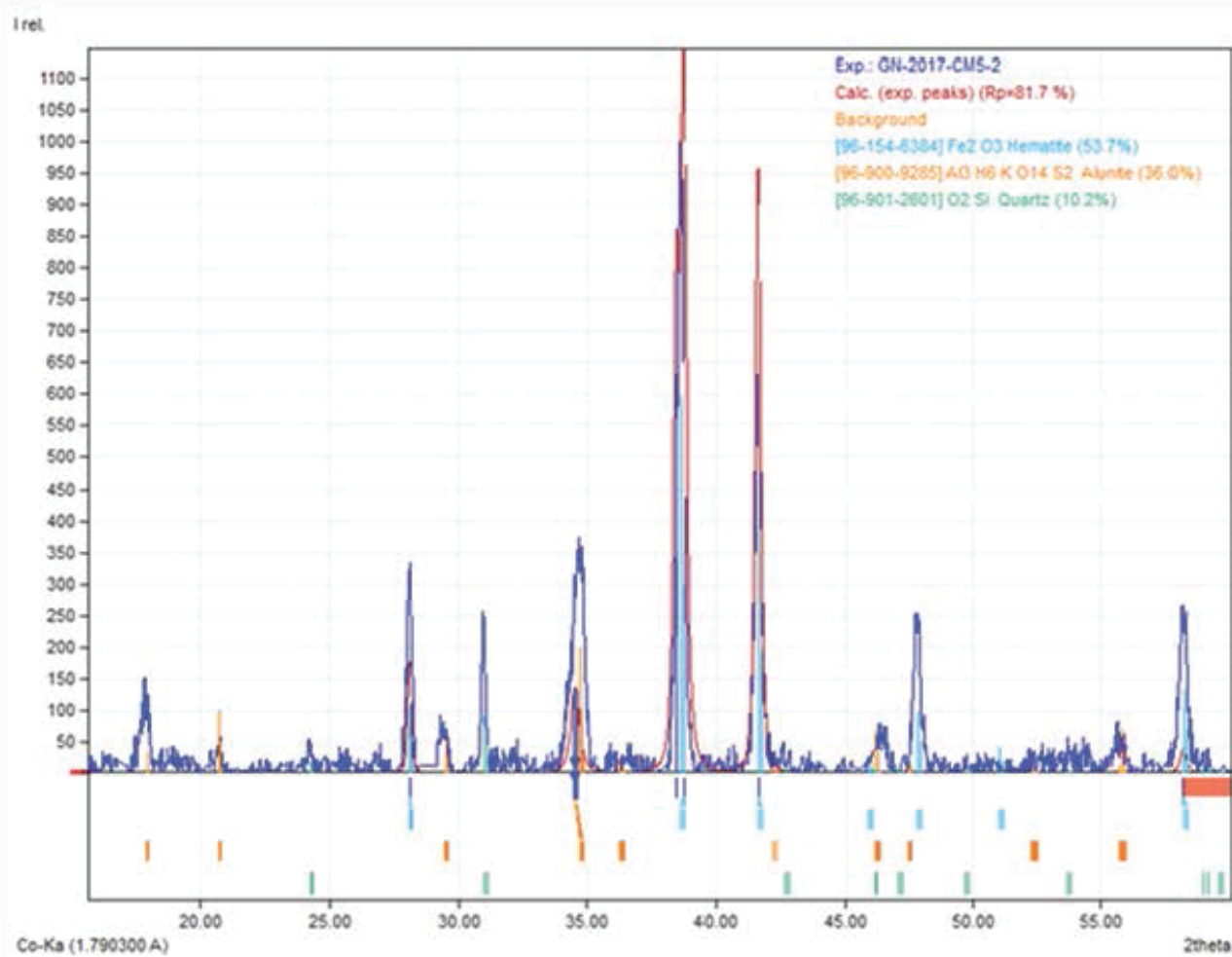


Point 4:

Full scale counts: 1649

2019-078#5(5)_pt1





Suggested mineral phases

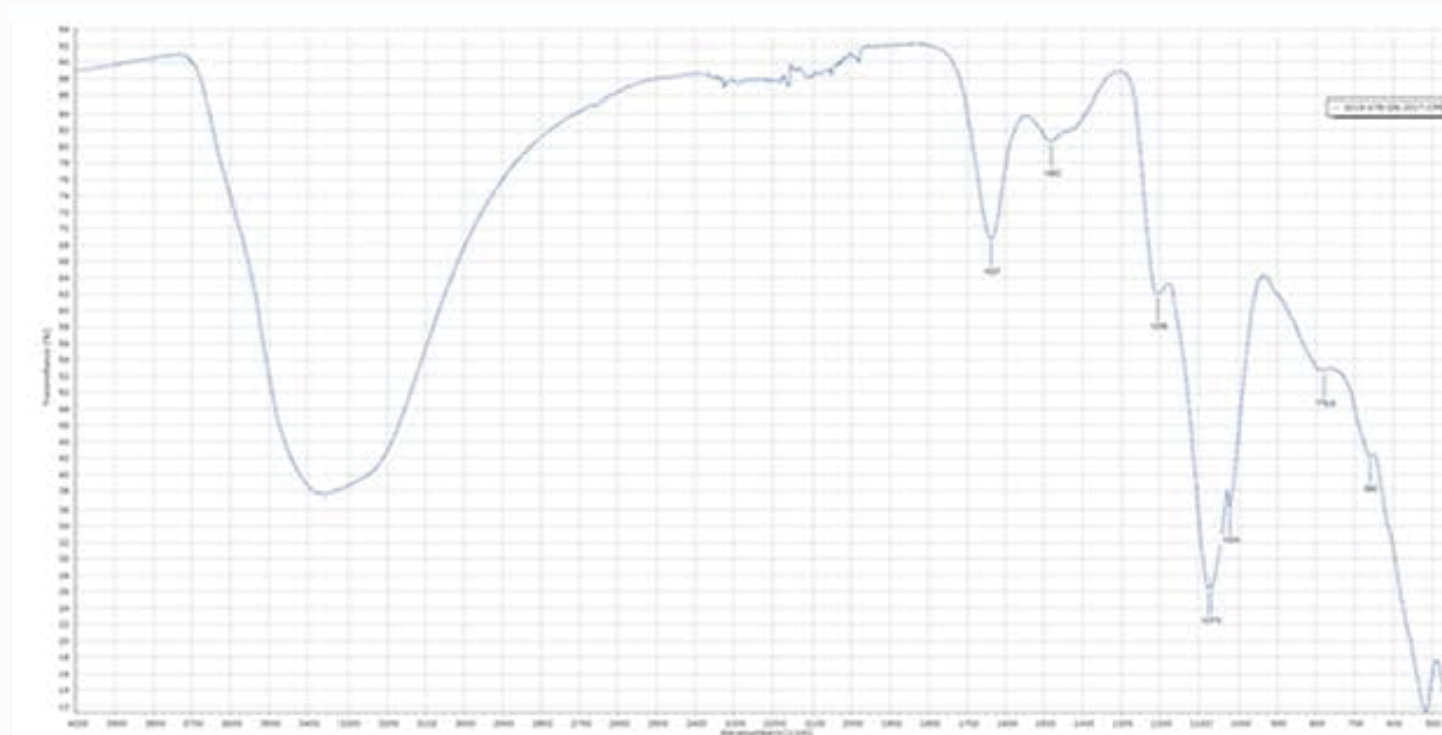
Identified:

hematite, Fe₂O₃ (53.7%)

alunite, Al₃H₆KO₁₄S₂ (36%)

quartz, SiO₂ (2%)

Non identified mineral phases present around 17.00, 29.00, 46.00, 47.00, 55-56.00, 58.00 2theta.



FTIR results

Absorption bands visible: **3361 vb**; **1637 msh**; 1482 w; 1205 wsh; *1073 vsh*; *1024 vsh*; 779.5 w; 660 msh; **510 vsh**.

* Hematite: reference in IRUG Database, sample number IMP00364 <http://www.irug.org/jcamp-details?id=824>

Corresponding absorption bands: **3600 – 3000 b (3446 peak)**; **1614 w**; **538 vsh**; **468 vsh**.

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: 1452 w; 1162 w; *1033 vsh*; 920 msh.

* Silicon oxide: reference Reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: *1077-1022 vsh* (in spectra *1073 vsh*; *1024 sh*)

* 660 msh - unknown

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4.

Corresponding absorption bands *1030 sh*, *795 w*, *531 sh*, *431 sh*)

The weak broad band positioned at 1482, could be calcium carbonate (Cornell & Schwermann 2003, p. 143)

(b - broad; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM05

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

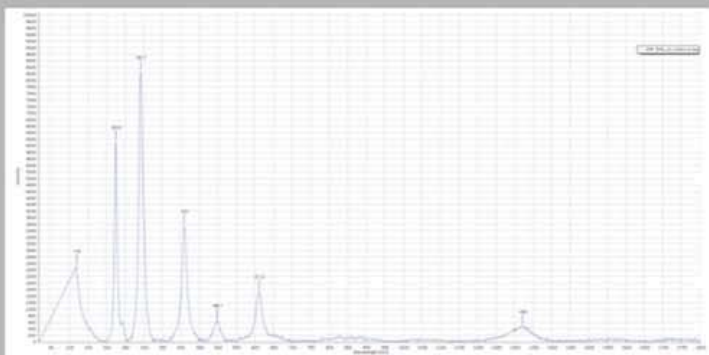
XRD

FTIR

RS

Conclusion

RS spectra 1

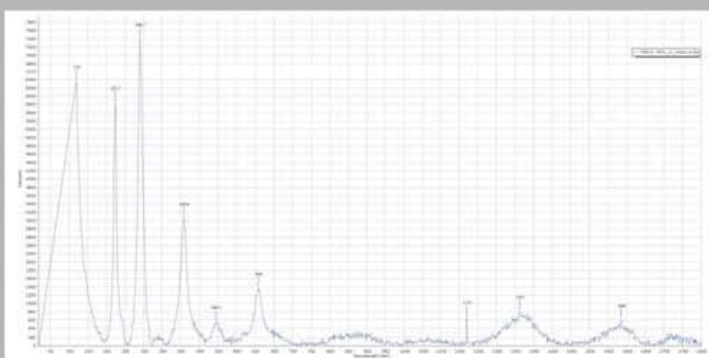


RS results 1

Settings: 30%, 1s, 10 accumulation

Peaks: 119 m; 224,8 s; 291,7 vs; 410 m; 498,7 w; 611,2 m; 1322 w.

RS spectra 2

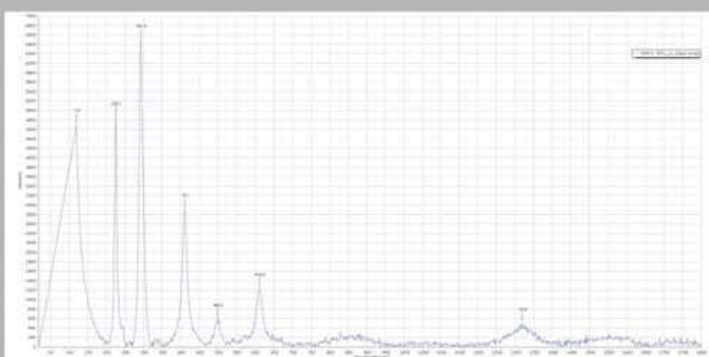


RS results 2

Settings: 30%, 1s, 10 accumulation

Peaks: 119 s; 223,7 s; 290,7 vs; 408,6 m; 494,1 w; 609 m; 1170 w; 1312 w; 1585 w.

RS spectra 3



RS results 3

Settings: 30%, 1s, 10 accumulation

Peaks: 119 s; 225,1 s; 291,8 vs; 411 m; 498,2 w; 610,4 m; 1319 w.

Summary

The Raman spectra corresponds to red ochre - Iron (III) oxide chromophore (Fe_2O_3 + clay + silica). Band wavenumbers and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174).

The intensive peak at 119 cm^{-1} , and 143 cm^{-1} in the point one, suggests existence of the lead-based component. Reference: lead based pigments of IRUG database. Wide massive peak from 1200 to 1400 cm^{-1} belongs to clay minerals. 1172 cm^{-1} in the point 2 is not identified.

GN-2017-CM06

Sample information

Location of sample

Northwestern part of C20 / content of barrel 7

Date of recovery (YYYY-MM-DD)

2017-09-24

Condition upon recovery

Sampled *in situ*

Sample description

Powder of fine consistency

Colour

Red

Storage condition

Stored in a glass jar which contains seawater. Kept in a dark space on a room temperature

Cross / thin section

n/a

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

Yes

RS

Yes

UHPLC

n/a

Photo documentation

Photography of underwater location



Sample condition



GN-2017-CM5

Photogrammetry

n/a

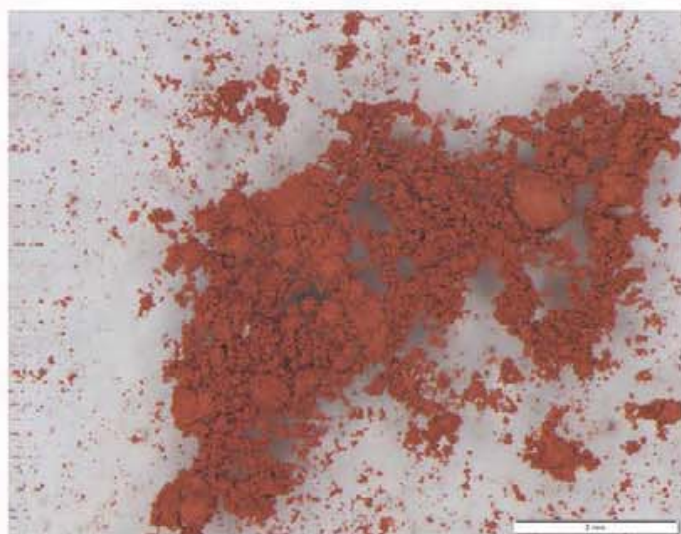
Notes

/

To conduct in future projects

/

Microscope photo 1



Texture description

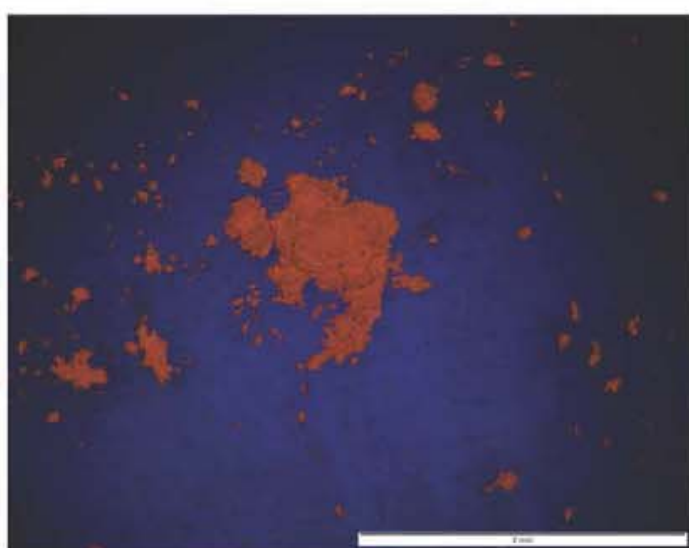
Colour: homogenous

Particles: red fine-grained particles, not possible to describe size and shape at this scale.

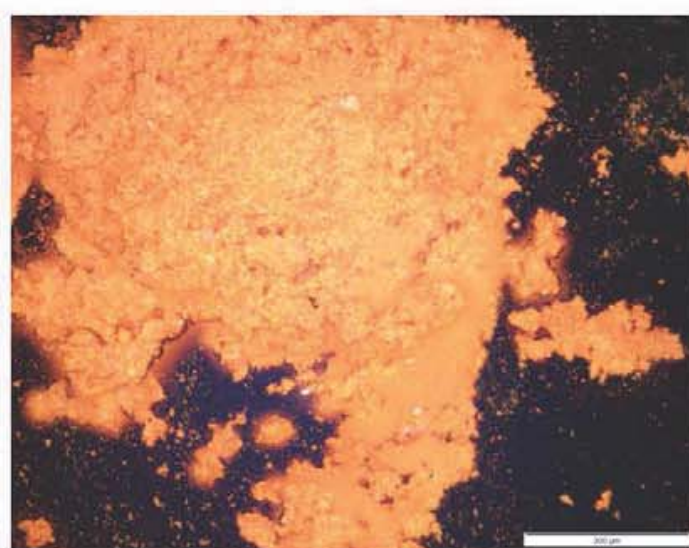
- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope, UV illumination.

Particles:
- red (various colours and shape) = 70%;
- white particles = 10%.

Microscope photo 2



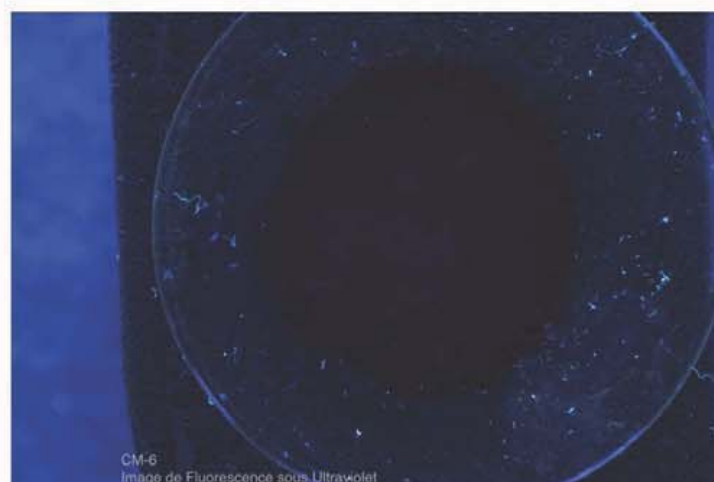
Microscope photo 3



Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



Microscope

UVL-VIS-IR-IRfc

XRF

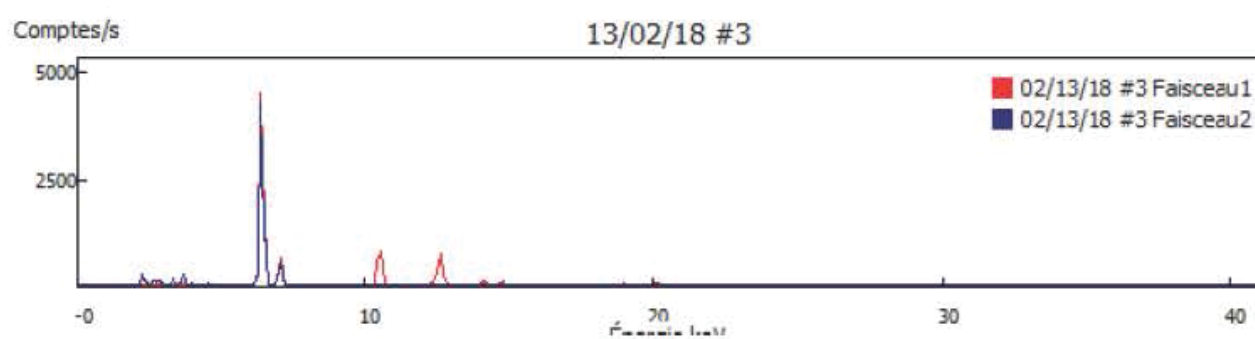
SEM-EDX

XRD

FTIR

RS

Conclusion

**Chemical elements**

Light Elements (49.48%)

Other: Fe (26.27%), Al (9.45%), S (3.78%), Si (4.83%), Pb (2.03%), K (1.46%), Ca (1.65%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

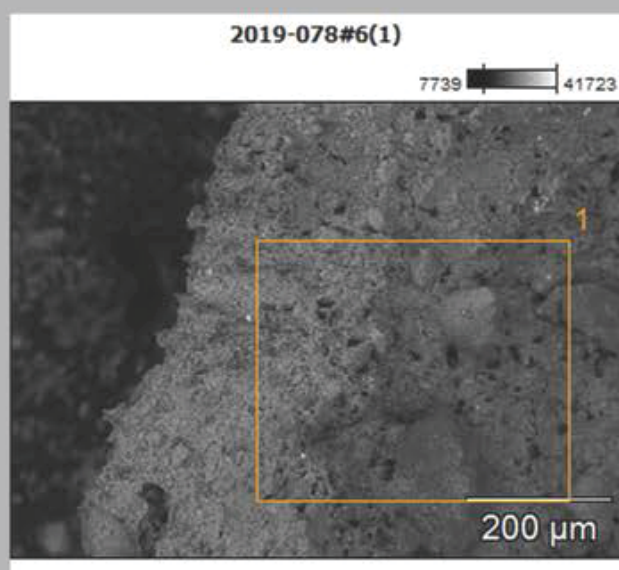
RS

Conclusion

Pt 1: Chemical elements

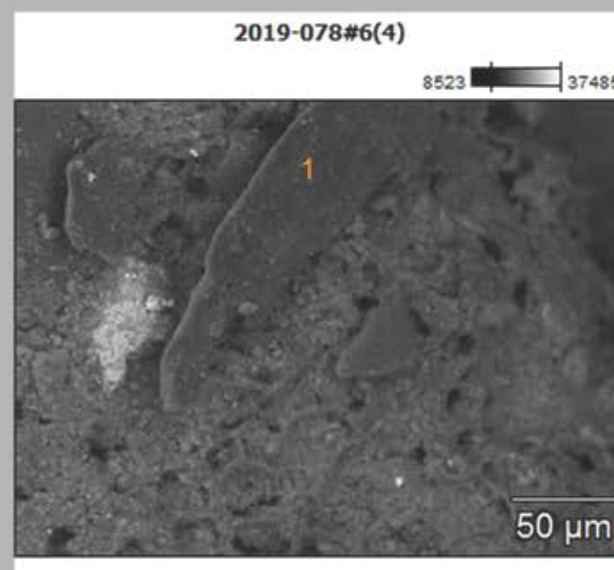
Magnification: 150

SA 1-1: C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Fe / Fe, O, Al, Ca

Pt 1: BSE image**Pt 2: Chemical elements**

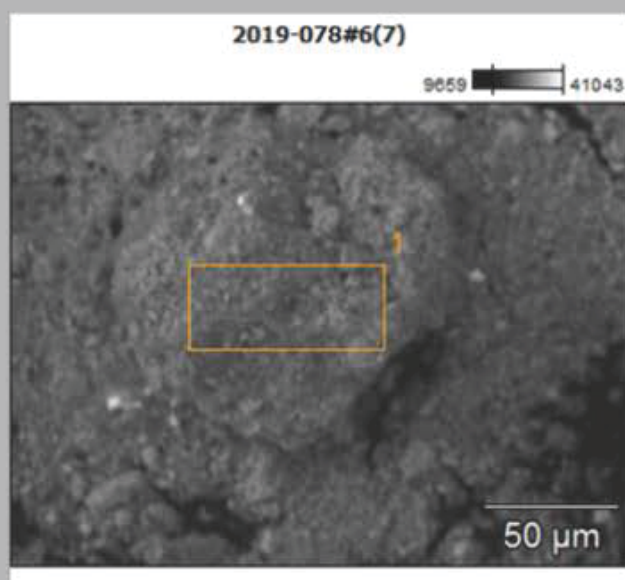
Magnification: 1500

Pt 2-1: C, O, Na, Al, Si, S, Cl, K, Ca, Fe / C, O, Al, Si, Fe

Pt 2: BSE image**Pt 3: Chemical elements**

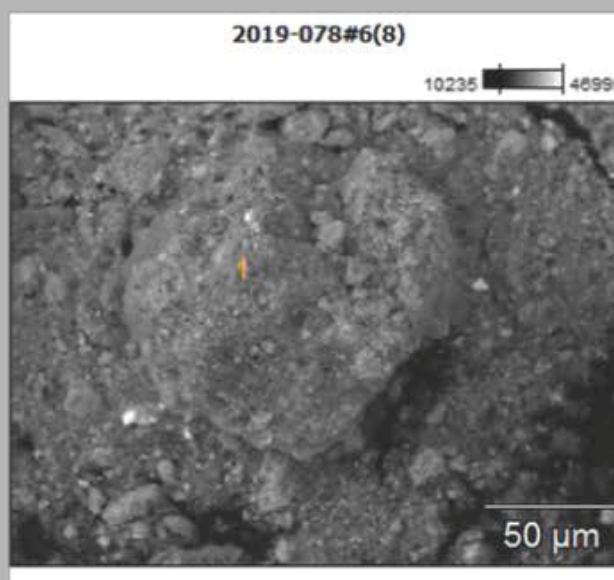
Magnification: 550

SA 3-1: C, O, F/Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe / O, Al, Fe

Pt 3: BSE image**Pt 4: Chemical elements**

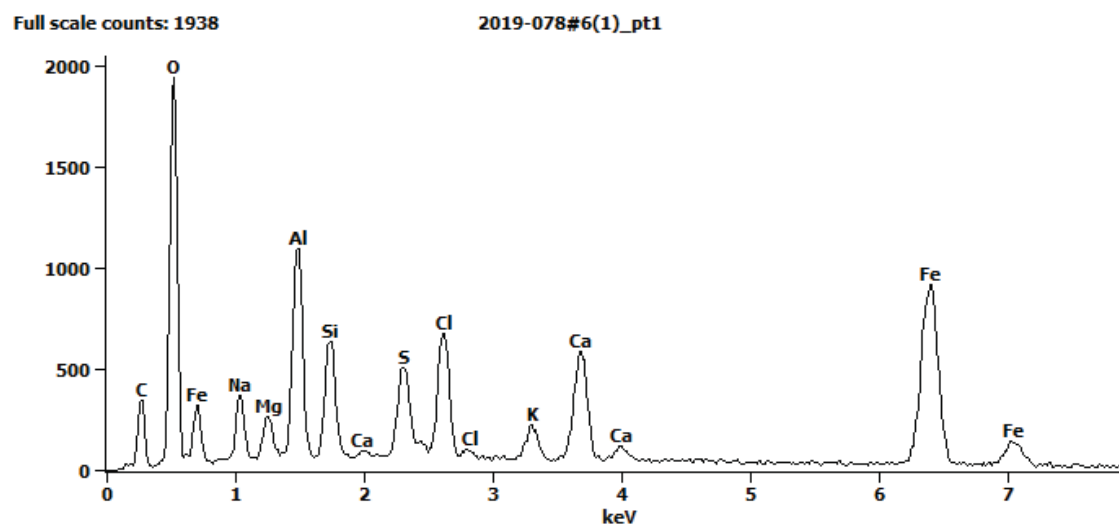
Magnification: 550

Pt 4-1: C, O, Na, Mg/As, Al, Si, P, S, Cl, K, Ca, Fe / O, Al, Si, S, Fe

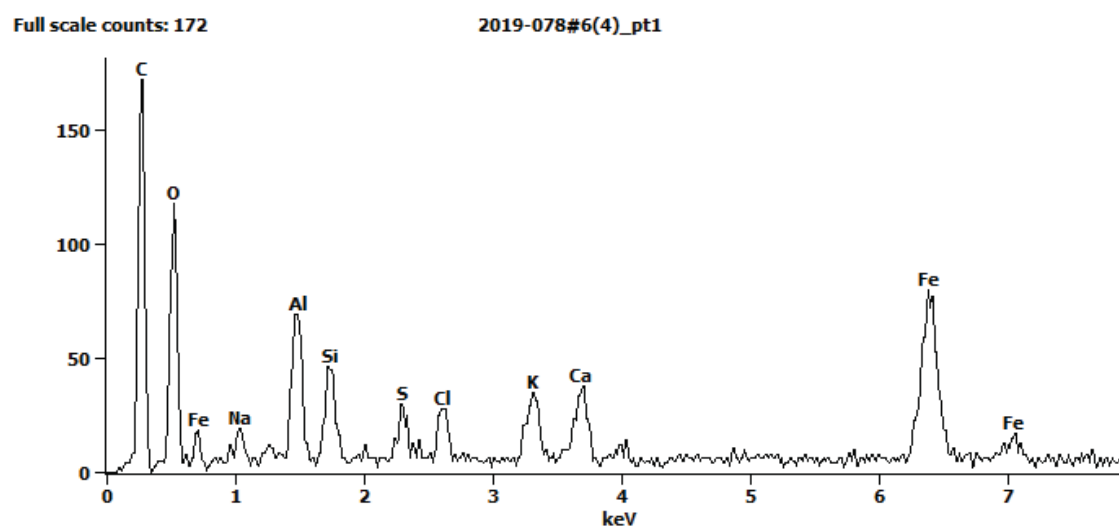
Pt 4: BSE image

GN-2017-CM06

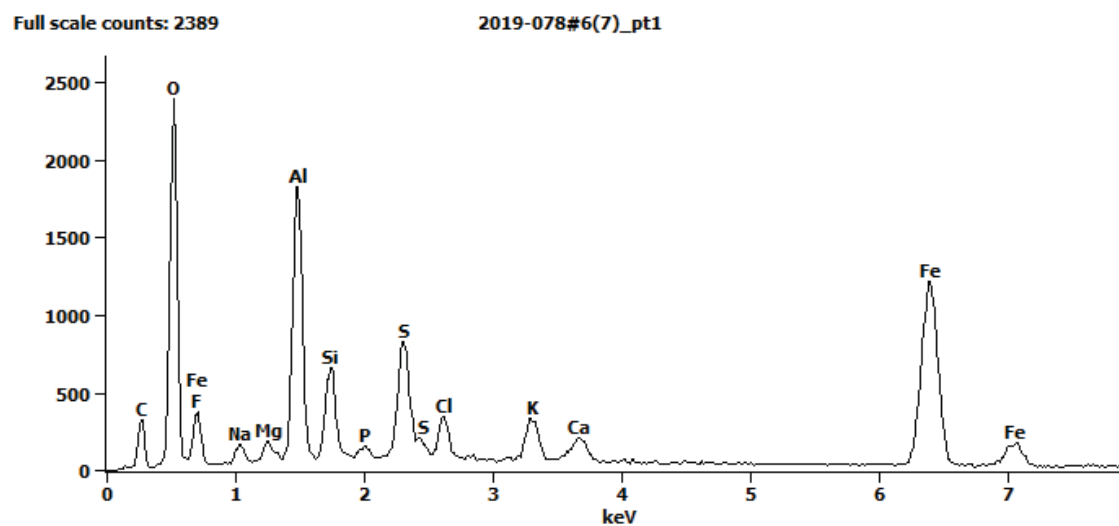
Surface area 1:



Point 2:

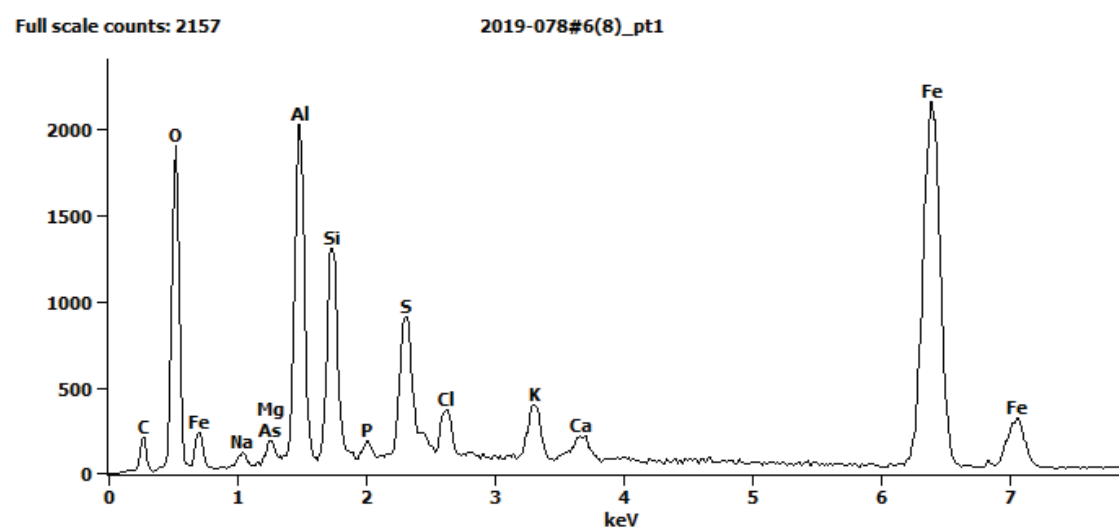


Surface area 3:



GN-2017-CM06

Point 4:



GN-2017-CM06

Microscope

UML-VIS-IR-IRfc

XRF

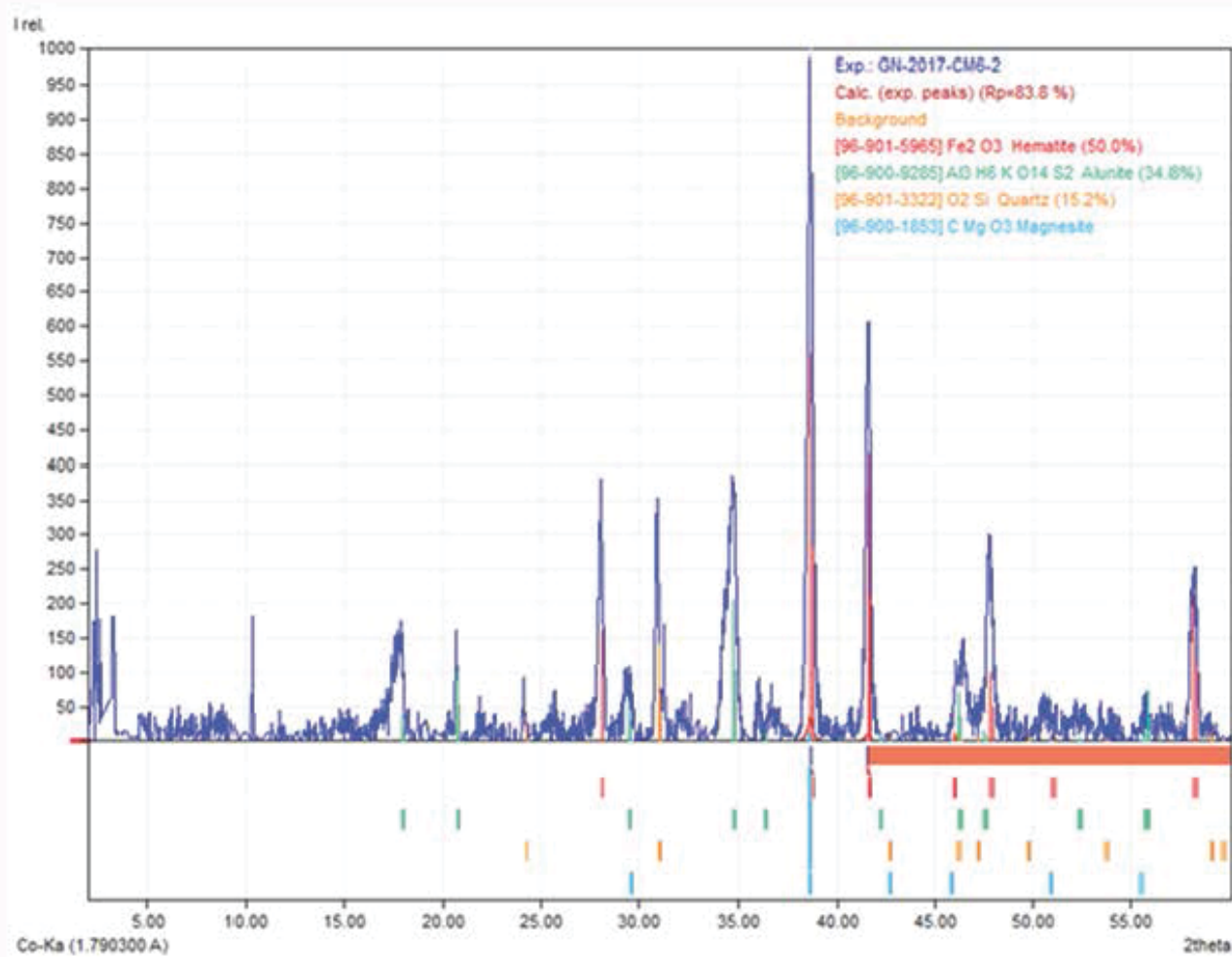
SEM-EDX

XRD

FTIR

RS

Conclusion



Suggested mineral phases

Identified:

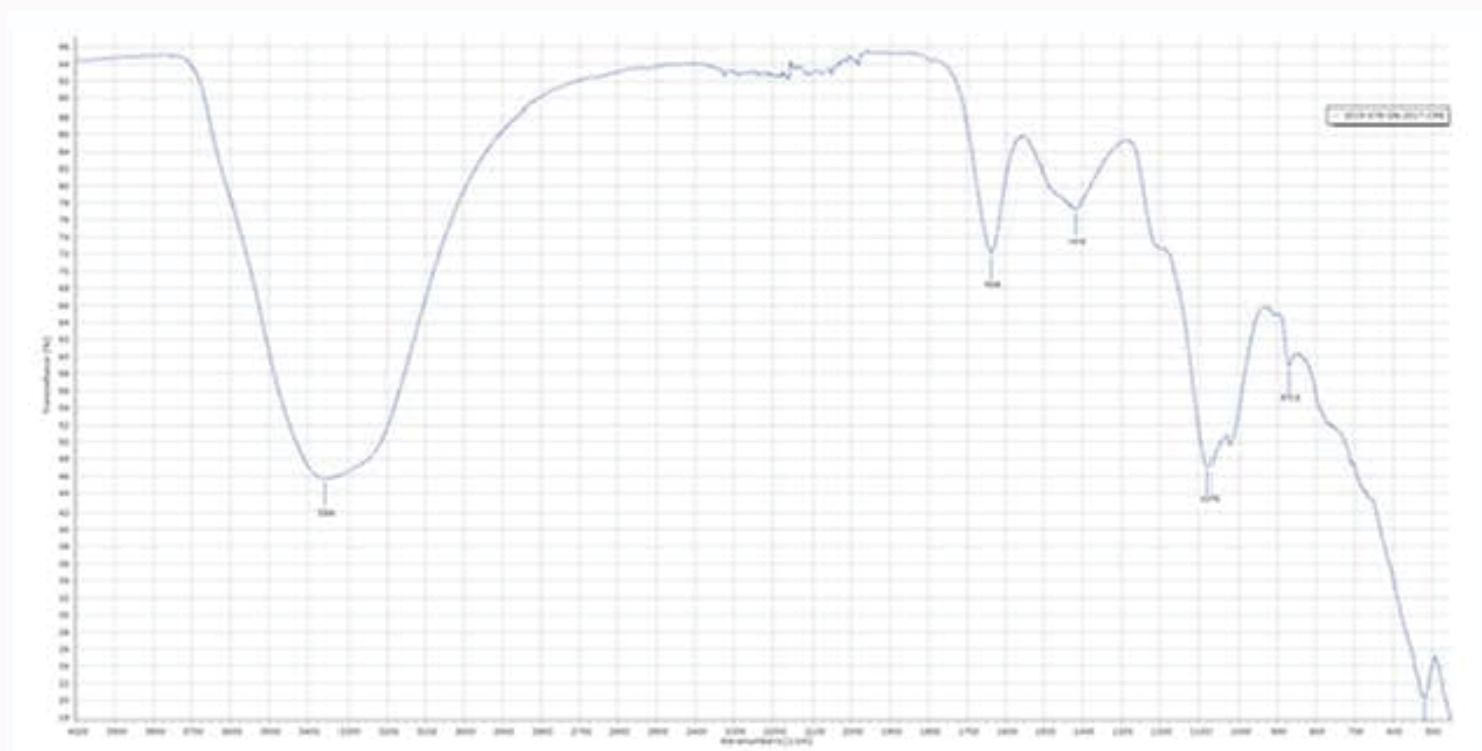
hematite, Fe₂O₃ (50.0%)

alunite, Al₃H₆KO₄S₂ (34.8%)

quartz, SiO₂ (15.2%)

magnesite (MgCO₃) (?)

Non identified mineral phases present around 10 - 11.00, broad peak from 15 - 18.00, 34.00 2theta.



FTIR results

Absorption bands visible: **3354 vb**; **1638 msh**; 1416 mh; 1076 vsh; 870 msh; **540 vsh**;

* Hematite: reference in IRUG Database, sample number IMP00364 <http://www.irug.org/jcamp-details?id=824>

Corresponding absorption bands: **3600 – 3000 b (3446 peak)**; **1614 w**; **538 vsh**; **468 vsh**.

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: 1452 w; 1162 w; 1033 vsh; 920 msh.

* Silicon oxide: reference Reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: 1077-1022 vsh (in spectra 1073 vsh; 1024 sh)

* 660 msh - unknown

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4.

Corresponding absorption bands 1030 sh, 795 w, 531 sh, 431 sh)

The weak broad band positioned at 1416, could be calcium carbonate (Cornell & Schwermann 2003, p. 143)

(b - broad; sh - sharp; w - weak; m - medium; v - very)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

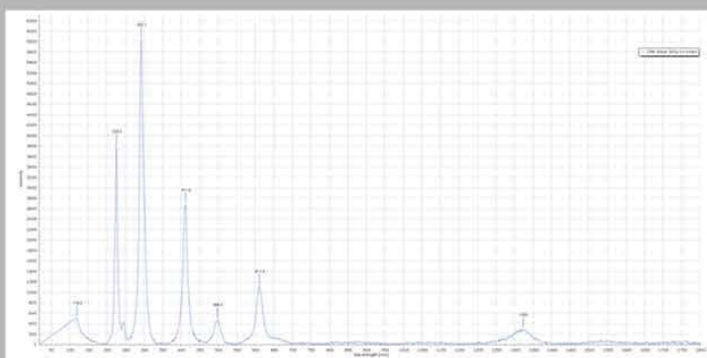
XRD

FTIR

RS

Conclusion

RS spectra 1



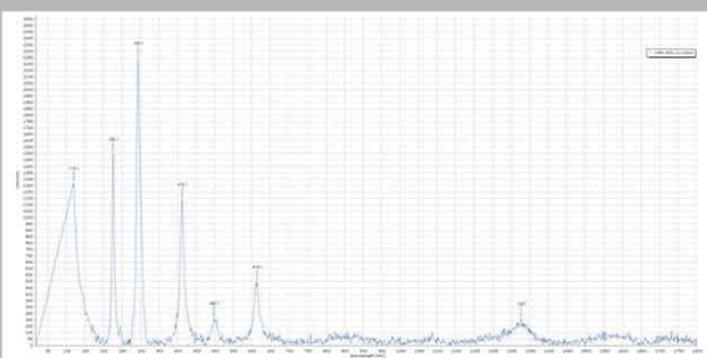
RS results 1

Black particle.

Settings: 30%, 1s, 10 accumulation

Peaks: 119,2 m; 225,3 s; 245,3 w; 292,1 vs;
411,2 m; 498,3 w; 611,4 w; 1323 w.

RS spectra 2



RS results 2

Red particle.

Settings: 30%, 1s, 10 accumulation

Peaks: 119 s; 226,1 s; 245,3 w; 293,1 vs;
412,1 m; 498,7 w; 613,1 m; 1327 w.

RS spectra 3

RS results 3

/

Summary

The Raman spectra corresponds to red ochre - Iron (III) oxide chromophore (Fe_2O_3 + clay + silica). Band wavenumbers (cm^{-1}) and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174). The intensive peak at 119 cm^{-1} , and 245 cm^{-1} in the point one, suggests existence of the lead-based component. Reference: lead based pigments of IRUG database.

Wide massive peak from 1200 to 1400 cm^{-1} belongs to clay minerals, including the peak on 1325 nm .

GN-2017-CM08

Sample information

Location of sample

B19.2 (underneath T276)
/ SW of ships' pump

Date of recovery
(YYYY-MM-DD)

2017-09-24

Condition upon recovery

The layer around was fine, silty sand mixed with the yellow colour and mercury drops. Sampled *in situ*

Sample description

Solid accumulation of the stones, yellow colour and sediment. Yellow powder mixed with sand-like particles

Colour

Bright yellow, grey

Storage condition

Recovered in glass jar

Cross / thin section

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

Yes

XRD

No

UVL-VIS-IR-IRfc

Yes

FTIR

No

XRF

Yes

RS

Yes

SEM-EDX

Yes

UHPLC

n/a

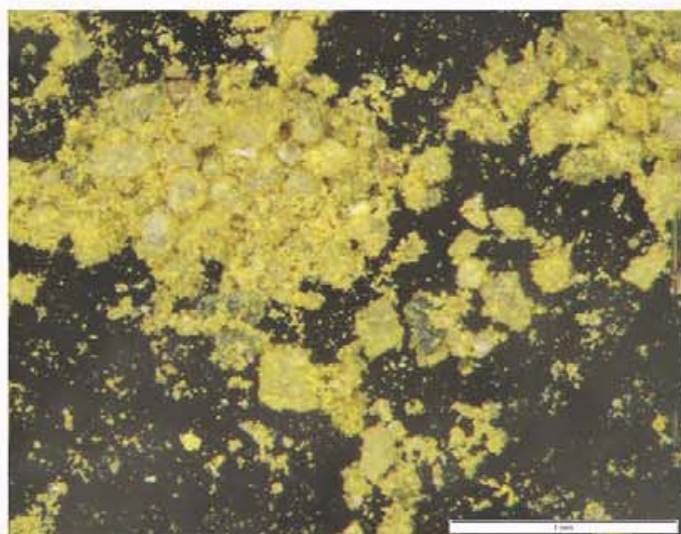
Notes

/

To conduct in future projects

/

Microscope photo 1



Texture description

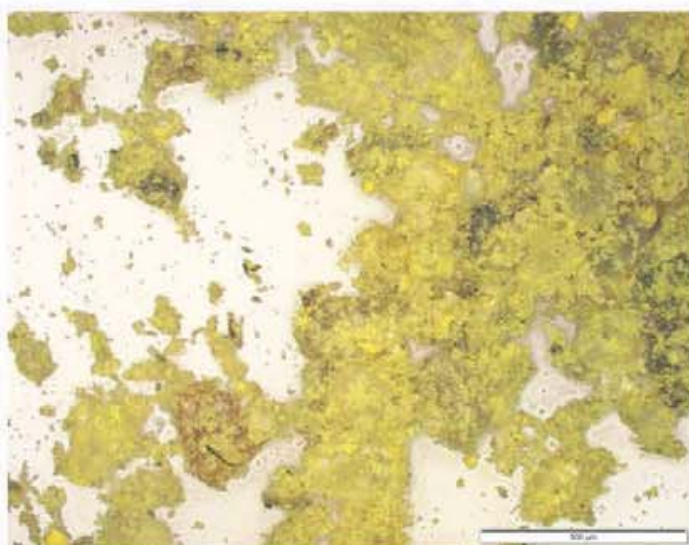
Colour: heterogeneous

- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope, UV illumination.

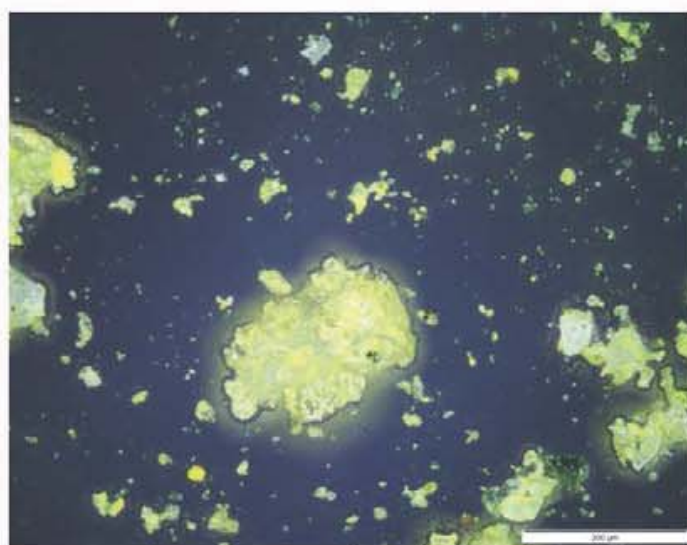
Particles:

- Different size, shape and colour (dark grey, light grey, brown) = 40%
size: 100-200 μm ;
- small particles of yellow colour = 30%
size: 10-20 μm .

Microscope photo 2



Microscope photo 3



GN-2017-CM08

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

Conclusion

Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



Microscope

UML-VIS-IR-IRfc

XRF

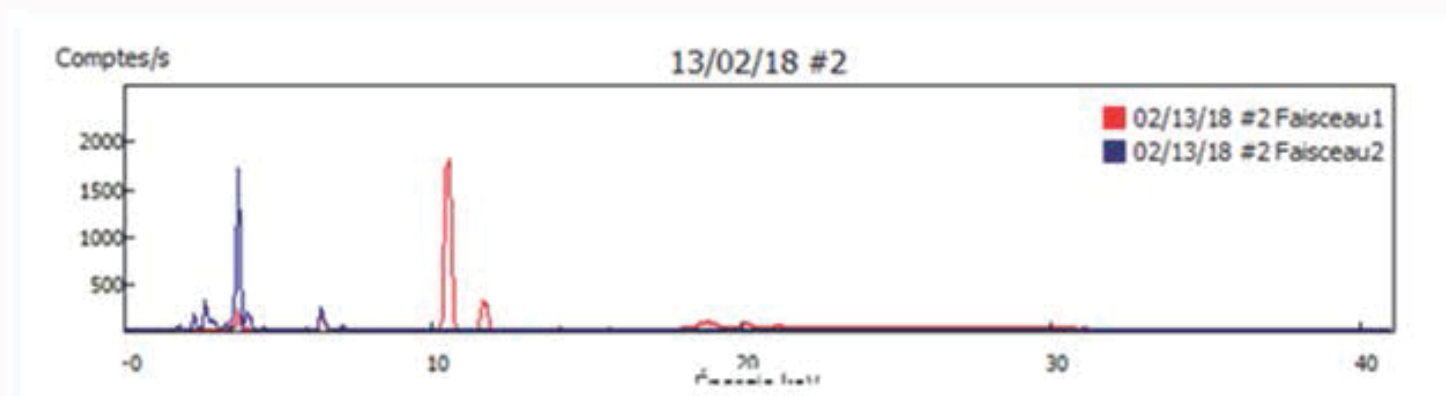
SEM-EDX

XRD

FTIR

RS

Conclusion

**Chemical elements**

Light Elements (60.35%)
Other: Ca (13.13%), Si (9.56%), Mg (7.5%), S (2.51%), Al (2.39%),
As (1.90%), Fe (1.74%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

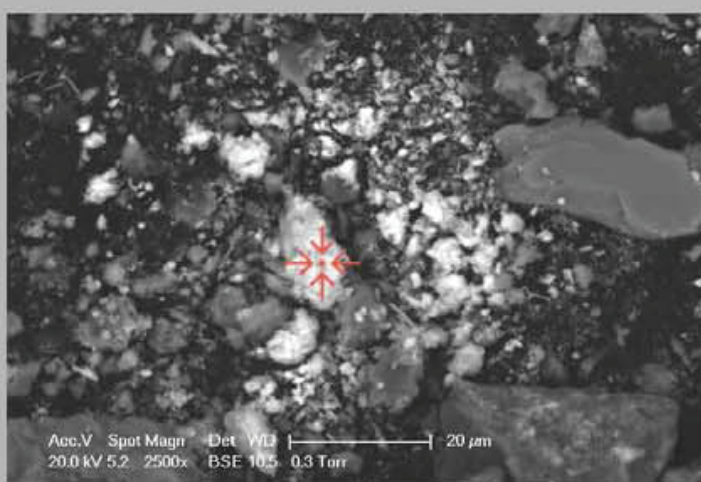
Conclusion

Pt 1: Chemical elements

Magnification: 2500

Pt 1: C, Na, Mg, Al, Si, S, K, Ca, Fe, As / Mg, S

Pt 1: BSE image

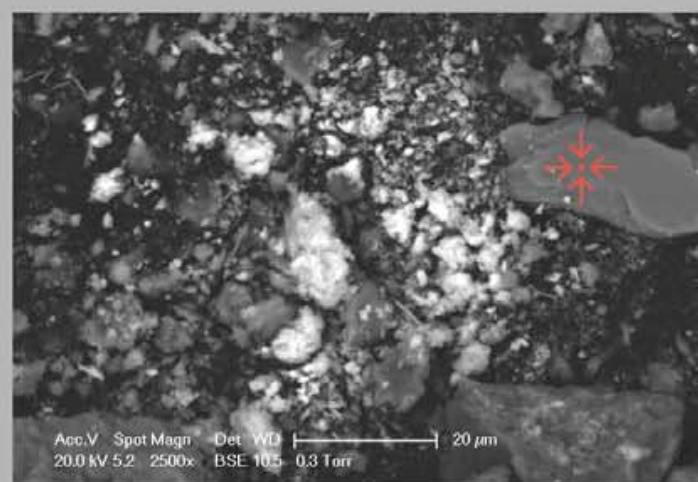


Pt 2: Chemical elements

Magnification: 2500

Pt 2: C, Mg, Al, Si, S, Ca, Mn, Fe / Al, Si

Pt 2: BSE image



Pt 3: Chemical elements

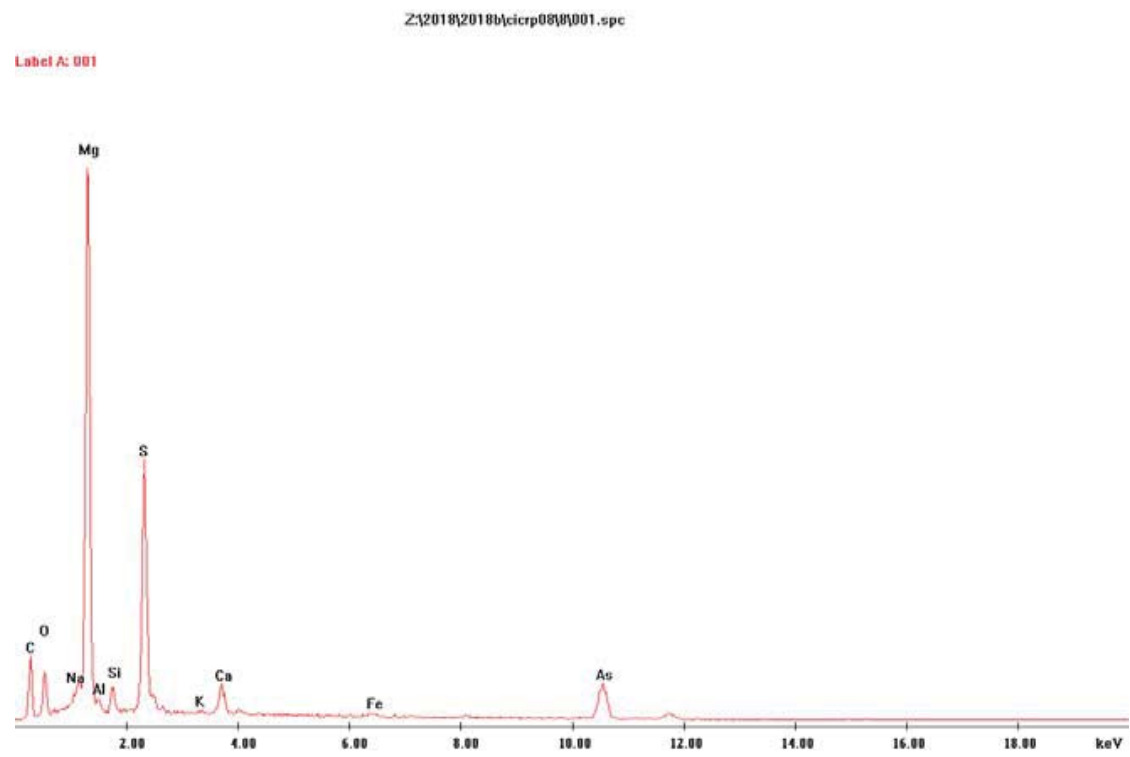
Pt 3: BSE image

Pt 4: Chemical elements

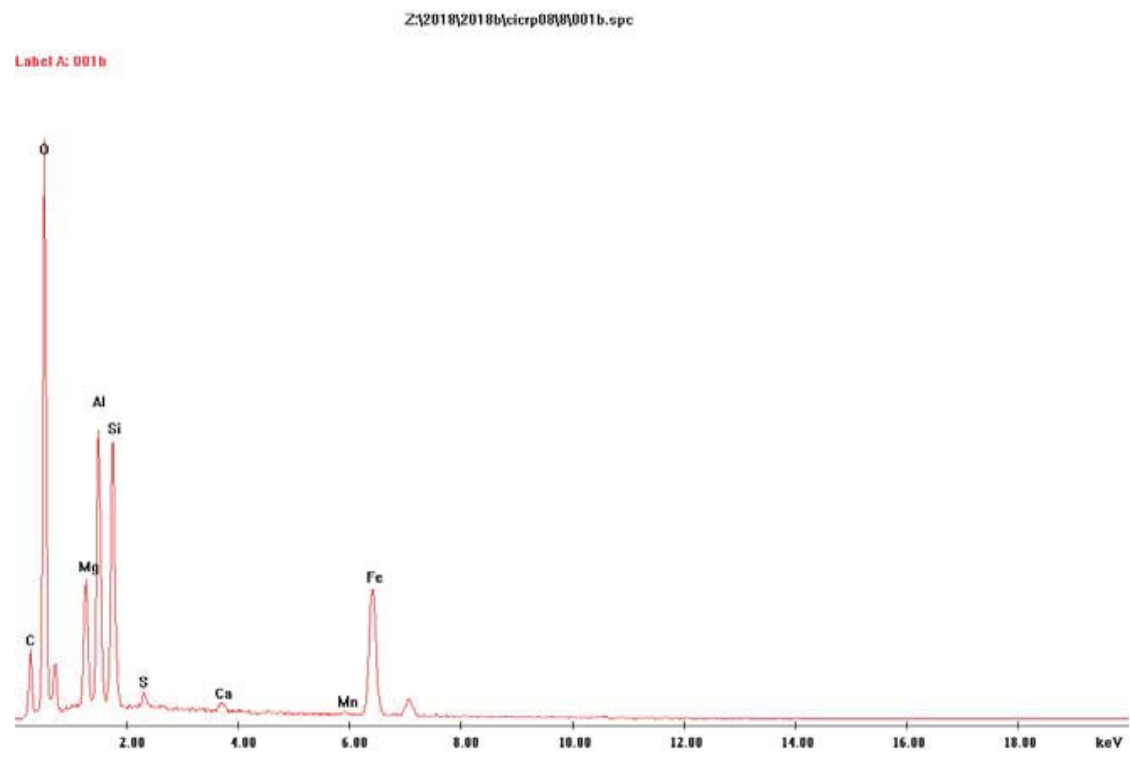
Pt 4: BSE image

GN-2017-CM08

Point 1:



Point 2:



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

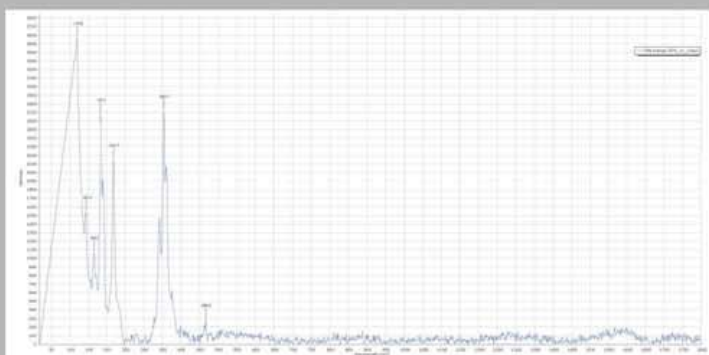
XRD

FTIR

RS

Conclusion

RS spectra 1



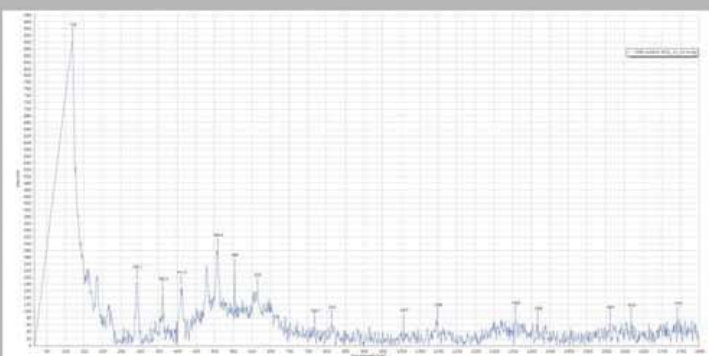
RS results 1

1) Orange particle

Settings: 25%, 1s, 10 accumulation

Peaks: 118,9 vsh; 142,4 msh; 164,2 msh; 183,1 vsh; 218,7 vsh; 353,7 vsh; 466,2 wsh.

RS spectra 2



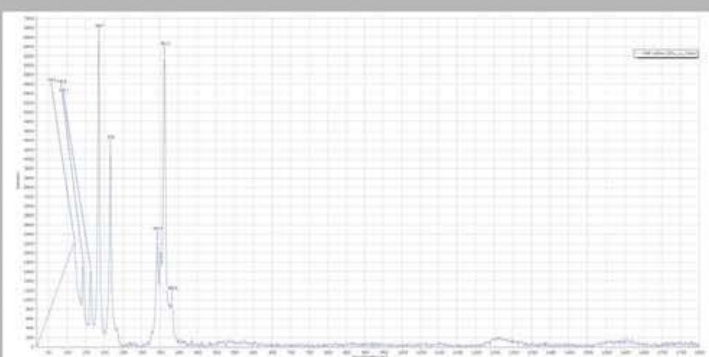
RS results 2

2) Reddish particle

Settings: 25%, 1s, 10 accumulation

Peaks: 119 vsh; 292,1 msh; 360,4 msh; 411,9 msh; 508,2 msh; 554 msh; 615 wsh; 768,7 wsh; 814 wsh; 1007 wsh (...)

RS spectra 3



RS results 3

3) Yellow particle

Settings: 25%, 1s, 10 accumulation

Peaks: 118,9 msh; 142,5 msh; 163,1 msh; 184,7 vsh; 216 vsh; 341,9 msh; 361,2 vsh; 380 wsh.

Summary

- 1) Orange particle- realgar (according to Bell, Clark & Gibbs, p. 2174)
- 2) Realgar - unknown?
- 3) Yellow particle - realgar

GN-2017-CM14

Sample information

Location of sample

On transition between northern C18 and C19 / content of barrel 4

Date of recovery (YYYY-MM-DD)

2017-09-01

Condition upon recovery

Sampled *in situ*

Sample description

Powder of fine consistency

Colour

Red

Storage condition

Stored in a glass jar which contains sea water. Kept in a dark space on a room temperature

Cross / thin section

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

No

UVL-VIS-IR-IRfc

No

XRF

No

SEM-EDX

Yes

XRD

No

FTIR

Yes

RS

Yes

UHPLC

n/a

Notes

/

To conduct in future projects

/

Microscope photo 1

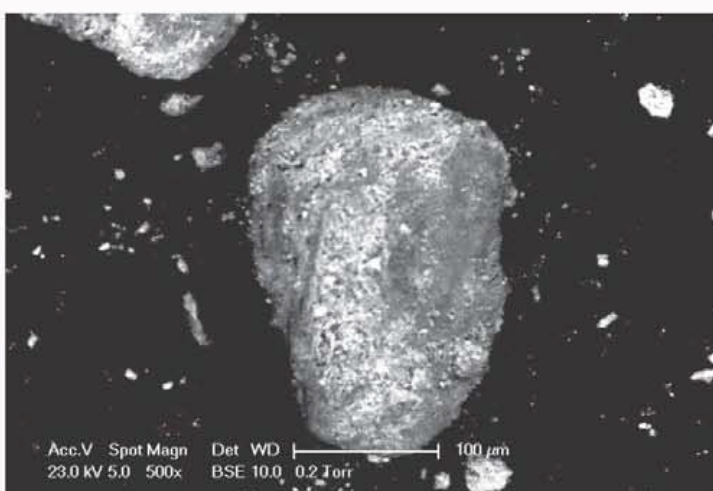


Texture description

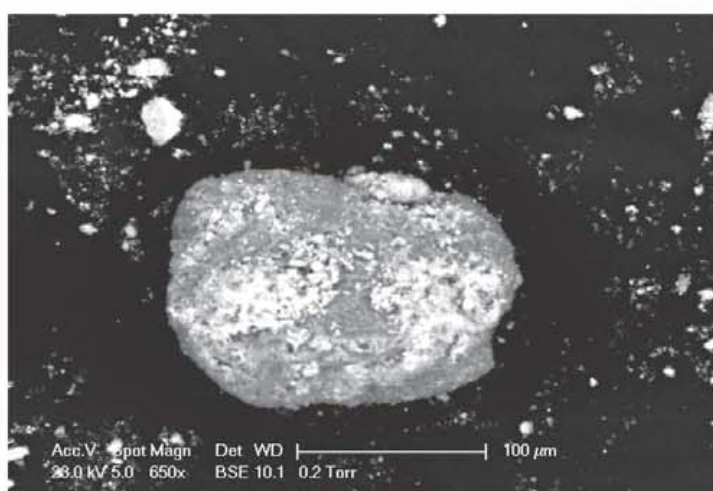
- 1) Binocular
- 2) & 3) SEM

Grain-like, rounded particles of 100 μ m with fine-grains

Microscope photo 2



Microscope photo 3



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

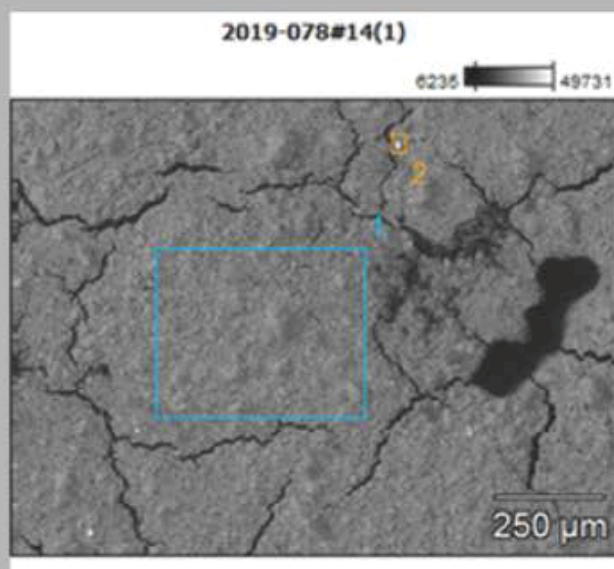
Conclusion

Pt 1: Chemical elements

Magnification: 90

SA 1-1: C, O, F/Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ba, Fe / O, Al, Fe

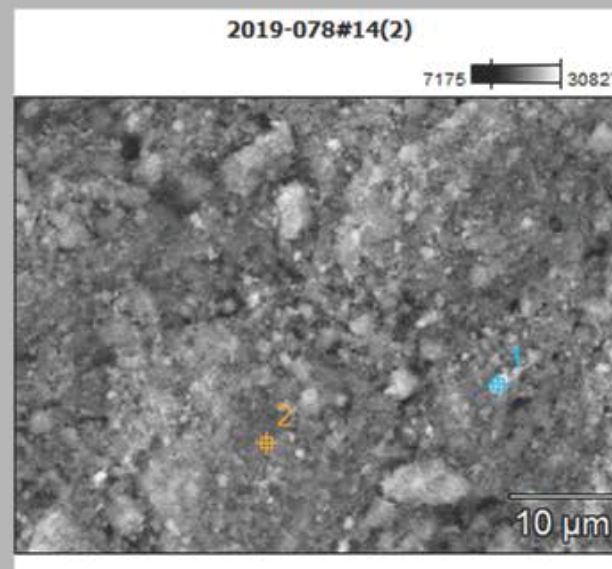
Pt 1-2: C, O, F/Fe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ba, Fe / O, Al, Fe

Pt 1: BSE image**Pt 2: Chemical elements**

Magnification: 2200

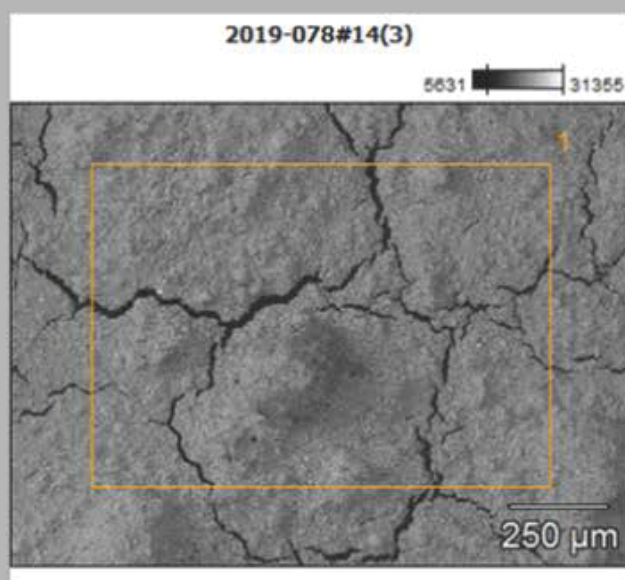
Pt 2-1: C, O, F/Fe, Na, Mg, Al, Si, P, S, Cl, K, Fe / O, Al, Fe

Pt 2-2: C, O, Na, Mg/As, Al, Si, P, S, Cl, K, Fe / O, Al, S, Fe

Pt 2: BSE image**Pt 3: Chemical elements**

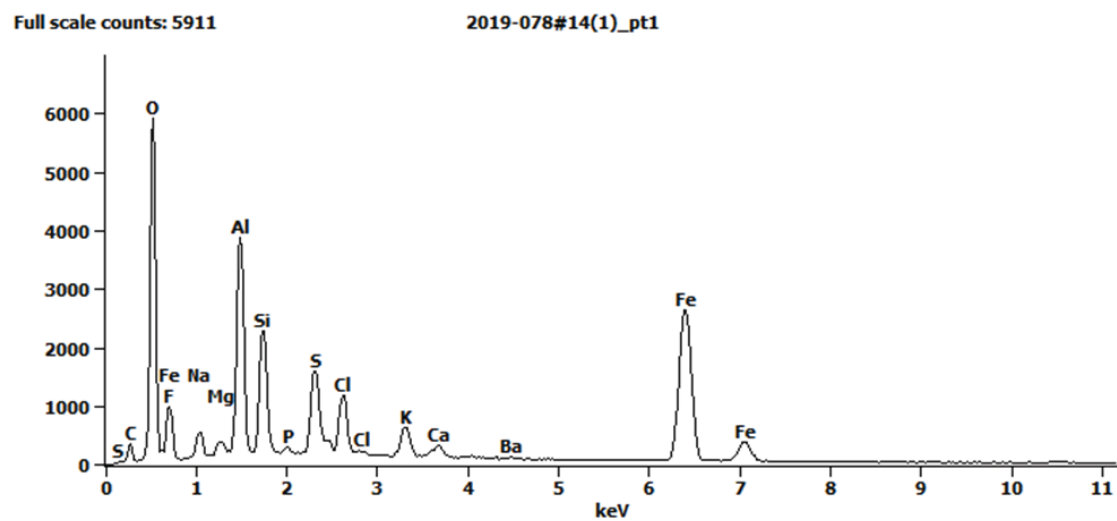
Magnification: 80

SA 3-1: C, O, F/Fe, Na, Mg/As, Al, Si, P, S, Cl, K, Ca, Fe / O, Al, Si, Fe

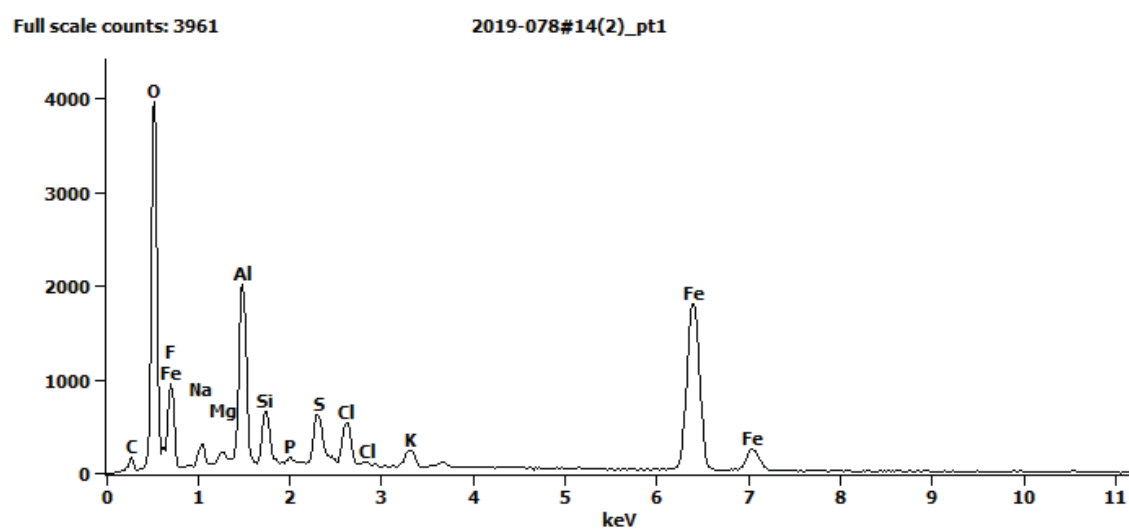
Pt 3: BSE image**Pt 4: Chemical elements****Pt 4: BSE image**

GN-2017-CM14

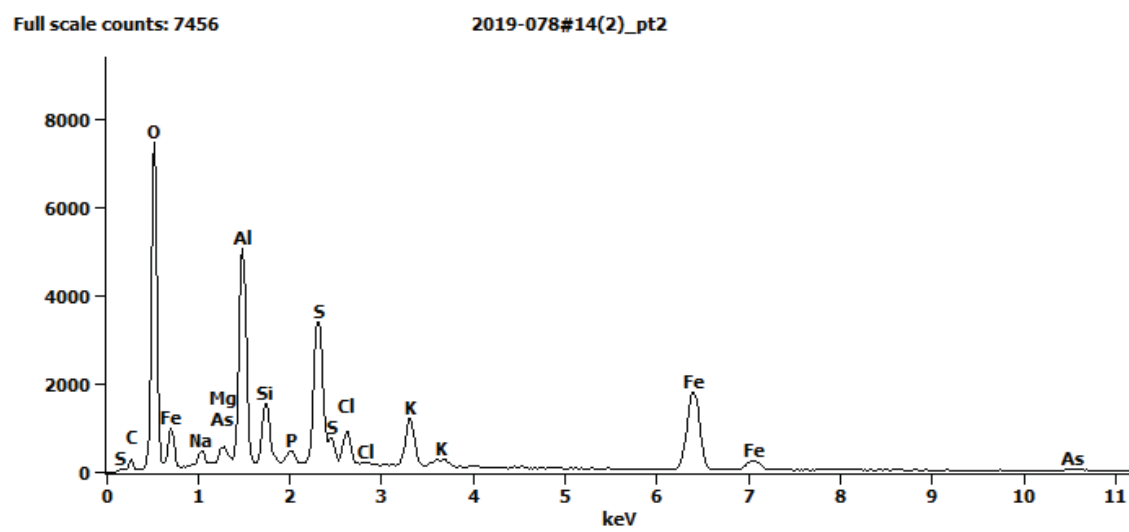
Surface area 1:



Point 2-1:

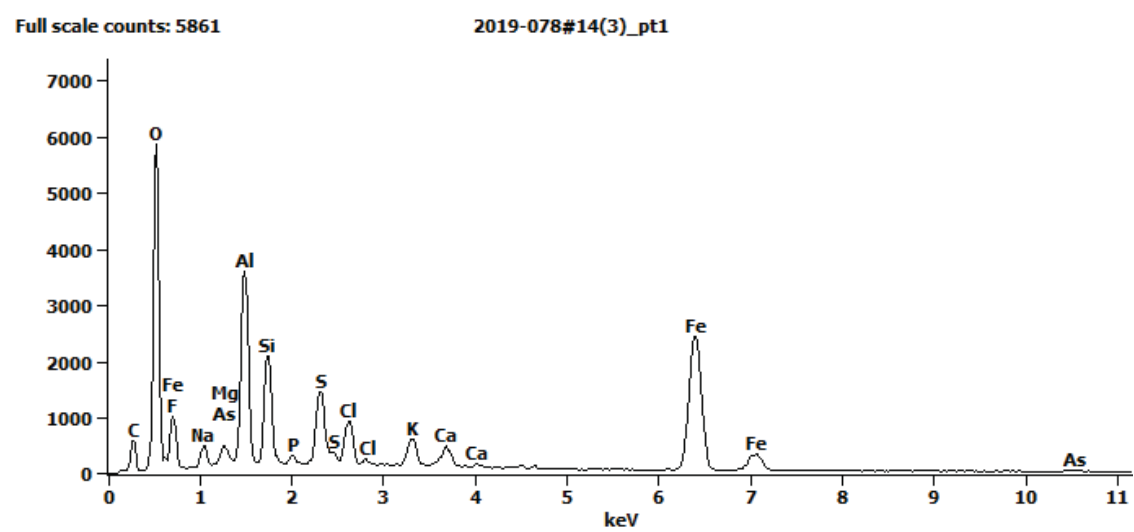


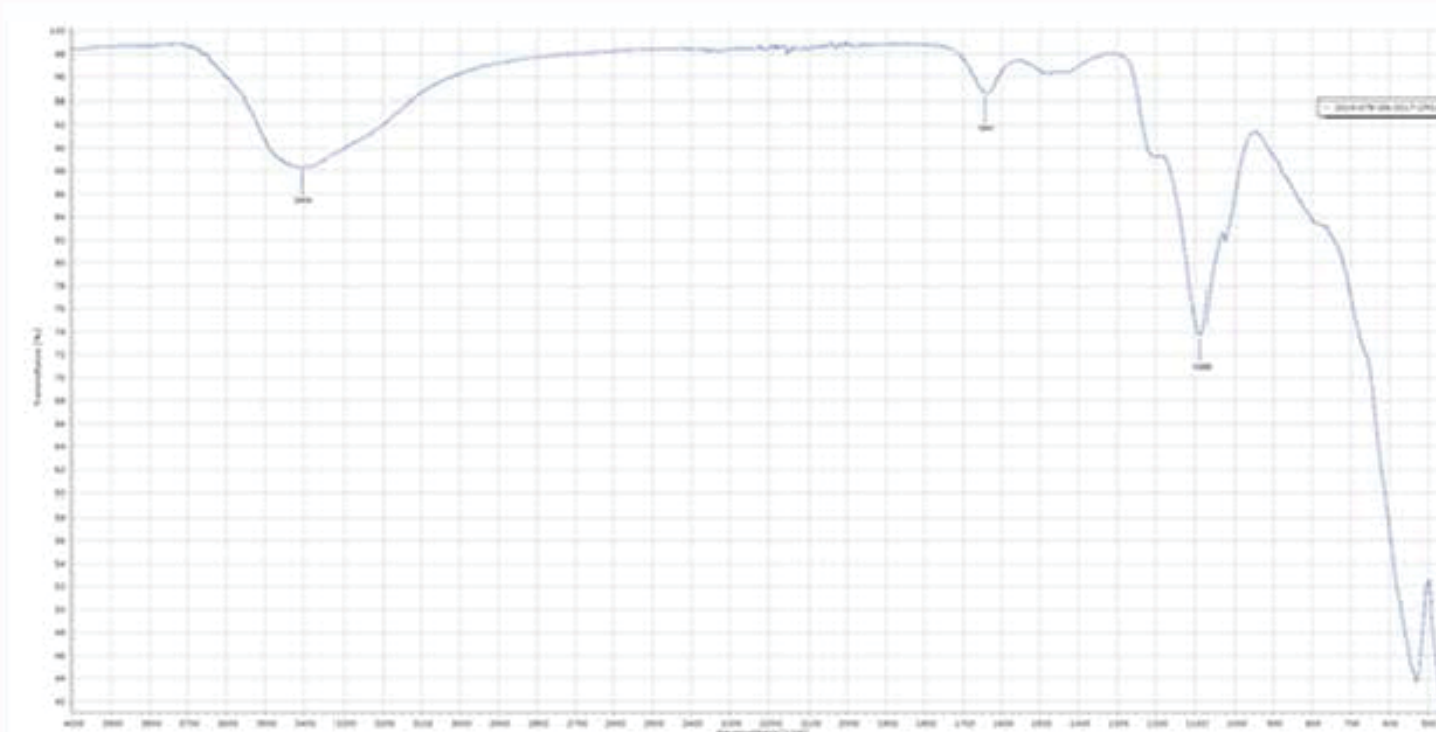
Point 2-2:



GN-2017-CM14

Surface area 3:





FTIR results

Absorption bands visible on: **3404 vb**; **1641 w**; 1205 msh; 1086 vsh; 1021 msh; **533 vsh**.

* Hematite: reference in IRUG Database, sample number IMP00364 <http://www.irug.org/jcamp-details?id=824>

Corresponding absorption bands: **3600 – 3000 b (3446 peak)**; **1614 w**; **538 vsh**; **468 vsh**.

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: 1452 w; 1162 w; 1033 vsh; 920 msh.

* Silicon oxide: reference Reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: 1077-1022 vsh (in spectra 1073 vsh; 1024 sh)

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4.

Corresponding absorption bands 1030 sh, 795 w, 531 sh, 431 sh)

The weak broad band positioned at 1482, could be calcium carbonate (Cornell & Schwermann 2003, p. 143)

(b - broad; sh - sharp; w - weak; m - medium; v - very)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

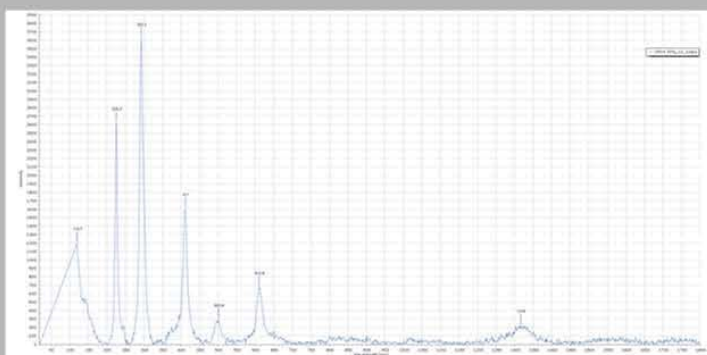
XRD

FTIR

RS

Conclusion

RS spectra 1

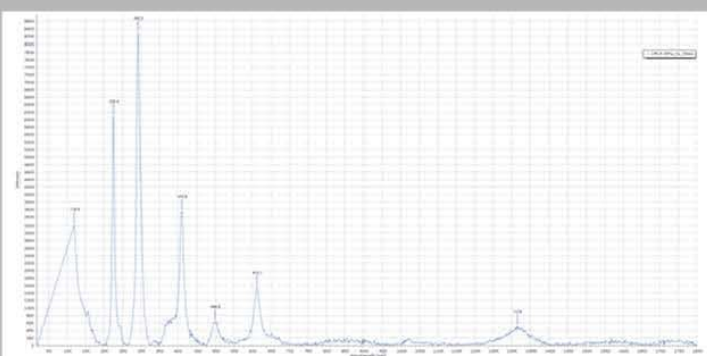


RS results 1

Settings: 30%, 1s, 10 accumulation

Peaks: 118,7 m; 143,6 w; 225 s; 245,3 w; 292,2 vs;
411 m; 400,5 w; 610,6 m; 1316 w.

RS spectra 2

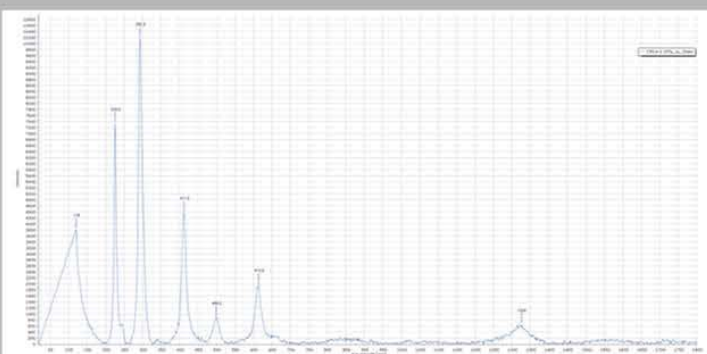


RS results 2

Settings: 30%, 1s, 30 accumulation

Peaks: 118,9 m; 156,76 m; 225,4 s; 243,6 w; 292,2
vs; 410,5 m; 498,6 w; 612,1 m; 1316 w.

RS spectra 3



RS results 3

Settings: 30%, 1s, 30 accumulation

Peaks: 119 s; 225,6 s; 245,13 w; 292,8 vs; 411,6
m; 498,2 w; 613,5 m; 1325 w.**Summary**

The Raman spectra corresponds to red ochre - Iron (III) oxide chromophore (Fe_2O_3 + clay + silica). Band wavenumbers (cm^{-1}) and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174).

The intensive peak at 119 cm^{-1} , and the weak peak at $243\text{-}245 \text{ cm}^{-1}$ in the point one, suggests existence of the lead-based component. Reference: lead based pigments of IRUG database. Wide massive peak from 1200 to 1400 cm^{-1} belongs to clay minerals, including the peak on 1325 cm^{-1} .

GN-2017-CM15

Sample information

Location of sample

D15.4

Date of recovery (YYYY-MM-DD)

2017-08-14

Condition upon recovery

Found in the dark grey sediment where is no hull anymore. In the same layer with lead seals, pins, glass beads

Sample description

Ball of approximate diameter of 1.5 cm

Colour

Dark purple, with lustre and white inclusions

Storage condition

Recovered in the plastic bag, later replaced in the glass container

Cross / thin section

Yes

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

No

SEM-EDX

Yes

XRD

Yes

FTIR

No

RS

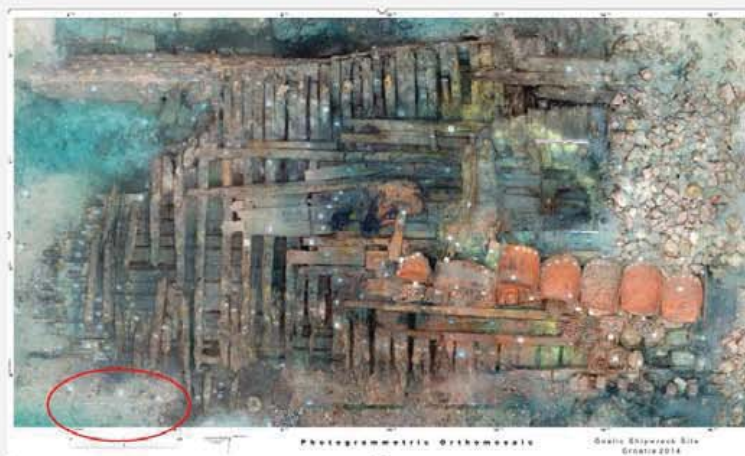
Yes

UHPLC

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

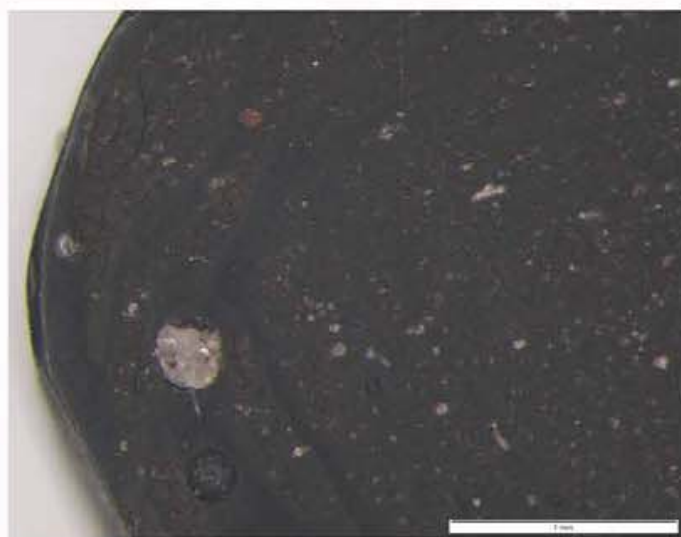
Notes

/

To conduct in future projects

SEM-EDX, RS

Microscope photo 1



Texture description

Colour: heterogeneous
Irregular shaped rounded particles; dark brown, purple or black, it gives impression of 'luster'.

- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope.

Particles:

- Dark brown / purple (50%);
- Black (20%);
- White particles - 10% ranging from 0.3 to 0.01 mm;
- One red particle in the crack of the sample embedded in epoxy resin.

Microscope photo 2



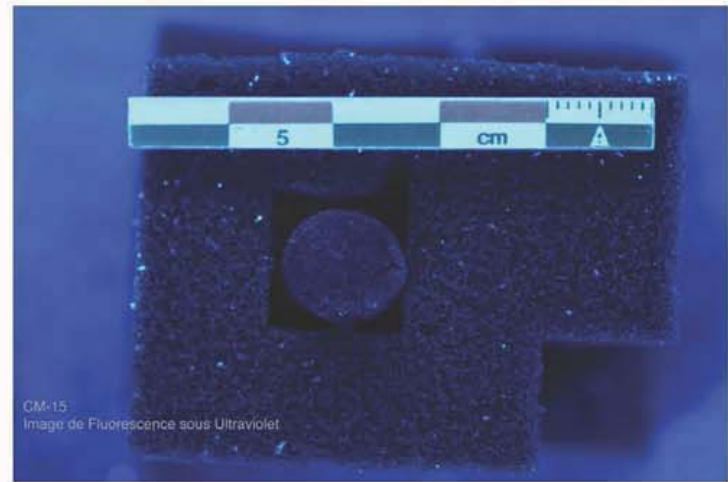
Microscope photo 3



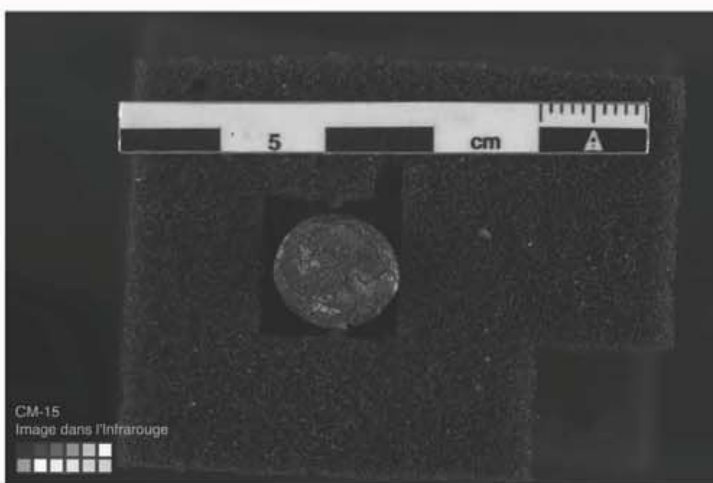
Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

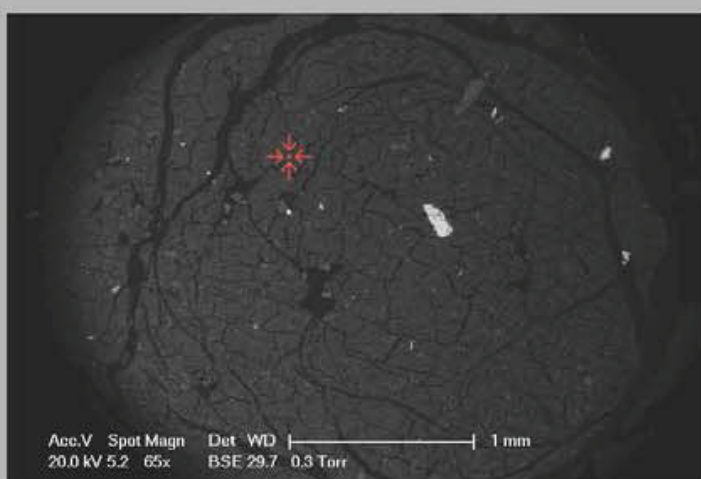
Conclusion

Pt 1: Chemical elements

Magnification: 140

Pt 1-1: C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca / C, O, Al, Si, S

Pt 1: BSE image

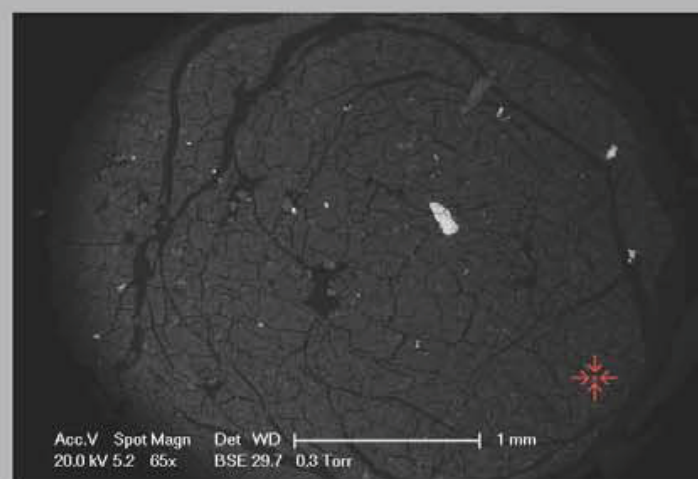


Pt 2: Chemical elements

Magnification: 140

Pt 1-2: C, N, O, Na, Mg, Al, Si, S, Cl, K, Ca, Fe, Cu / C, S

Pt 2: BSE image

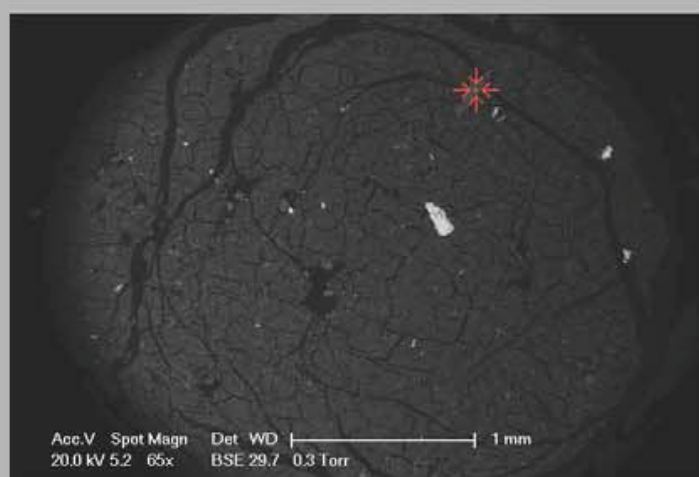


Pt 3: Chemical elements

Magnification: 140

Pt 1-3: C, N, O, Al, Si, P, S, Cl, Ca / C, Al

Pt 3: BSE image

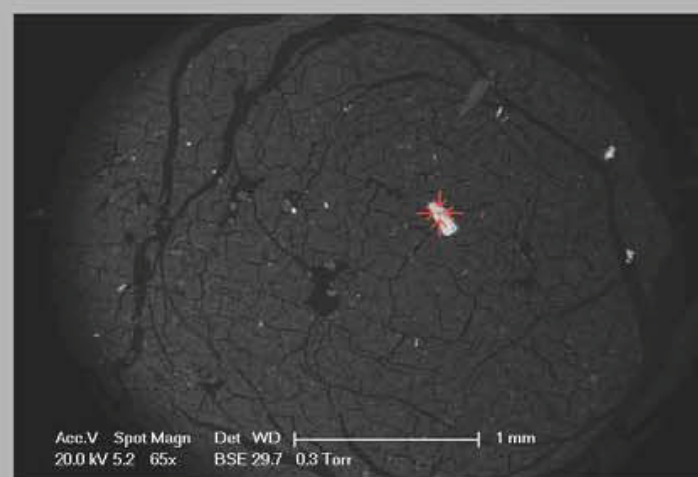


Pt 4: Chemical elements

Magnification: 140

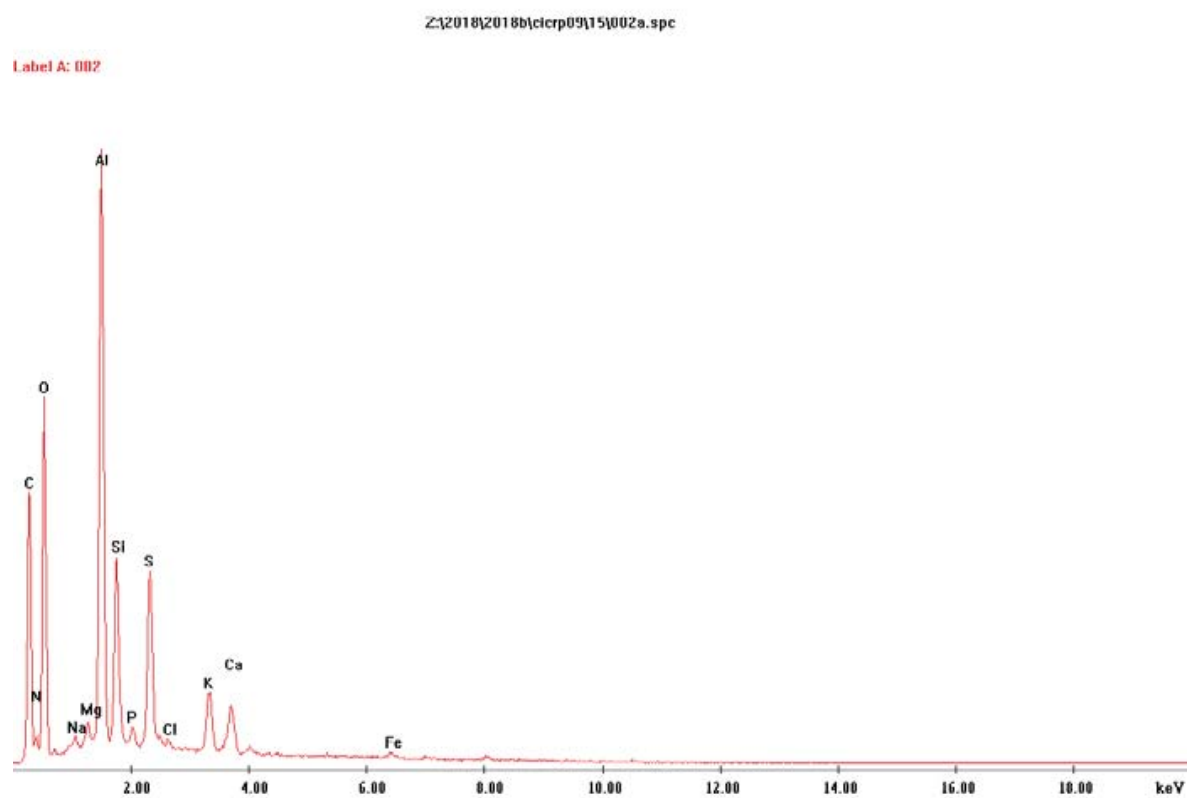
Pt 1-4: C, N, O, Na, Mg, Al, Si, P, S, K, Ca, Fe, Cu / O, Al, Si, S

Pt 4: BSE image

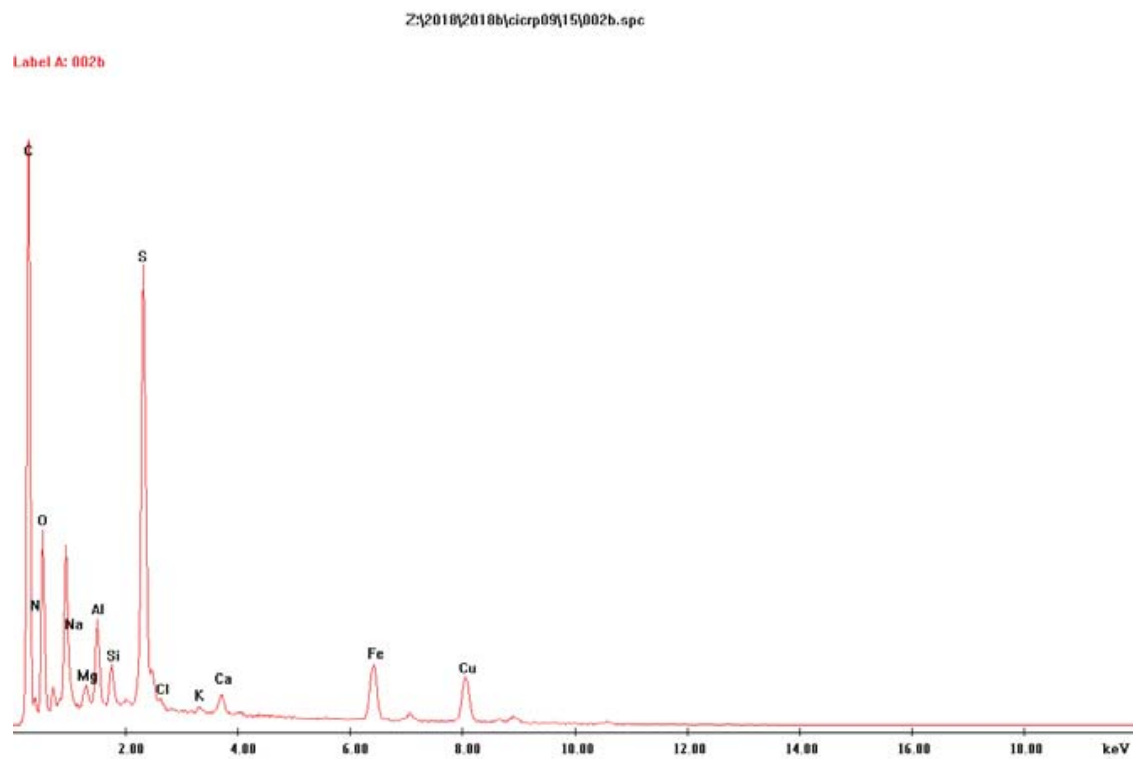


GN-2017-CM15

Point 1-1:

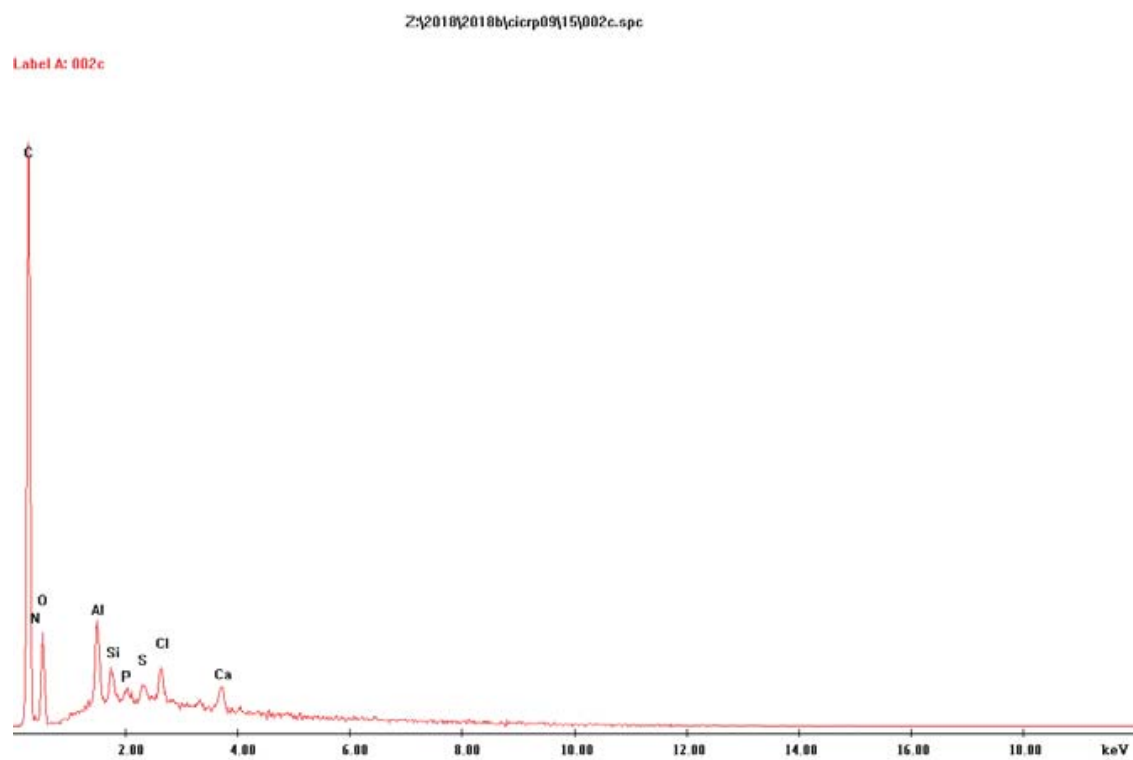


Point 1-2:

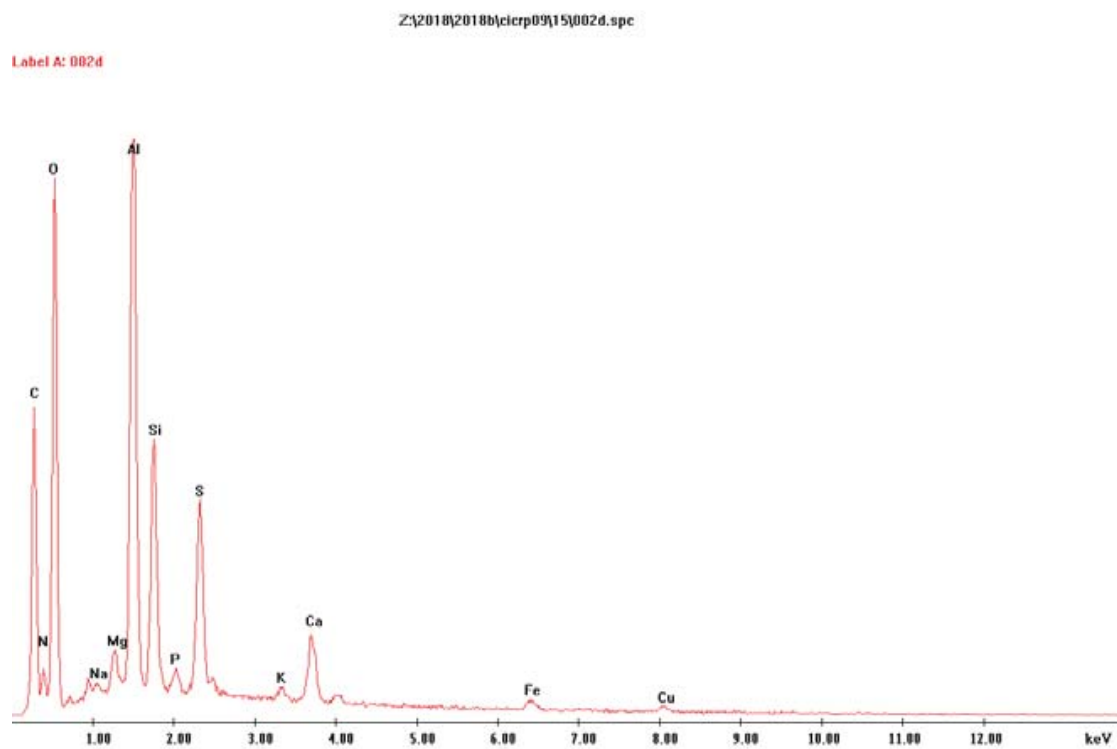


GN-2017-CM15

Point 1-3:



Point 1-4:



GN-2017-CM16

Sample information

Location of sample

D15.3

Date of recovery (YYYY-MM-DD)

2017-08-12

Condition upon recovery

Found in the dark grey sediment where is no hull anymore, in the same layer with lead seals, pins, glass beads

Sample description

Fragments of ball

Colour

Dark purple, with luster and white inclusions

Storage condition

Recovered in the plastic bag, later replaced in the glass container

Cross / thin section

n/a

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

No

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

Yes

RS

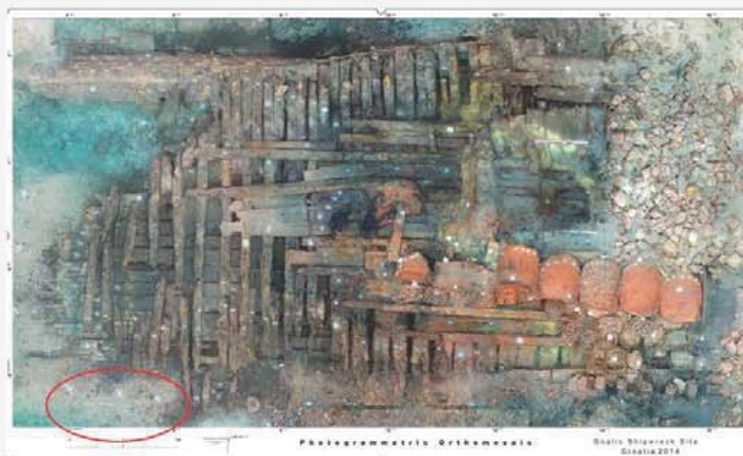
No

UHPLC

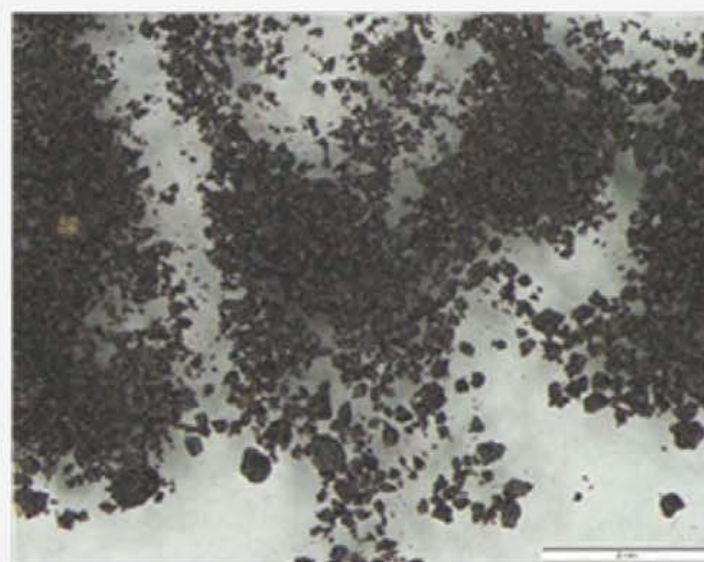
n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

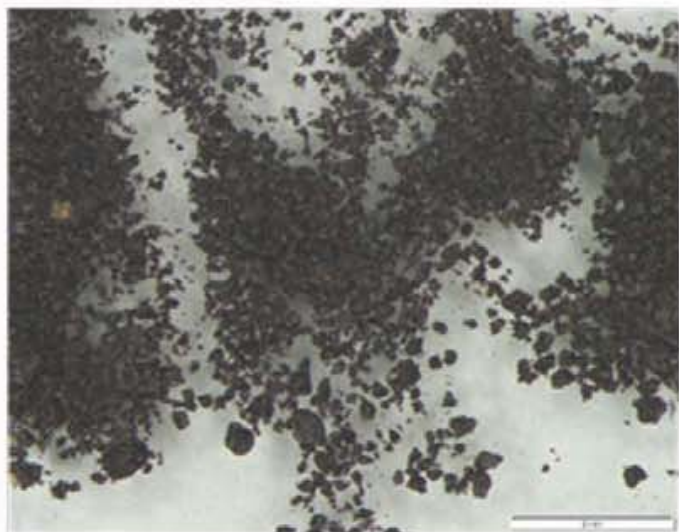
Notes

/

To conduct in future projects

SEM-EDX, RS

Microscope photo 1

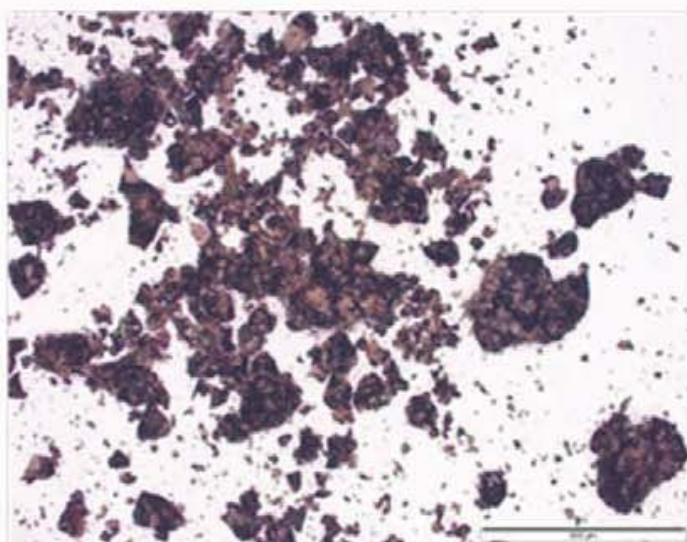


Texture description

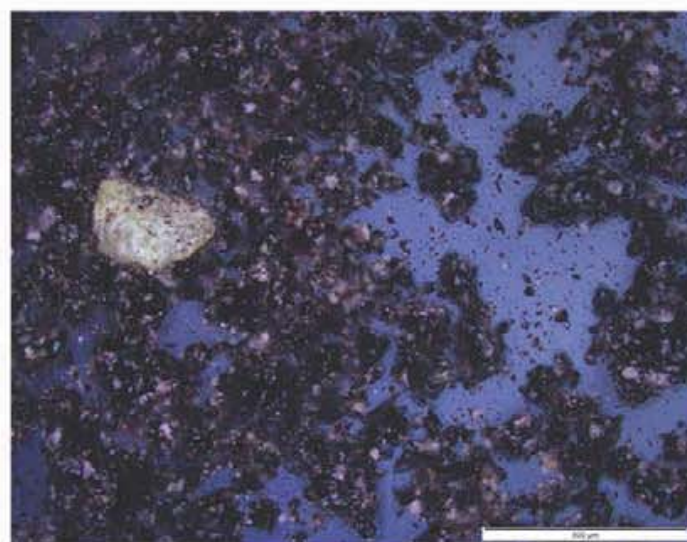
Colour: heterogeneous
Irregular shaped rounded particles
Colour: heterogeneous - dark brown, purple or black, it gives impression of 'luster'.
Particles of approximate size of 150-200 μm .

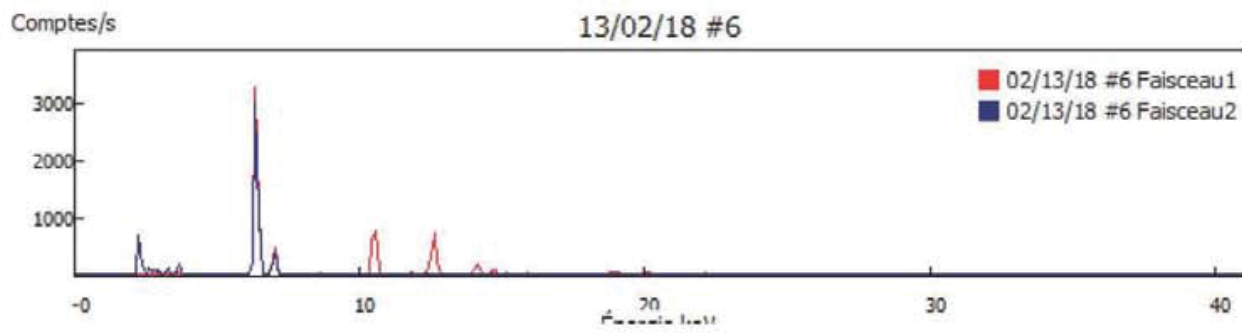
Particles:
- Dark purple/brown with light purple dots on the top; dimensions: 0.25 - 0.5 mm (50%);
- Light purple (is this creating the impression of lustre?) (30%);
- Brown/orange particle: less than 10% (around 0.25 mm).

Microscope photo 2



Microscope photo 3





Chemical elements

Light elements (79.55%)
Other: S (5.32%), Al (4.68%), Si (2.4%), Ca (2.12%), Fe (2.11%),
Pb (1.59%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

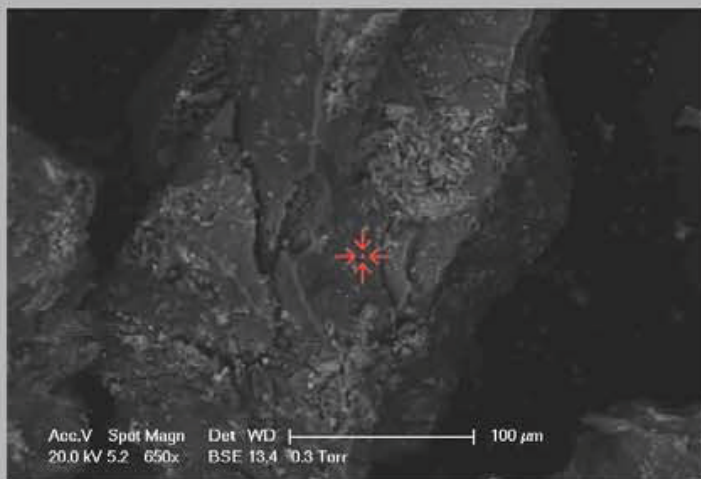
Conclusion

Pt 1: Chemical elements

Magnification: 650

Pt 1: C, O, Fe, Na, Mg, Al, Si, P,S, K, Ca, Fe, Cu /
C, O,Al, Si, S

Pt 1: BSE image

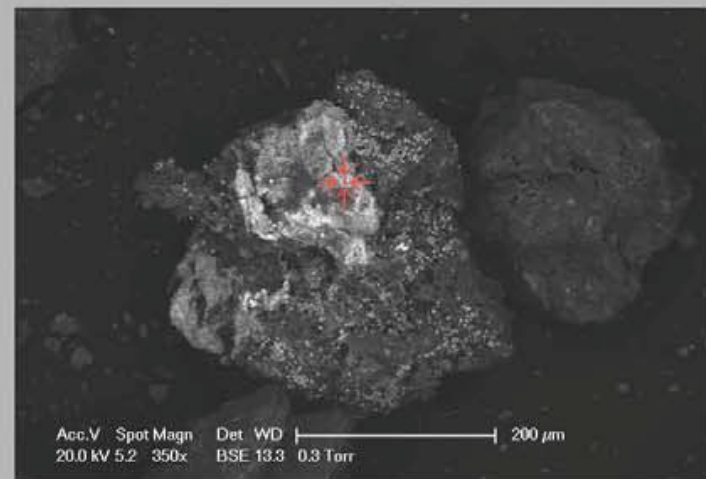


Pt 2: Chemical elements

Magnification: 350

Pt 2: C, O, Fe, Na, Mg, Al, Si, S, K, Ca, Fe,
Cu, Hg / C, O, Al, Si, S

Pt 2: BSE image

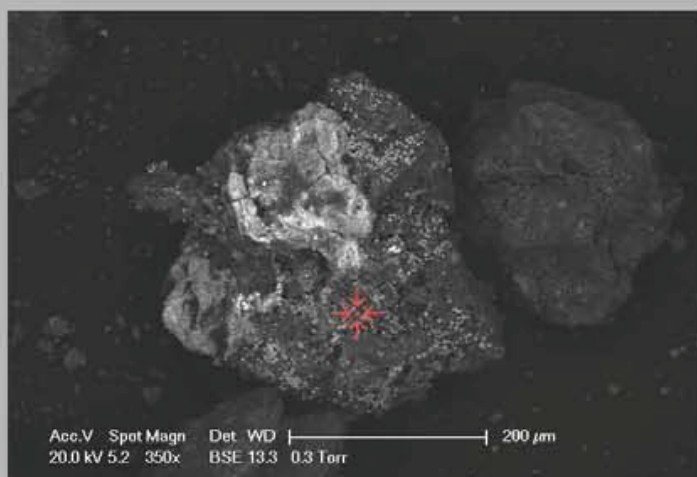


Pt 3: Chemical elements

Magnification: 350

Pt 3: C, O, Na, Mg, Al, Si, S, K, Ca, Fe, Cu,
Hg / C, O, Al, S, Fe

Pt 3: BSE image

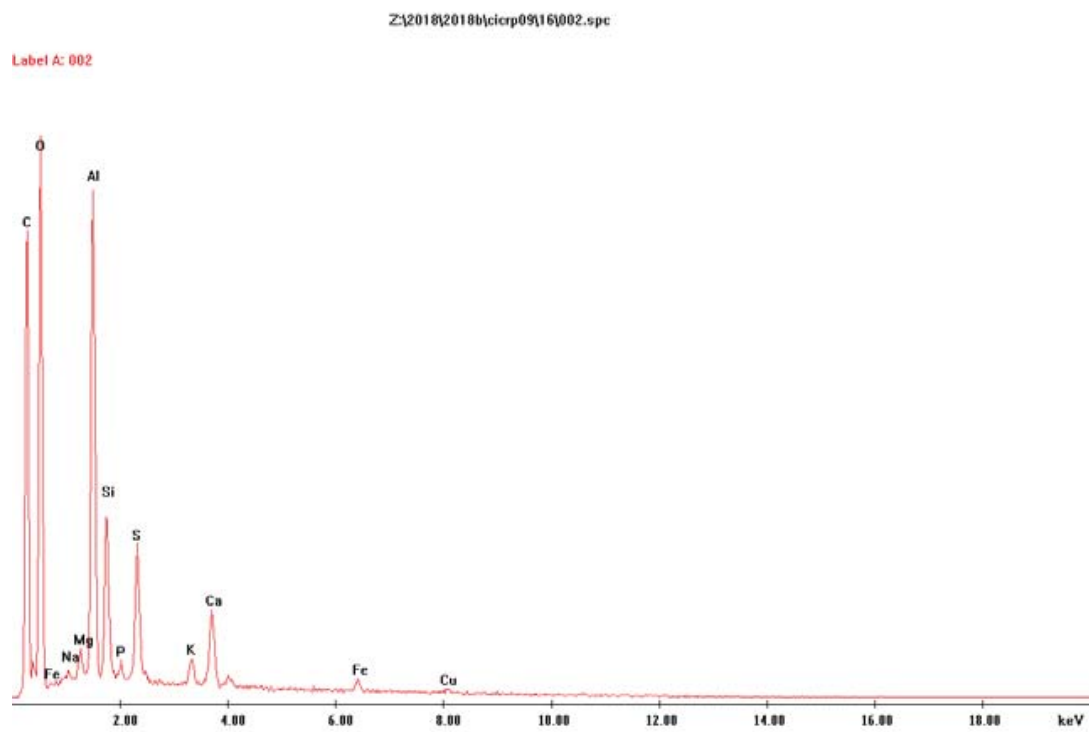


Pt 4: Chemical elements

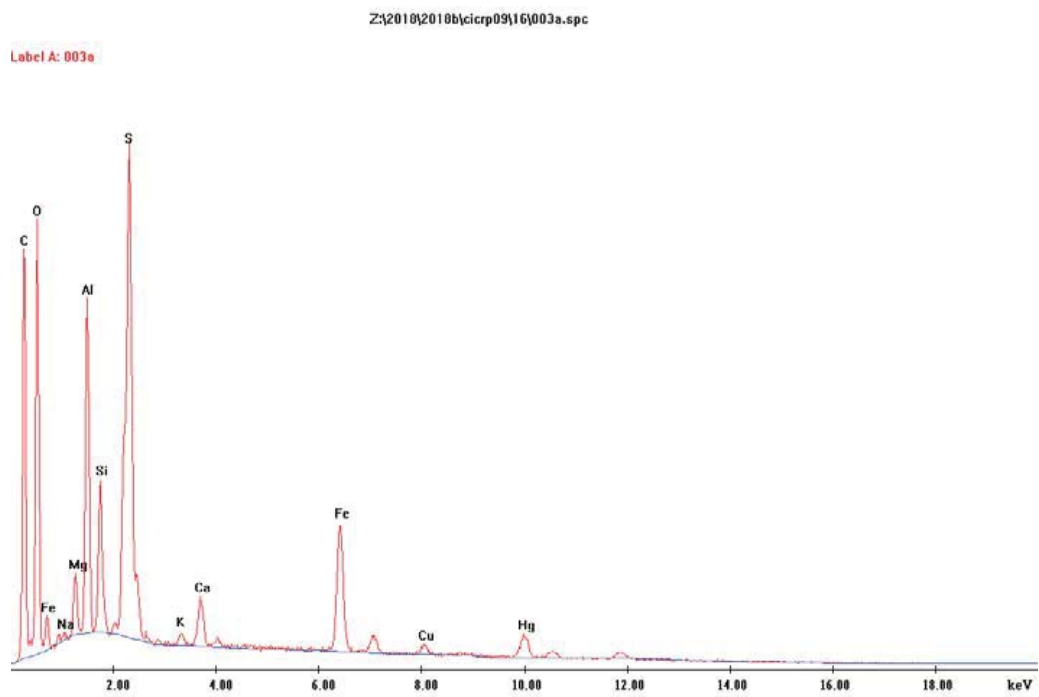
Pt 4: BSE image

GN-2017-CM16

Point 1:



Point 2-1:

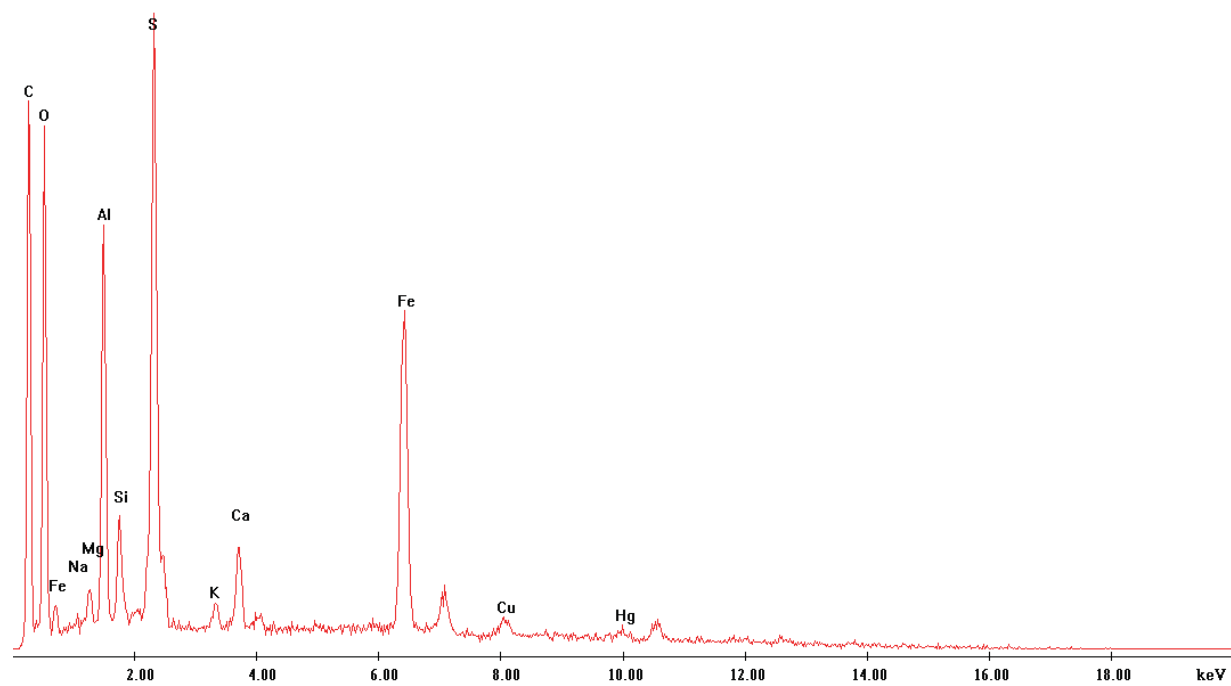


GN-2017-CM16

Point 2-2:

Z:\2018\2018b\cicrp09\16\003b.spc

Label A: 003b



G N-2017-CM16

Microscope

UVL-VIS-IR-IR.fc

XRF

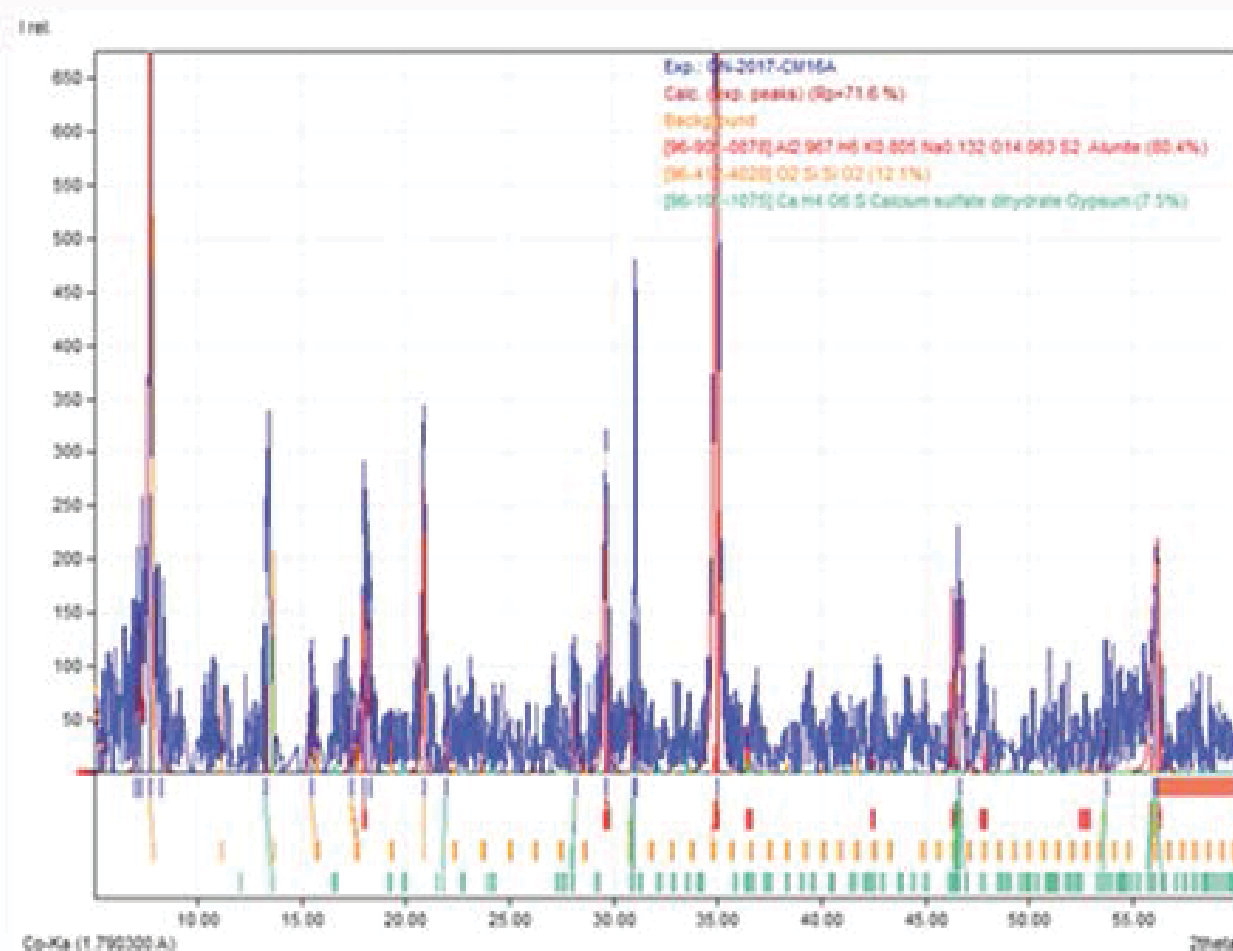
SEM-EDX

XRD

FTIR

RS

Conclution



Suggested mineral phases

Alunite (80.4%)
Quartz (12.1%)
Calcium sulphate dihydrate Gypsum (7.5%)



FTIR results

Peaks: 2963 vb; 1635 msh; 1531 msh; 1393 vsh; 1231 wsh; 1082 vsh; 951,8 vsh; 843,9 wsh;

Wool might be present.

Corresponding absorption bands: <http://www.irug.org/jcamp-details?id=1671>

(b - broad; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM18

Sample information

Location of sample

B19/B20; South of the ship's pump, in the area with fine sediment

Date of recovery (YYYY-MM-DD)

2017-09-06

Condition upon recovery

Recovered in a plastic bag

Sample description

Fine-grained powder mixed with sand

Colour

Yellow, grey

Storage condition

Recovered in plastic bag, and after three weeks repacked in the glass jar. The sea water was not replaced with tap water

Cross / thin section

No

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

No

FTIR

No

RS

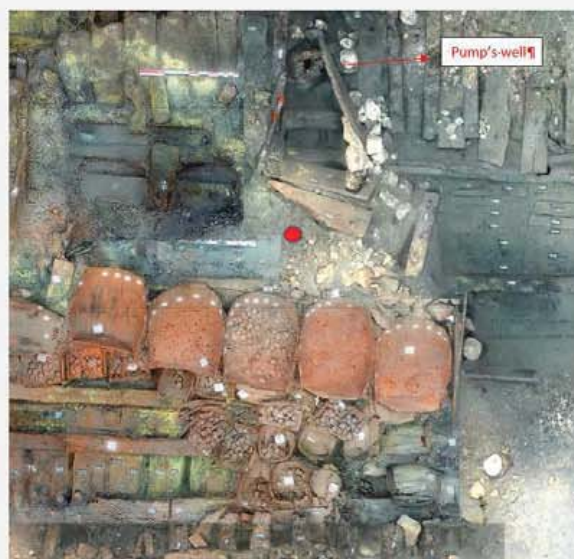
Yes

UHPLC

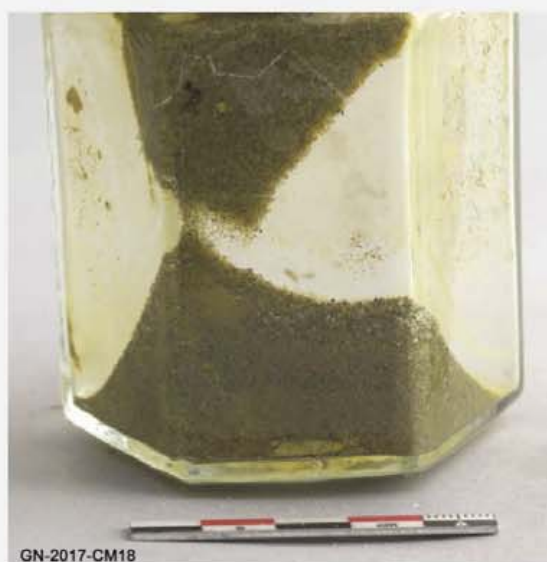
n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

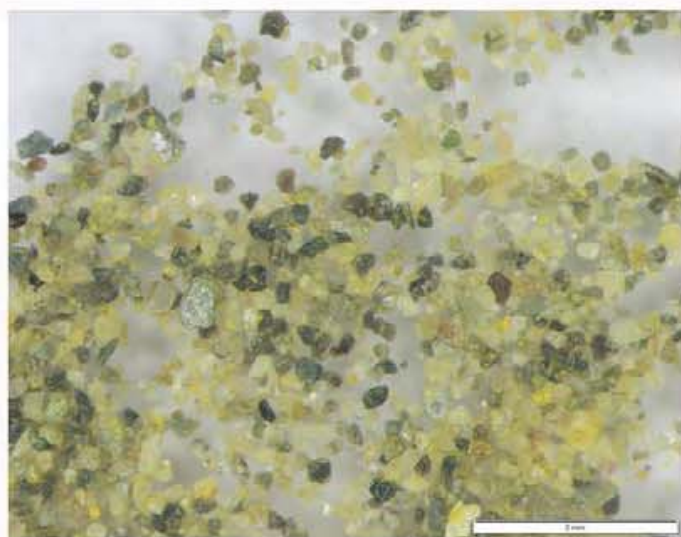
Notes

/

To conduct in future projects

XRD

Microscope photo 1



Texture description

Sand with fine-grained yellow colour
Heterogeneous composition:

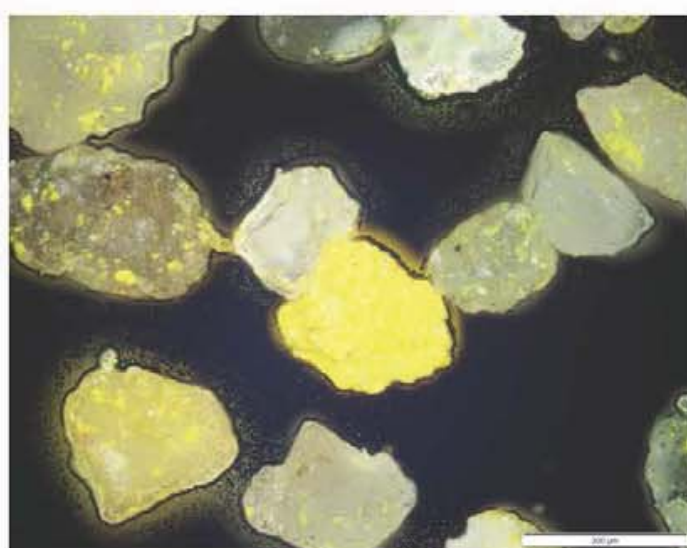
- Dark, white, and light gray particles 50-100 μm , the sand (around 75%);
- Particles and lumps of intensive yellow colours, less than 50 μm (25%).

- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope.

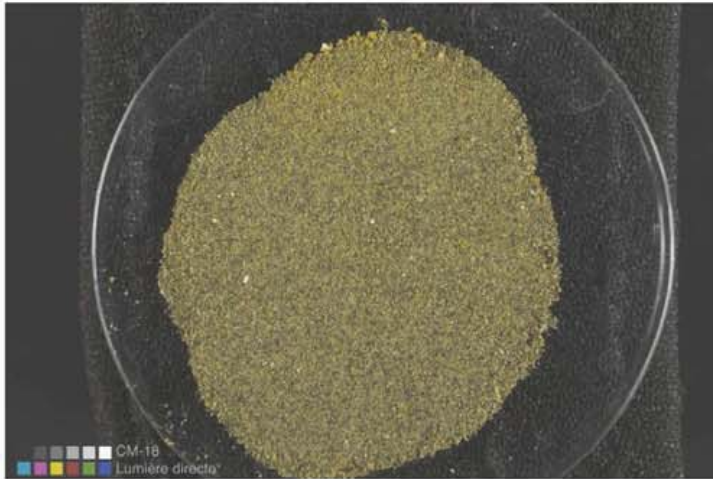
Microscope photo 2



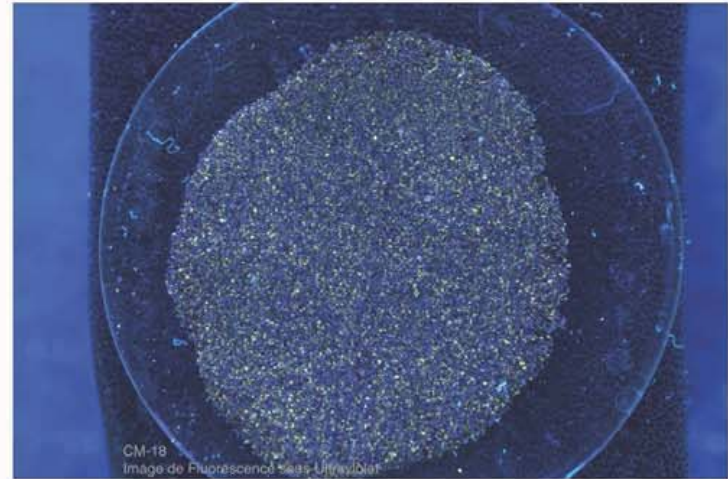
Microscope photo 3



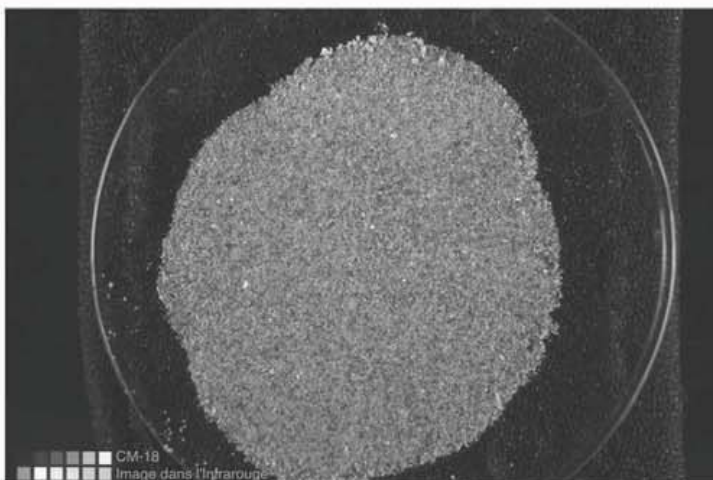
Visible light (VIS)



Ultraviolet light (UVL)

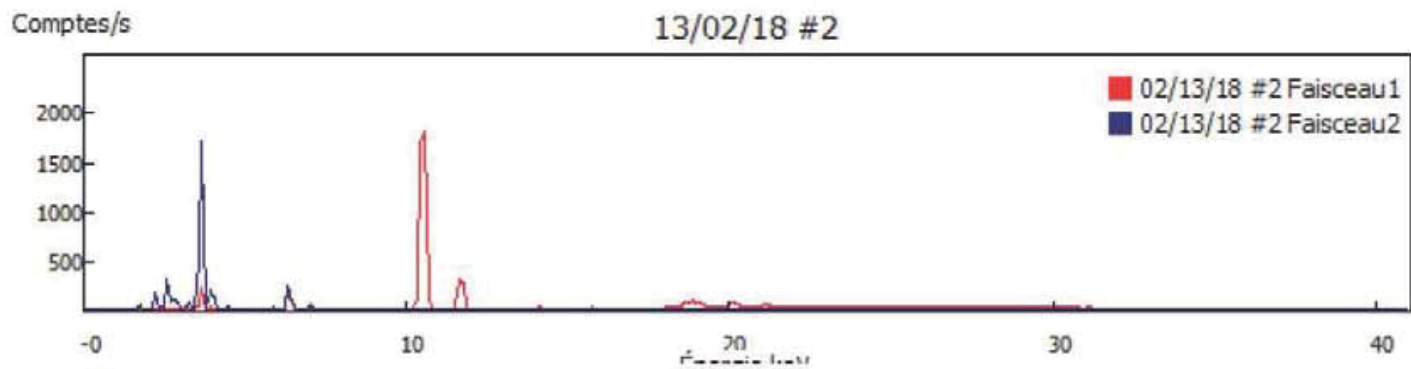


Infrared light (IR)



Infrared false colour (IRfc)





Chemical elements

Light elements (60.35%)
Other: Ca (13.13%), Si (9.56%), Mg (7.5%), S (2.51%), Al (2.39%),
As (1.9%), Fe (1.74%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

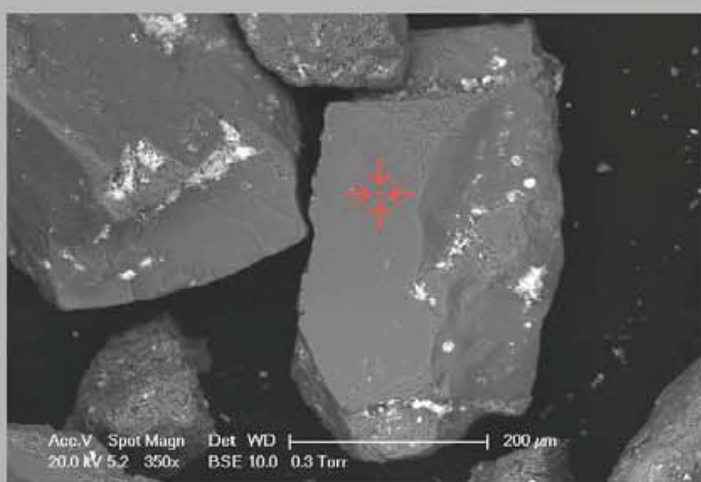
Conclusion

Pt 1: Chemical elements

Magnification: 350

Pt 1: Na, Mg, Al, Si, K / Si, Al

Pt 1: BSE image

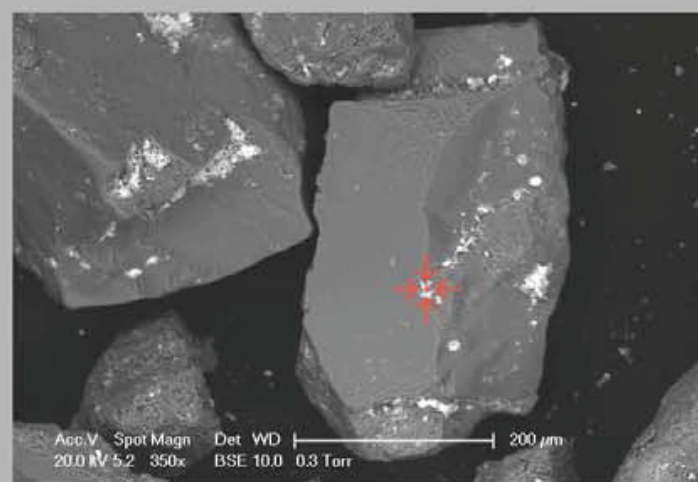


Pt 2: Chemical elements

Magnification: 350

Pt 2: Na, Mg, Al, Si, S, K, Ca, Fe, As / Mg, Si, S

Pt 2: BSE image



Pt 3: Chemical elements

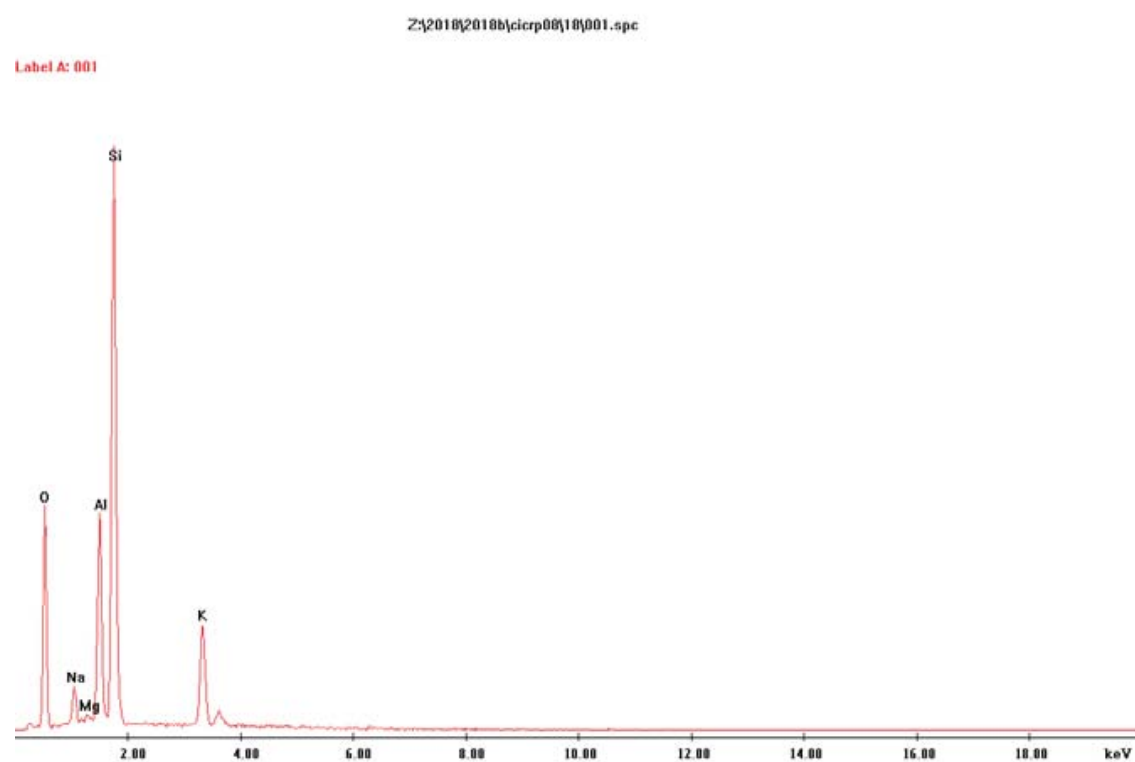
Pt 3: BSE image

Pt 4: Chemical elements

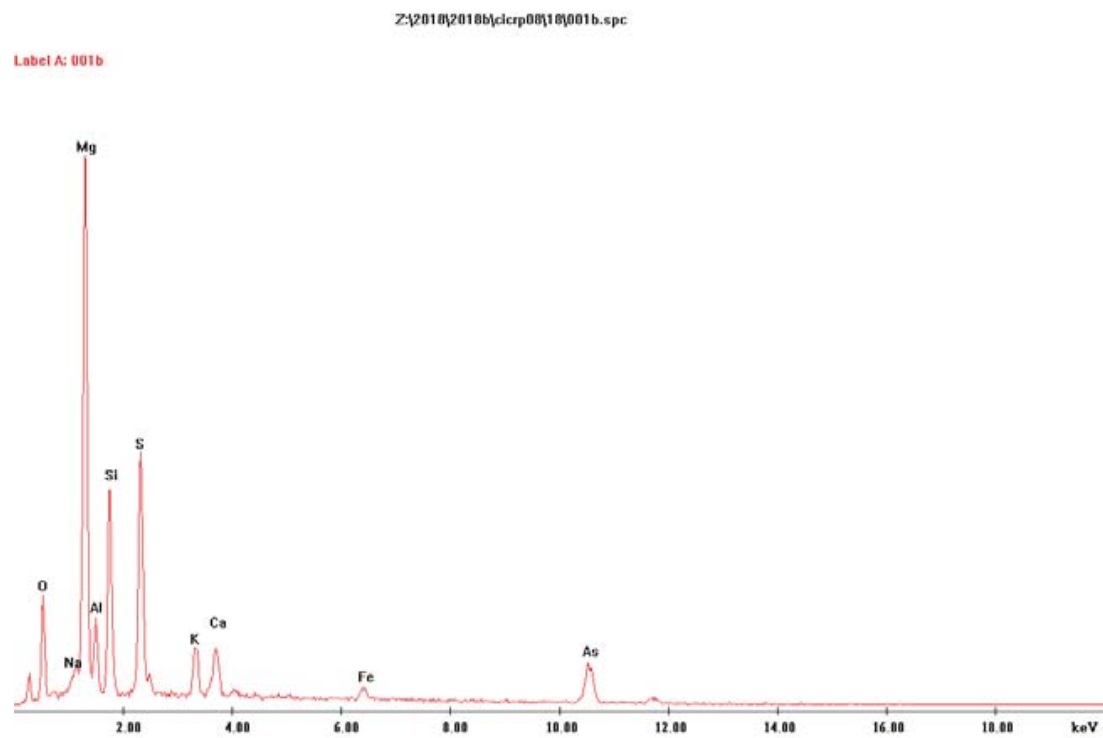
Pt 4: BSE image

GN-2017-CM18

Point 1:



Point 2-1:



GN-2017-CM18

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

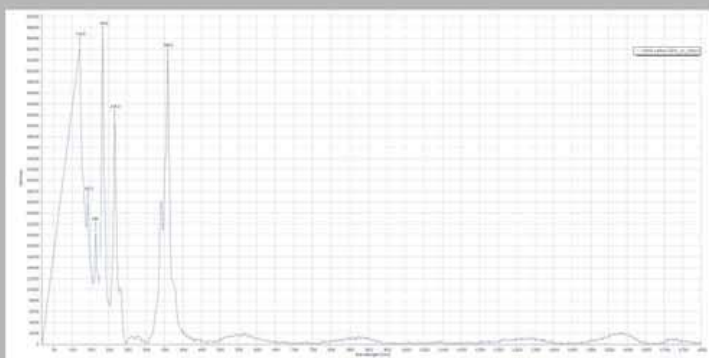
XRD

FTIR

RS

Conclusion

RS spectra 1



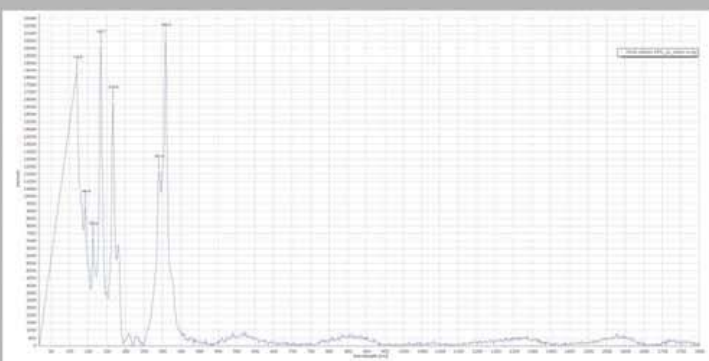
RS results 1

1) Yellow particle

Settings: 25%, 1s, 10 accumulation

Peaks: 118,9 vsh; 142,2 msh; 163,1 msh; 183,6 vsh; 216,3 vsh; 359,4 vsh.

RS spectra 2



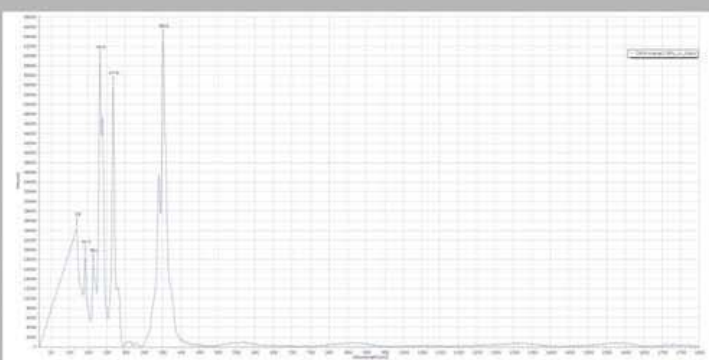
RS results 2

2) Yellow particle

Settings: 25%, 1s, 10 accumulation

Peaks: 118,9 vsh; 142,4 msh; 163,5 msh; 183,7 vsh; 216,8 vsh; 341,9 msh; 359,3 vsh.

RS spectra 3



RS results 3

3) Orange particle

Settings: 25%, 1s, 10 accumulation

Peaks: 119 msh; 141,9 wsh; 164,2 wsh; 181,6 vsh; 217,6 vsh; 352,5 vsh.

Summary

- 1) Yellow particle - realgar
- 2) Yellow particle - realgar
- 3) Orange particle - realgar

GN-2017-CM31

Sample information

Location of sample

Northern part of C18 / content of barrel 3

Date of recovery (YYYY-MM-DD)

2014-08 (unknown day)

Condition upon recovery

Recovered in summer of 2014 when the barrel was emptied

Sample description

Powder of fine consistency

Colour

Red

Storage condition

Kept in the lab and exposed to air to dry out then packed in plastic bag

Cross / thin section

/

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

No

UVL-VIS-IR-IRfc

No

XRF

No

SEM-EDX

Yes

XRD

No

FTIR

Yes

RS

Yes

UHPLC

n/a

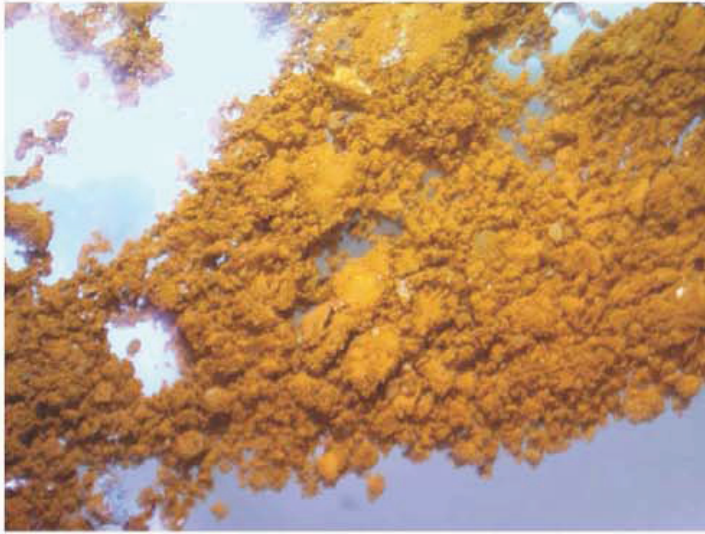
Notes

/

To conduct in future projects

/

Microscope photo 1



Texture description

Binocular observation:

Red fine-grained particles.

Microscope photo 2

Microscope photo 3

GN-2017-CM31

Microscope

LVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

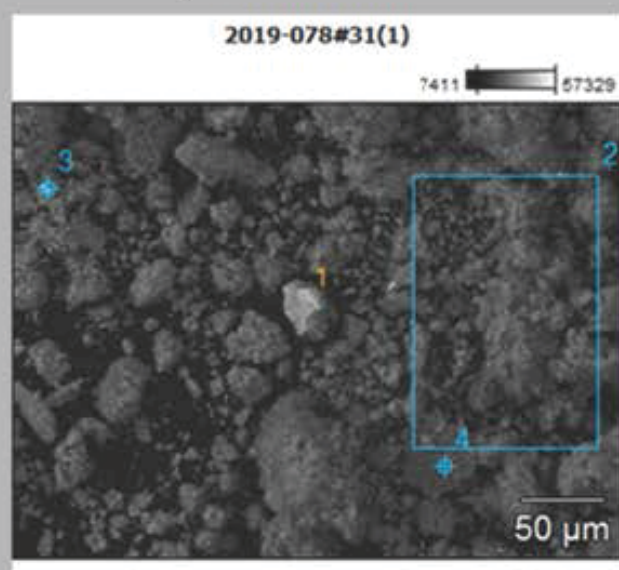
Conclusion

Pt 1: Chemical elements

Magnification: 350

Pt 1: C, Al, Si, S, K, Ba, Fe / **O, Al, S, Ba, Fe**

Pt 1: BSE image

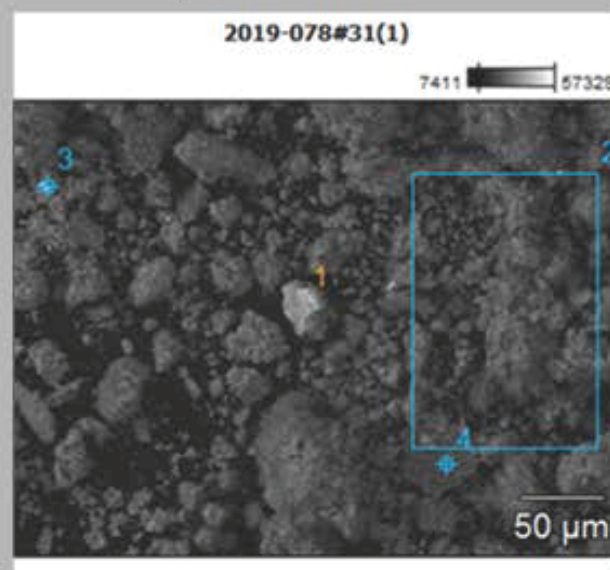


Pt 2: Chemical elements

Magnification: 350

Se 2: C, F/Fe, Na, Mg/As, Al, Si, P, S, Cl, K, Ca, Ba, Fe, As / **O, Al, Fe**

Pt 2: BSE image

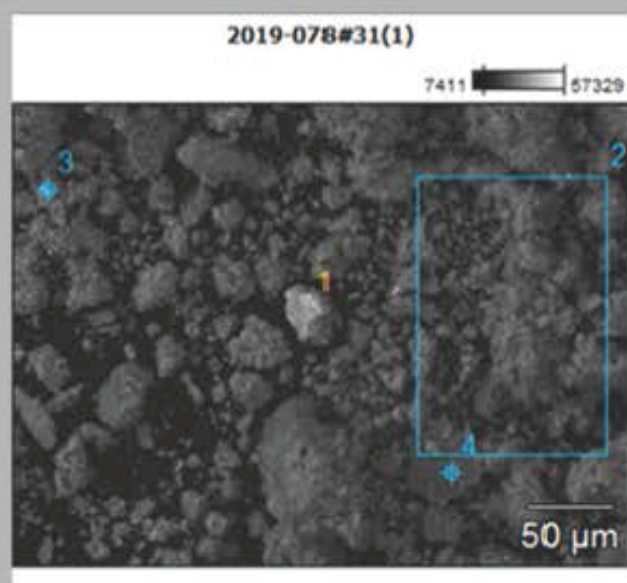


Pt 3: Chemical elements

Magnification: 350

Pt 3: C, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe / **C, O, Al, Fe**

Pt 3: BSE image

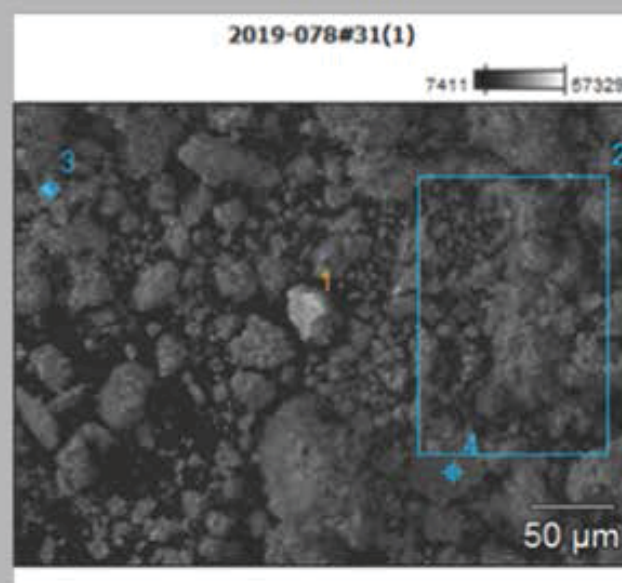


Pt 4: Chemical elements

Magnification: 350

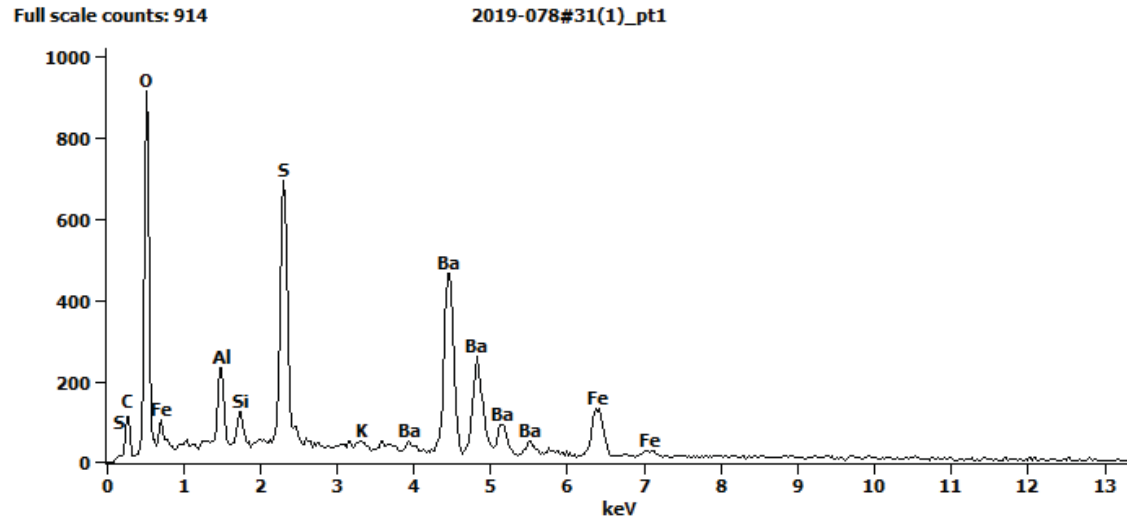
Pt 4: C, Na, Mg, Al, Si, P, S, Cl, K, Fe, As / **O, Al, Si**

Pt 4: BSE image

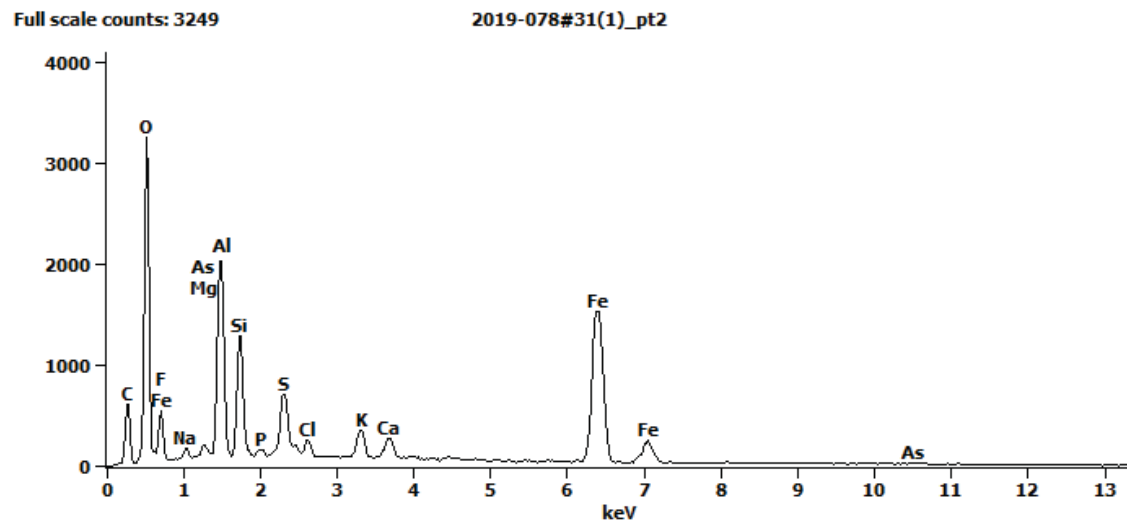


GN-2017-CM31

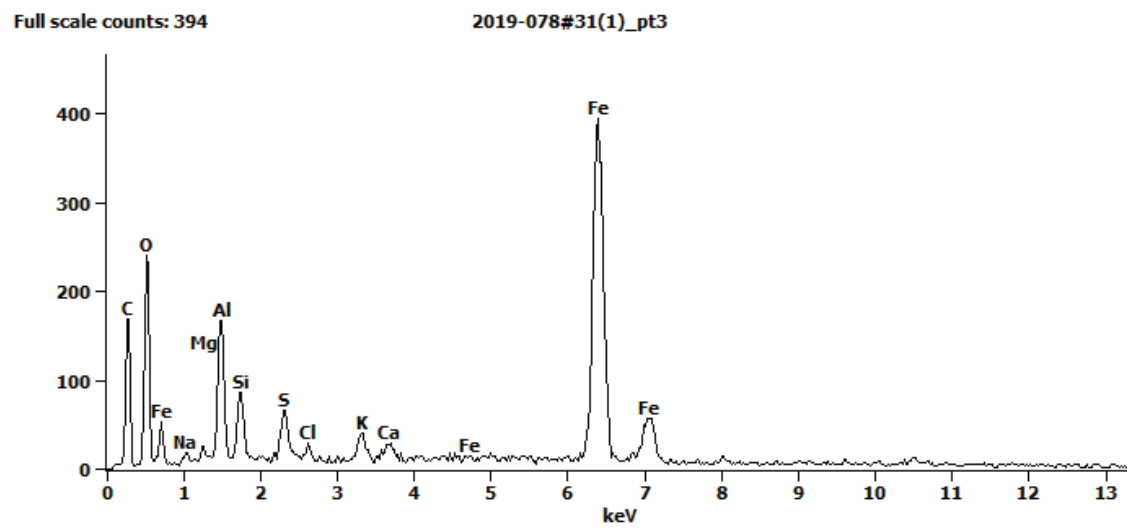
Point 1:



Surface area 2:

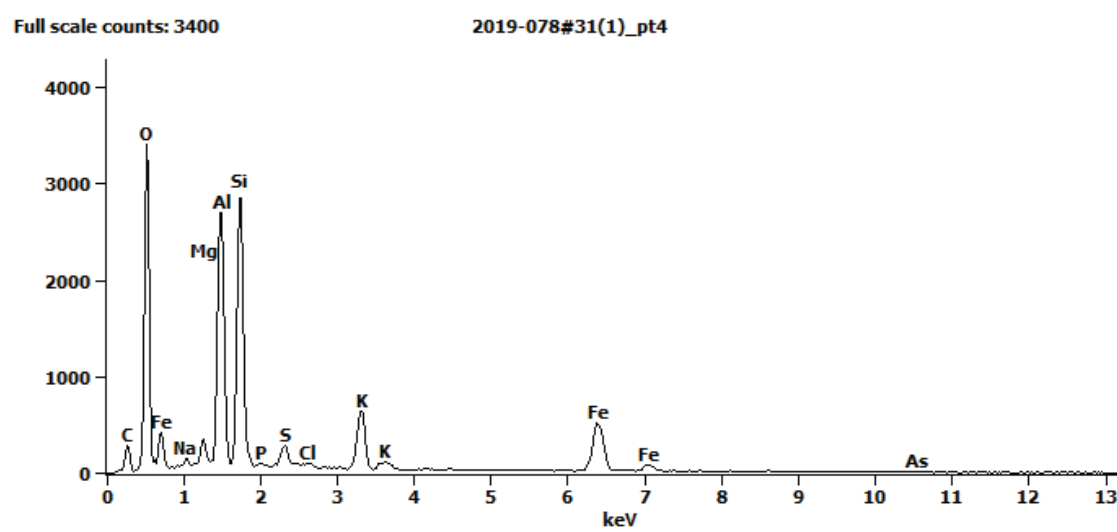


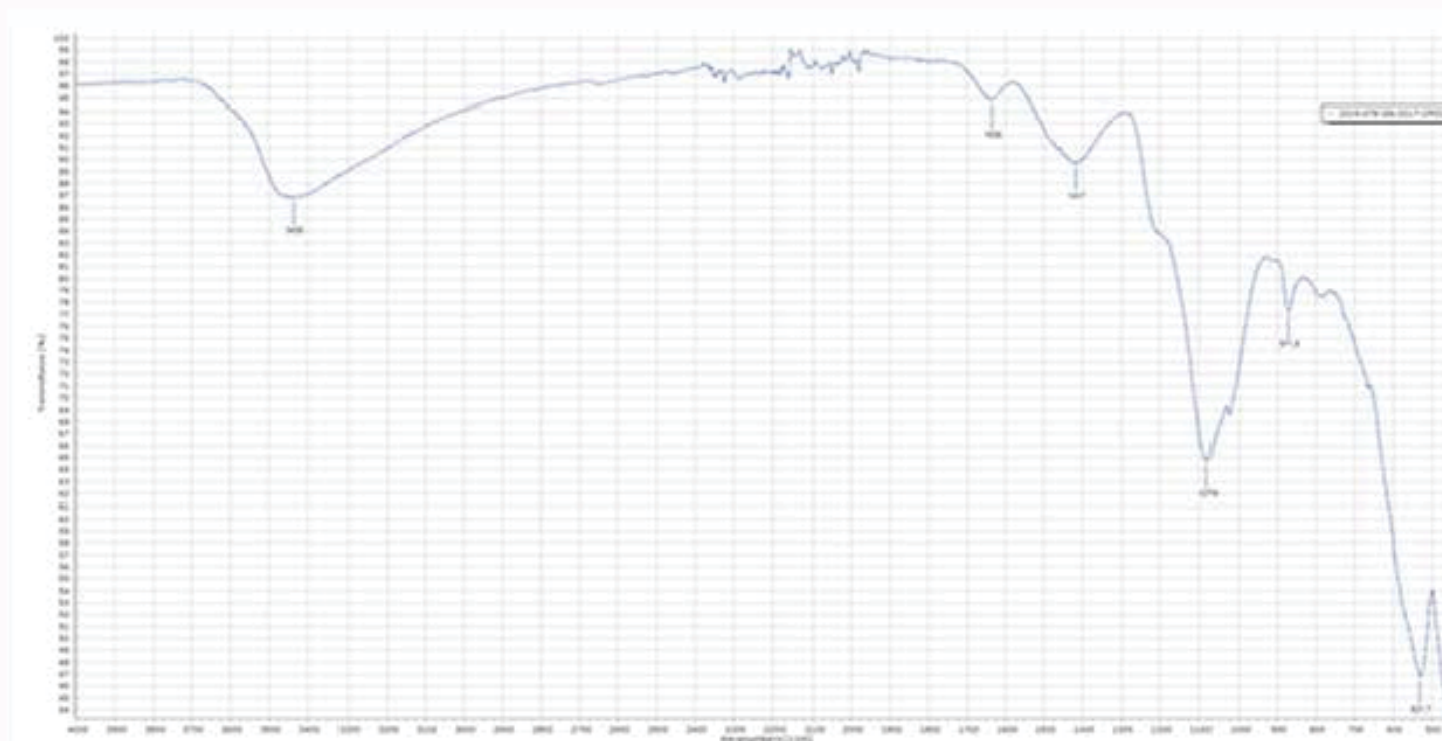
Point 3:



GN-2017-CM31

Surface area 4:





FTIR results

Absorption bands visible on: **3435 wb**; **1636 w**; 1417 wh; 1189 wsh; 1079 vsh; 1018 msh; 871 msh; 792 wsh; **527 vsh**.

* Hematite: reference in IRUG Database, sample number IMP00364 <http://www.irug.org/jcamp-details?id=824>

Corresponding absorption bands: **3600 – 3000 b (3446 peak)**; **1614 w**; **538 vsh**; **468 vsh**.

* Ochre, iron oxide: reference in IRUG Database, sample number IMP00023 <http://www.irug.org/jcamp-details?id=1956>

Corresponding absorption bands: 1452 w; 1162 w; 1033 vsh; 920 msh.

* Silicon oxide: reference Reference Čiuladienė et al. 2018, p. 248.

Corresponding absorption bands: 1022-1077 vsh (in spectra 1079 vsh; 1018 msh)

* 792 msh - unknown

Note: Also see the reference to red ochre in Čiuladienė et al. 2018, Fig. 4.

Corresponding absorption bands 1030 sh, 795 w, 531 sh, 431 sh)

The weak broad band positioned at 1482, could be calcium carbonate (Cornell & Schwermann 2003, p. 143)

(b - broad; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM31

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

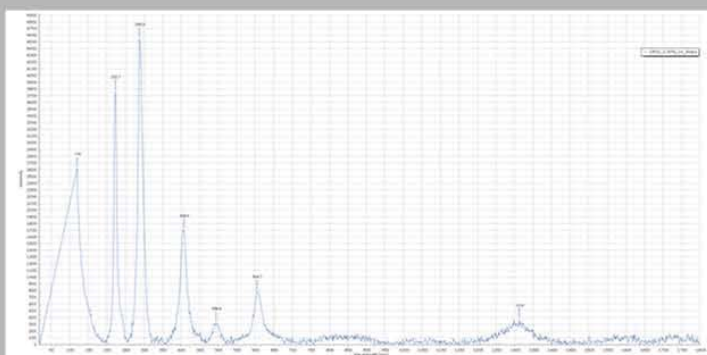
XRD

FTIR

RS

Conclusion

RS spectra 1

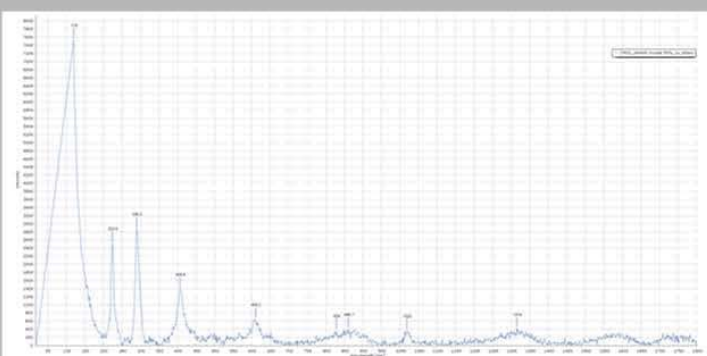


RS results 1

Settings: 30%, 1s, 30 accumulation

Peaks: 119 m; 222,7 s; 288,9 vs; 406,4 m; 495,5 w;
604,7 w; 1312 w.

RS spectra 2



RS results 2

Settings: 30%, 1s, 40 accumulation – whiteish crystal

Peaks: 119 s; 223,8 m; 290,2 m; 405,9 m; 608,2 w;
860 w; 1020 w, 1315 w.

RS spectra 3

RS results 3

Summary

The Raman spectra corresponds to red ochre - Iron (III) oxide chromophore (Fe_2O_3 + clay + silica). Band wavenumbers and relative intensities: 220 vs; 286 vs; 402 m; 491 w; 601 w (Bell, Clark & Gibbs 1997, p. 2174).

The intensive peak at 119 cm^{-1} suggests existence of the lead-based component. Reference: lead based pigments of IRUG database. Wide massive peak from 1200 to 1400 cm^{-1} is associated to clay minerals, including the peak on 1325 cm^{-1} . Wide massive peak from 750 to 950 cm^{-1} and weak peak 1020 cm^{-1} are not identified.

GN-2017-CM33

Sample information

Location of sample

C16 or B16

Date of recovery (YYYY-MM-DD)

2014-08

Condition upon recovery

Recovered from the site in a plastic bag, repacked in the laboratory

Sample description

Scarlet lump with silver, needle-like structure

Colour

Scarlet

Storage condition

Soaked in tap water

Cross / thin section

/

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

No

RS

No

UHPLC

n/a

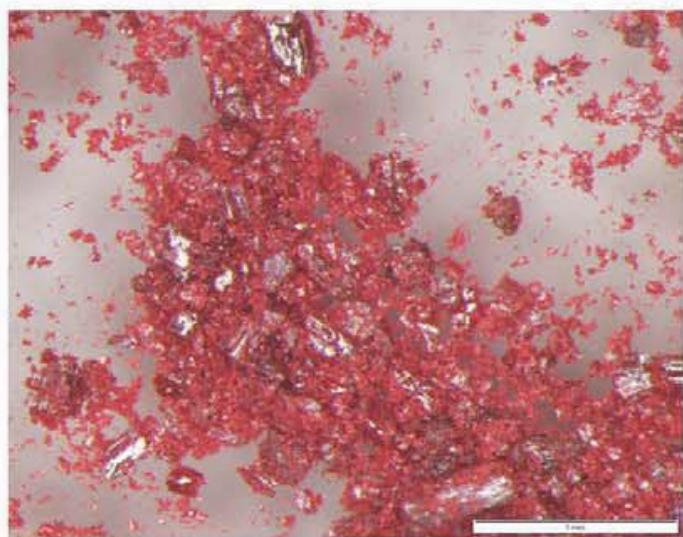
Notes

/

To conduct in future projects

FTIR, RS

Microscope photo 1

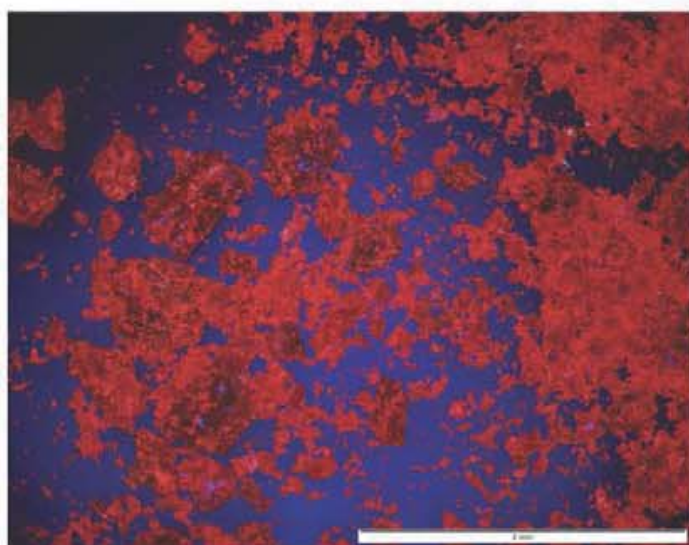


Texture description

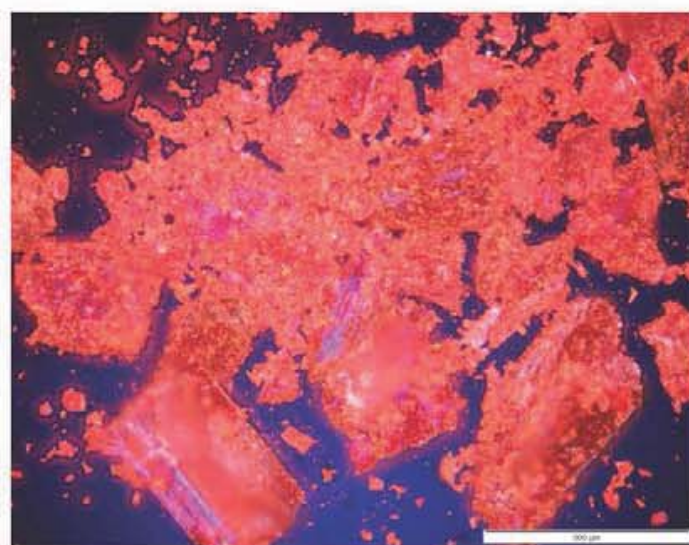
Regular, high relief scarlet particles of different sizes. Average of 300-500 μm .

- 1) Binocular;
- 2) Stereo microscope with UV illumination;
- 3) Stereo microscope with UV illumination.

Microscope photo 2



Microscope photo 3



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

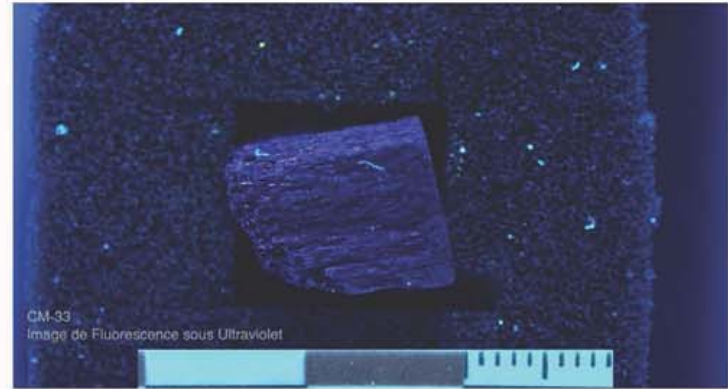
RS

Conclusion

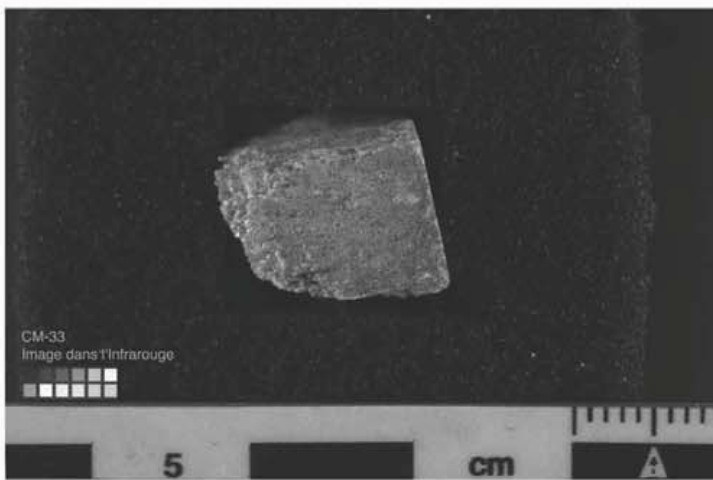
Visible light (VIS)



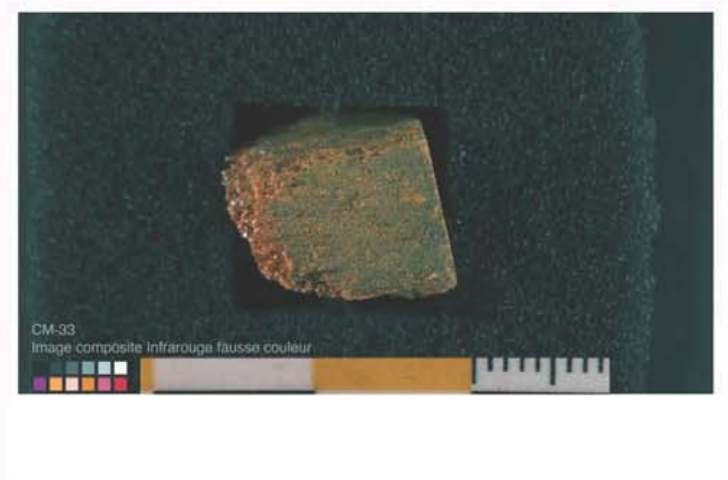
Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



GN-2017-CM33

Microscope

UVL-VIS-IR-IR.fc

XRF

SEM-EDX

XRD

FTIR

RS

Conduction

Chemical elements

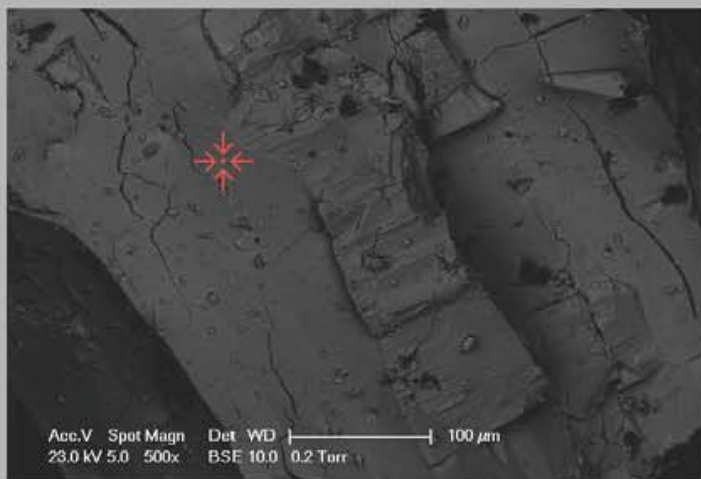
Light elements (11.37%)
Other: Hg (55.67%), S (23.4%), P (1.7%), Si (1.46%), K (1.23%),
Ca (0.66%), Ca (0.59%), Pb (0.11%), Fe (0.1%)

Pt 1: Chemical elements

Magnification: 500

Pt 1: C, Al, Si, S, Hg / S, Hg

Pt 1: BSE image

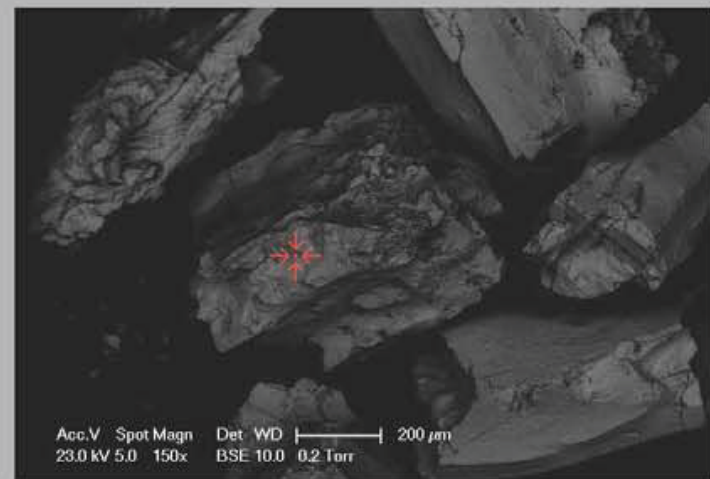


Pt 2: Chemical elements

Magnification: 150x

Pt 2: C, Al, Si, S, Hg / S, Hg

Pt 2: BSE image

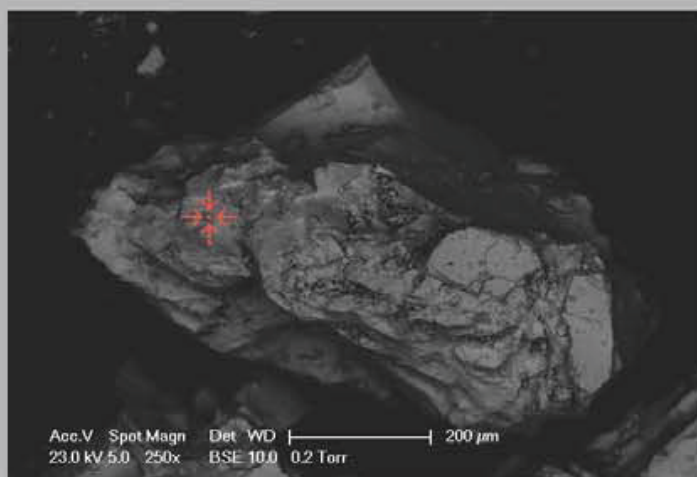


Pt 3: Chemical elements

Magnification: 250

Pt 3: C, Al, Si, S, Hg / S, Hg

Pt 3: BSE image

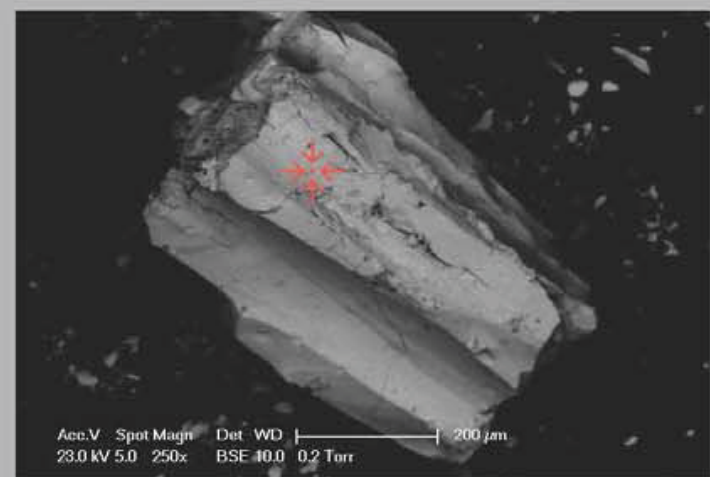


Pt 4: Chemical elements

Magnification: 250

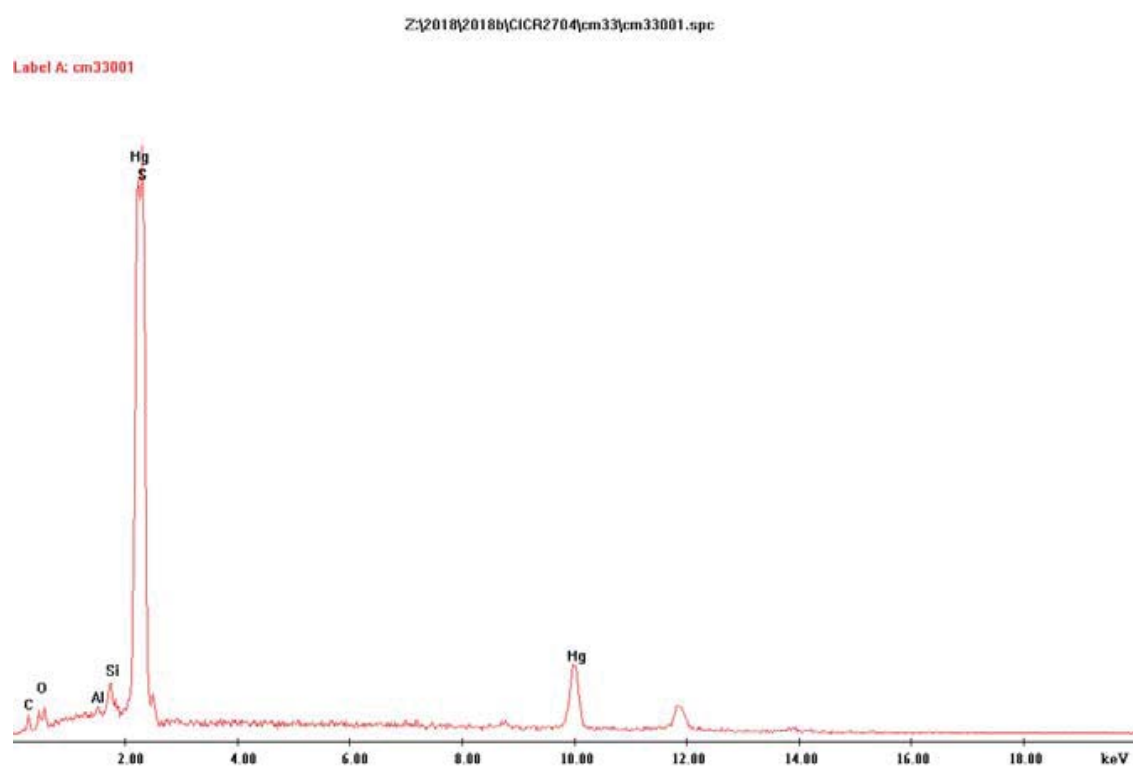
Pt 4: Pt 1: C, Al, Si, S, Hg / S, Hg

Pt 4: BSE image

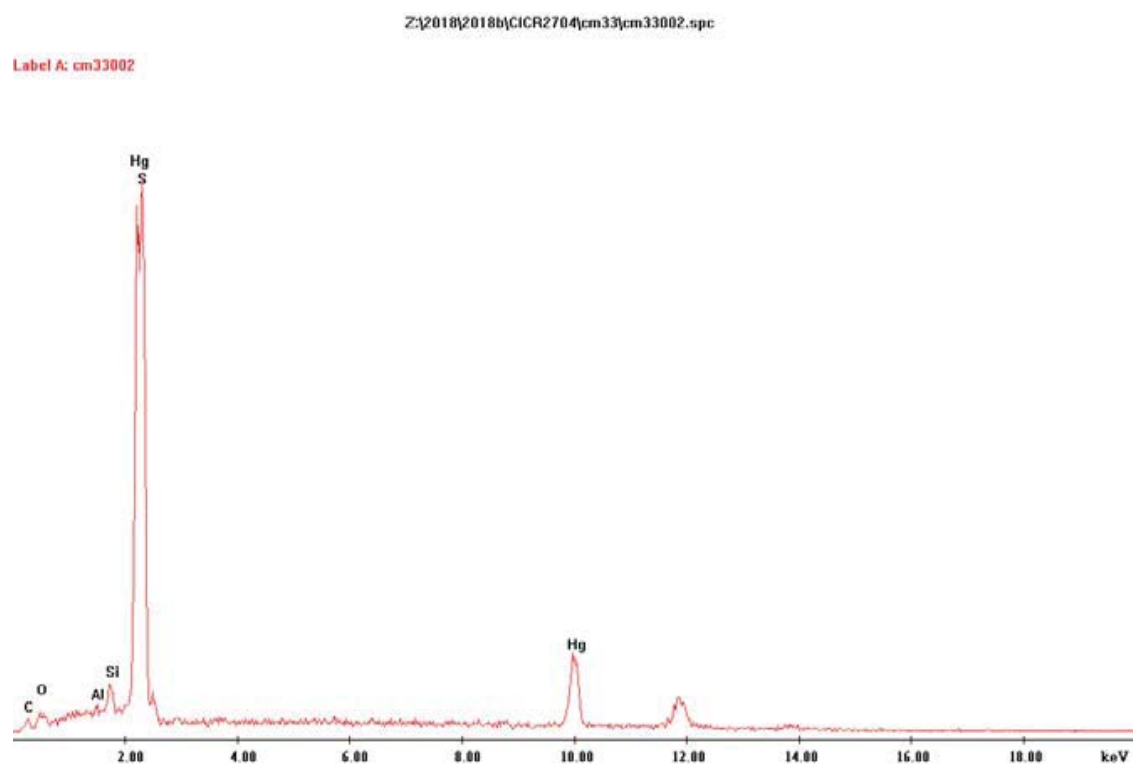


GN-2017-CM33

Point 1:

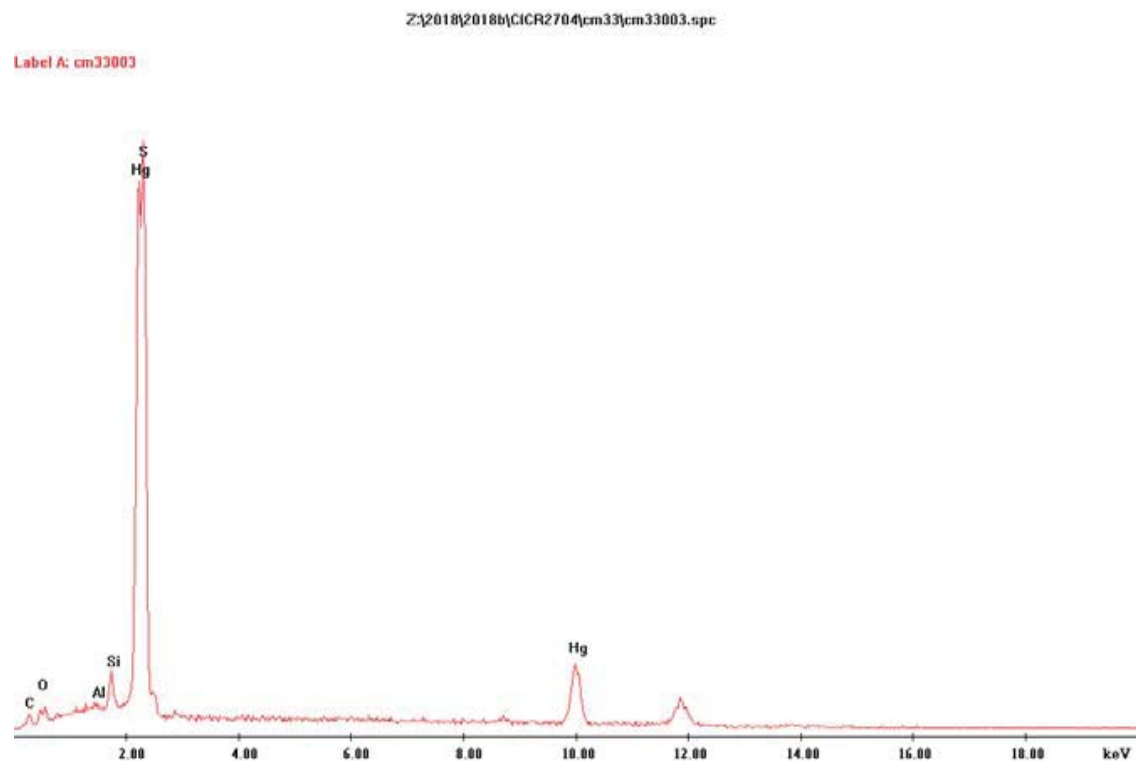


Point 2:

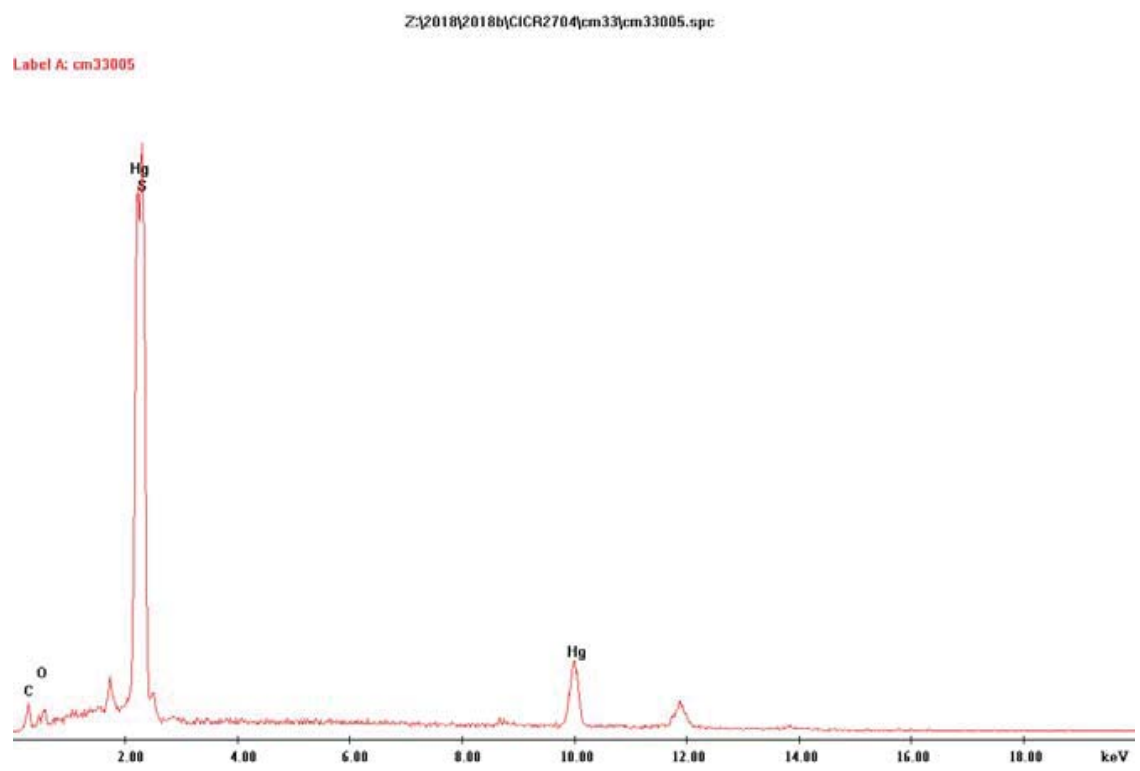


GN-2017-CM33

Point 3:



Point 4:



GN-2017-CM33

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

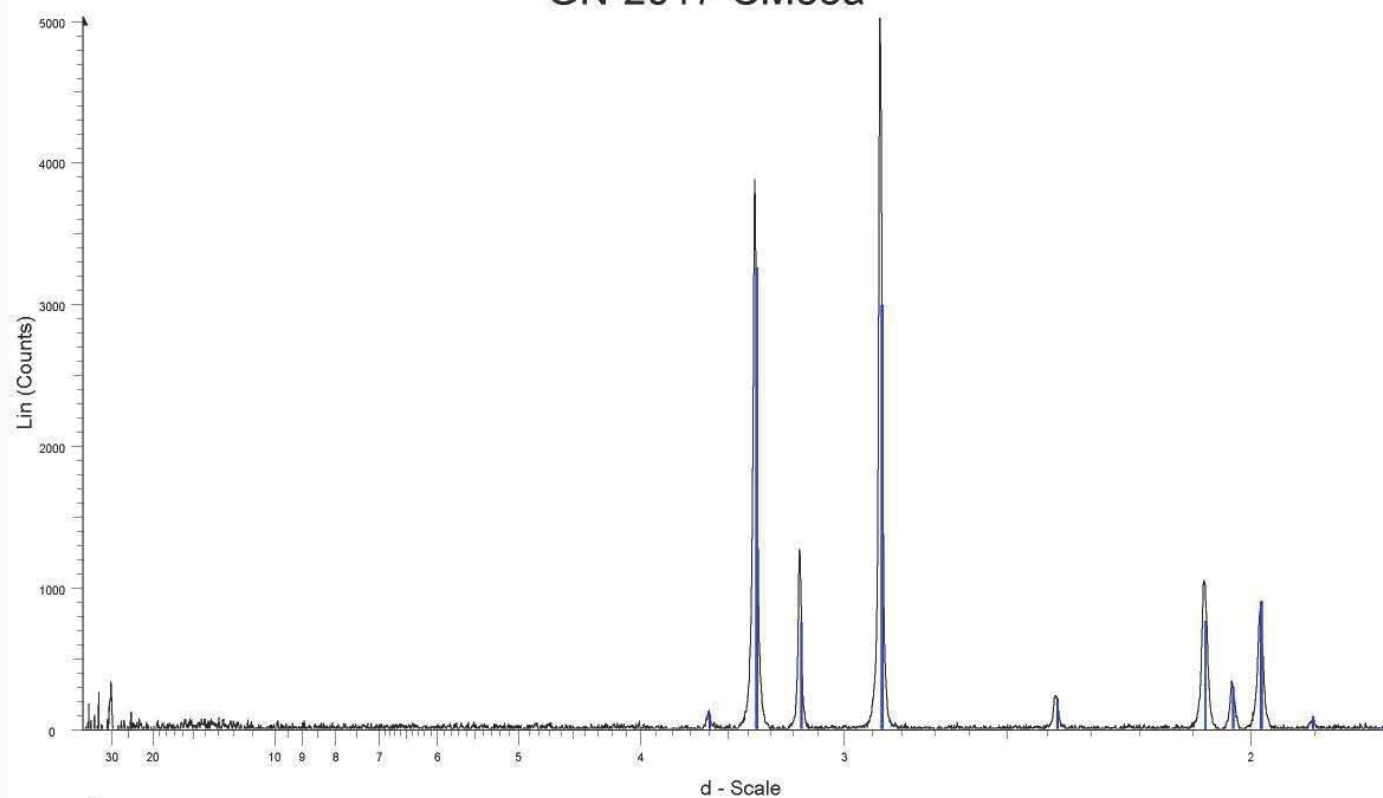
XRD

FTIR

RS

Conclusion

GN-2017-CM33a



GN-2017-CM33a - File: GN-2017-CM33a.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 60.007 ° - Step: 0.020 ° - Step time: 50. s - Temp.: 25 °C (Room) - Time Started: 13 s - 2-Theta: 2.000 ° - Theta: 1.000 ° - Chi: 0.00 ° - Phi: 0
Operations: Background 0.676, 1.000 | Import

01-071-5164 (I) - Cinnabar, syn - HgS - Y: 64.33 % - d x by: 1. - WL: 1.78897 - Hexagonal - a 4.14890 - b 4.14890 - c 9.49470 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3121 (152) - 3 - 141.540 - I/c PDF 12.3 - F

Suggested mineral phases

Mercury sulphide, HgS (100%)

GN-2017-CM35

Sample information

Location of sample

D16

Date of recovery (YYYY-MM-DD)

2014-08-01

Condition upon recovery

Recovered in plastic bag, soaked in tap water, and dried in the lab

Sample description

Lump of minium (lead III oxide) with alteration layer. Height 5 cm; length 9.6 cm; width 6 cm; weight 796.9 g

Colour

Orange / red core and grey alteration layer

Storage condition

Packed in plastic zip-bag

Cross / thin section

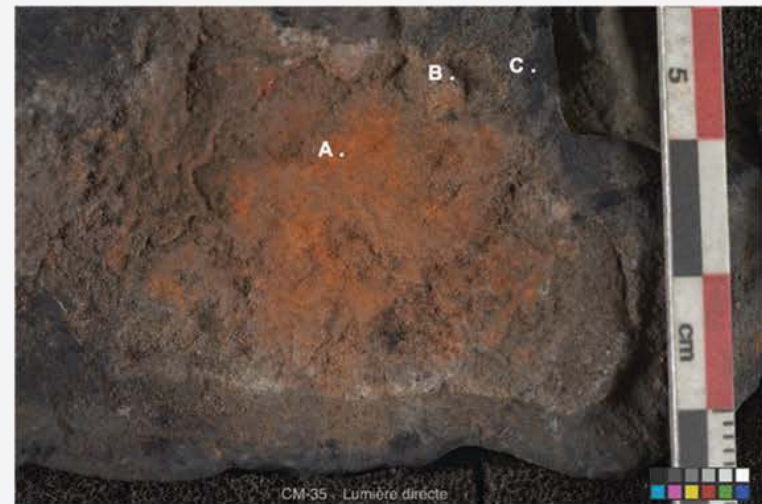
/

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

Yes

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

No

RS

No

UHPLC

n/a

Notes

Samples a (red core), and c (alteration layer) were analyzed.
Sample b (middle layer) was not analyzed.

To conduct in future projects

FTIR, RS

Microscope photo 1



Texture description

GN-2017-CM35A

Fine-grained texture, SEM shows irregular particles of 5-20 μm .

GN-2017-CM35C

Irregular crystals of approximately 150 μm , with fine grains of different contrast (heterogeneous mixture).

- 1) A - orange/red core, binocular, 0.8x;
- 2) B - light gray middle layer, binocular, 0.8x;
- 3) C - dark gray external layer, binocular, 0.8x.

Microscope photo 2



Microscope photo 3



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

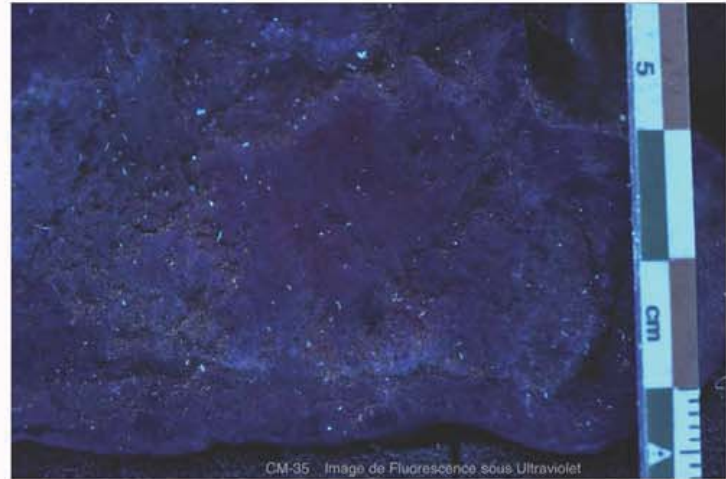
RS

Conclusion

Visible light (VIS)



Ultraviolet light (UVL)

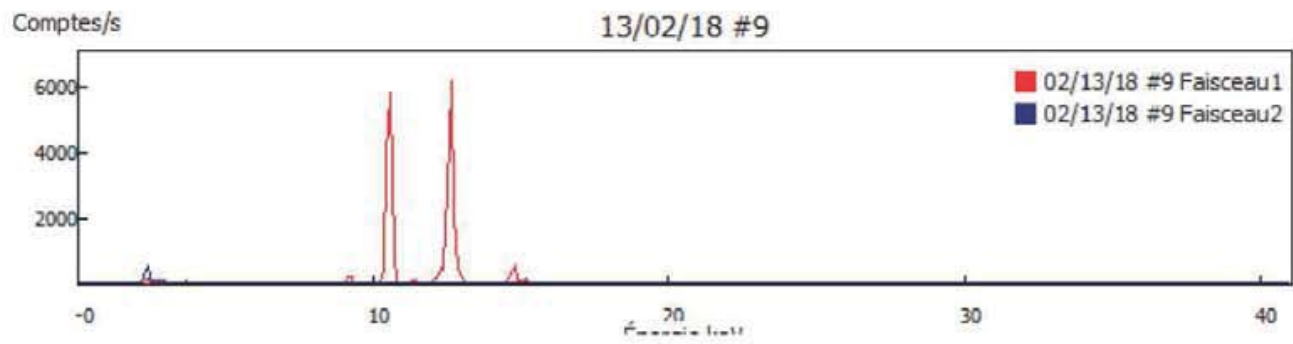


Infrared light (IR)



Infrared false colour (IRfc)





Chemical elements

A (spectra image)

Light elements (22%)

Other: Pb (54.88%), S (15.55%), Ca (2.06%) Si (1.98%), As (1.37%)

C

Light elements (20%)

Other: Pb (45.03%), S (23.60%), Ca (7.78%), Si (1.50%), As (1.13%)

GN-2017-CM35

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

Conclusion

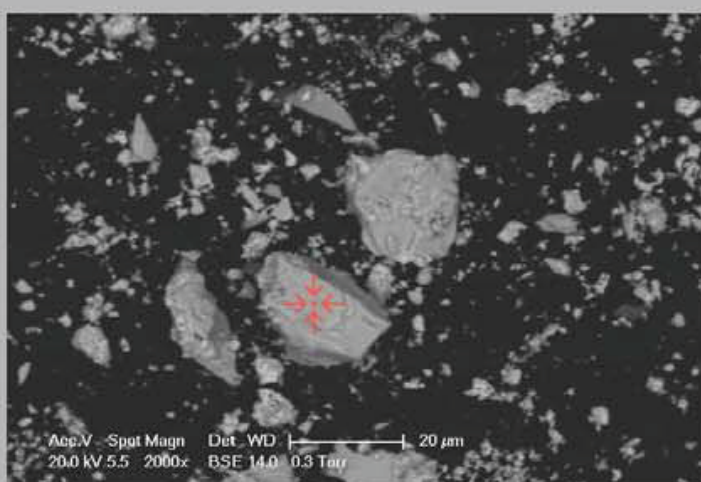
Pt 1: Chemical elements

GN-2017-CM35A

Magnification: 2000

Pt 1: Na, Mg, Al, Cl, Ca, Pb / S / Pb/S

Pt 1: BSE image



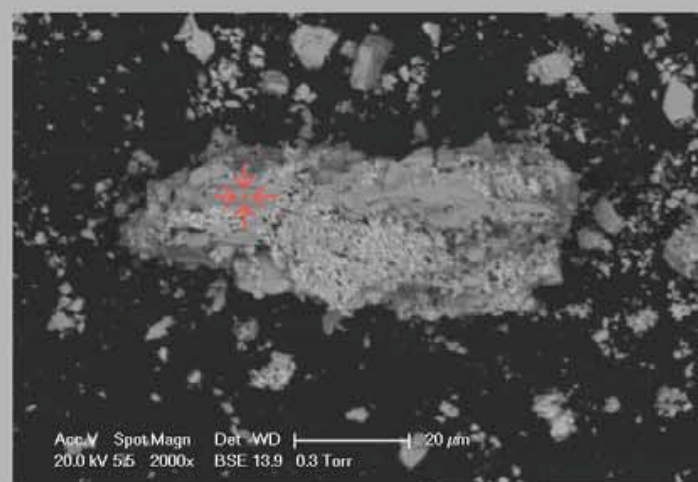
Pt 2: Chemical elements

GN-2017-CM35A

Magnification: 1200

Pt 2: Na, Mg, Al, S, Cl, Ca, Pb / S, Pb

Pt 2: BSE image



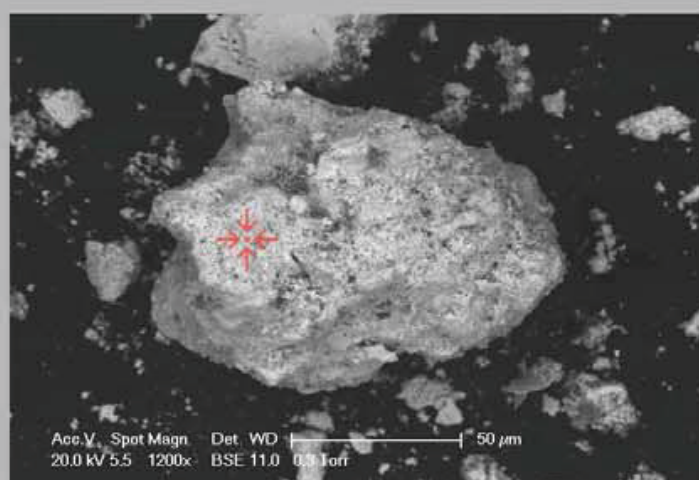
Pt 3: Chemical elements

GN-2017-CM35C

Magnification: 1200

Pt 3: C, Mg, Al, S, Cl, Ca, Pb / Pb/S

Pt 3: BSE image



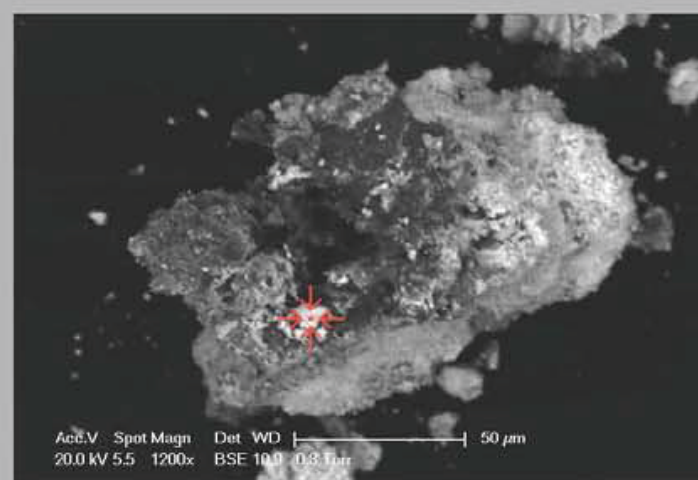
Pt 4: Chemical elements

GN-2017-CM35C

Magnification: 1200

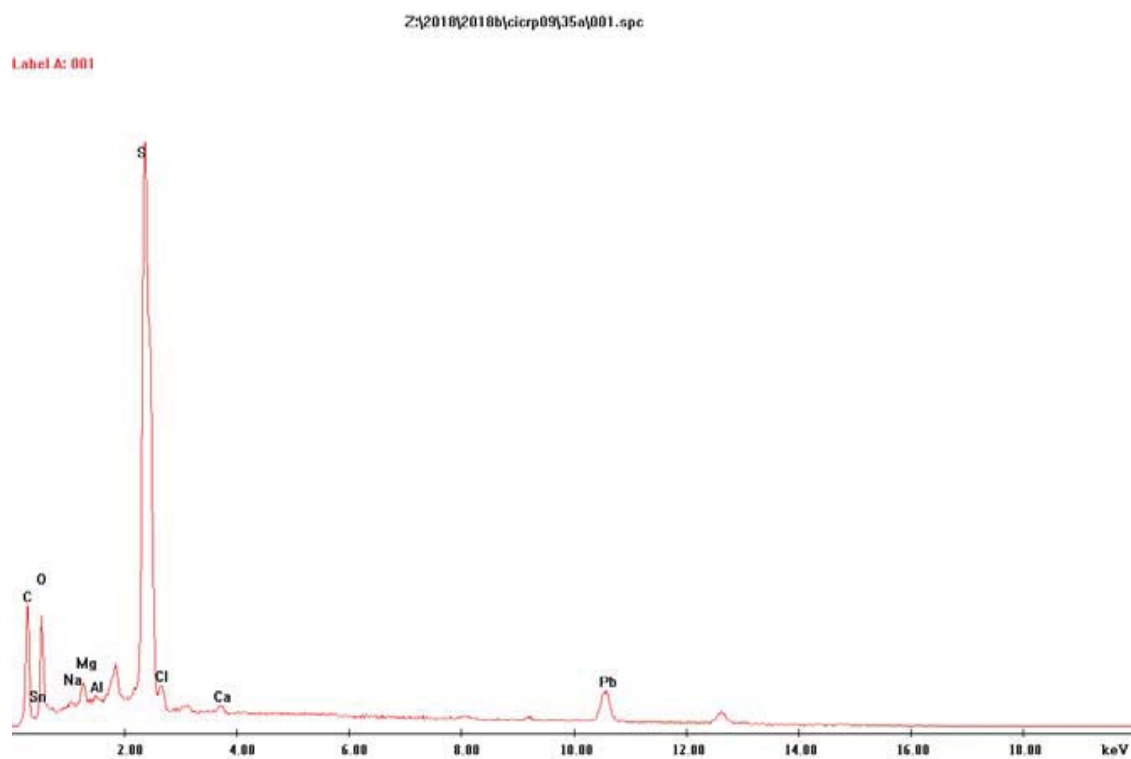
Pt 4: C, S, Cl, Ca, Pb / Ca, Pb

Pt 4: BSE image

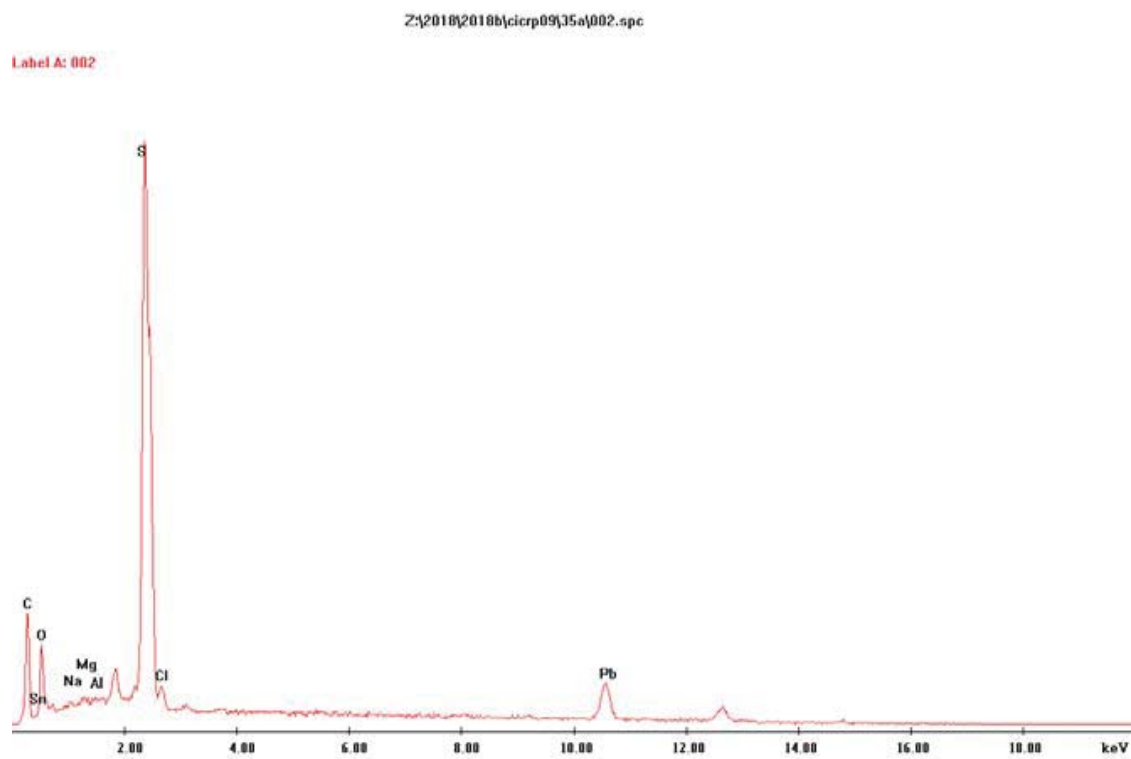


GN-2017-CM35

Point 1 (GN-2017-CM35A)

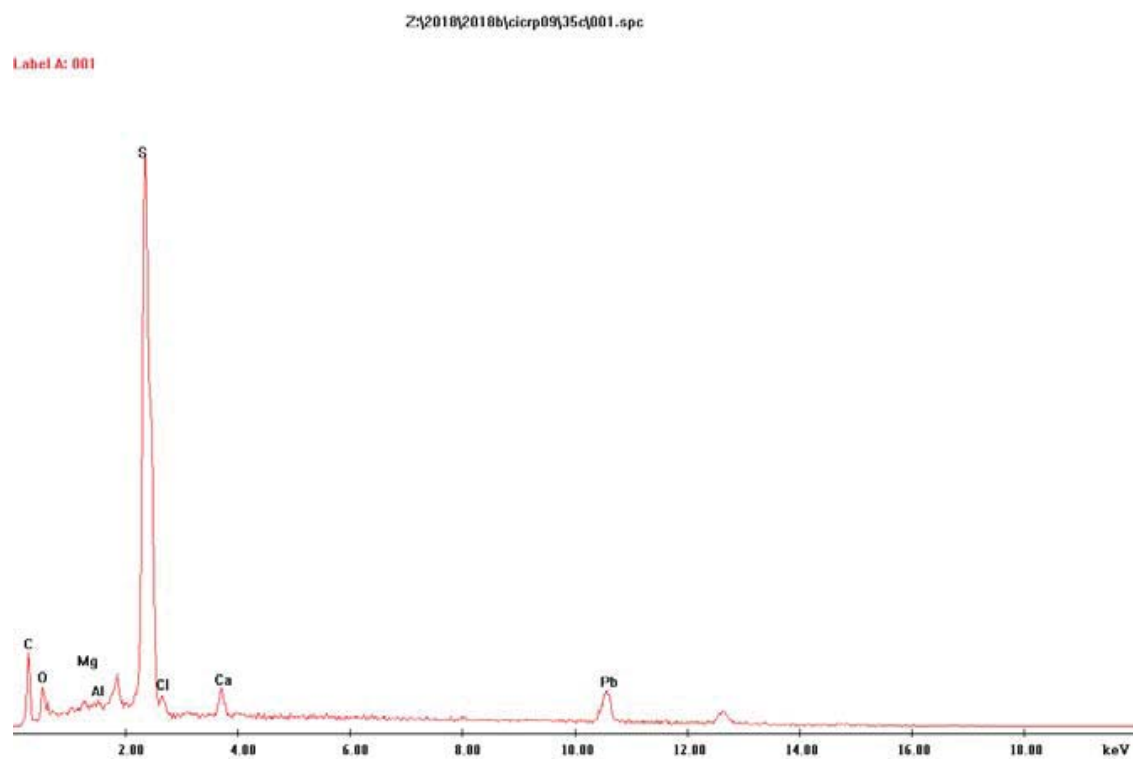


Point 2 (GN-2017-CM35A)

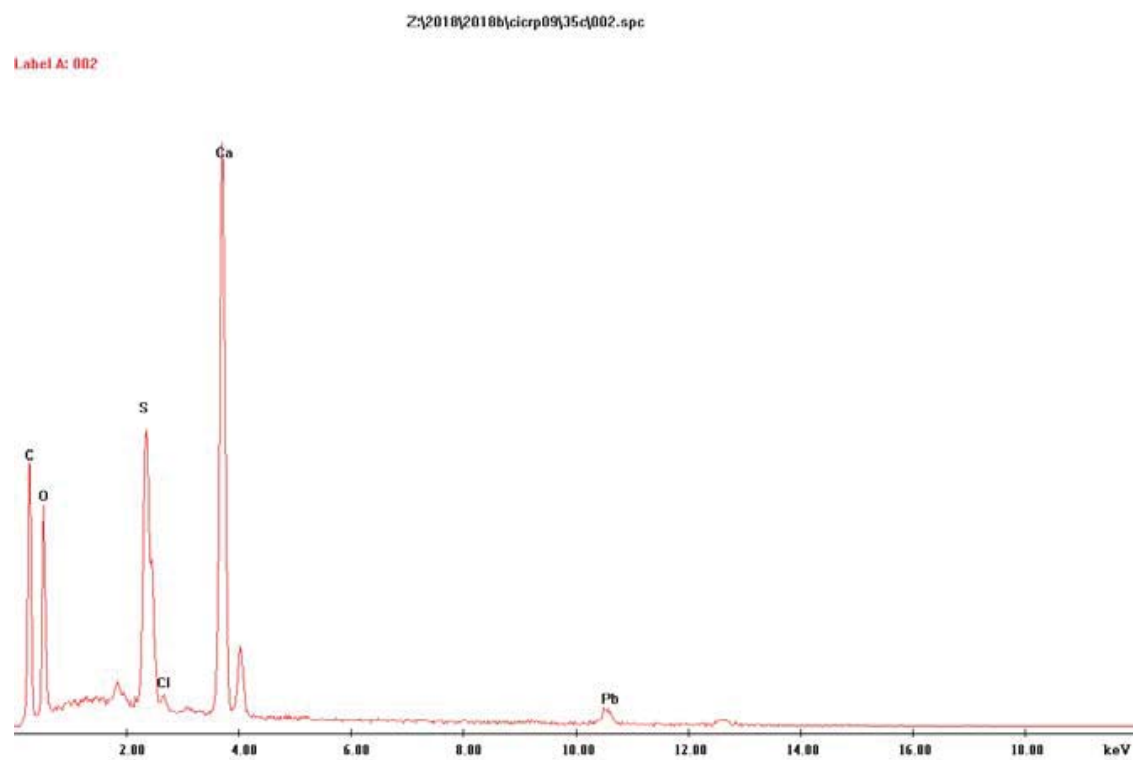


GN-2017-CM35

Point 3 (GN-2017-CM35B)



Point 4 (GN-2017-CM35B)



GN-2017-CM35

Microscope

UVL-VIS-IR-IRfc

XRF

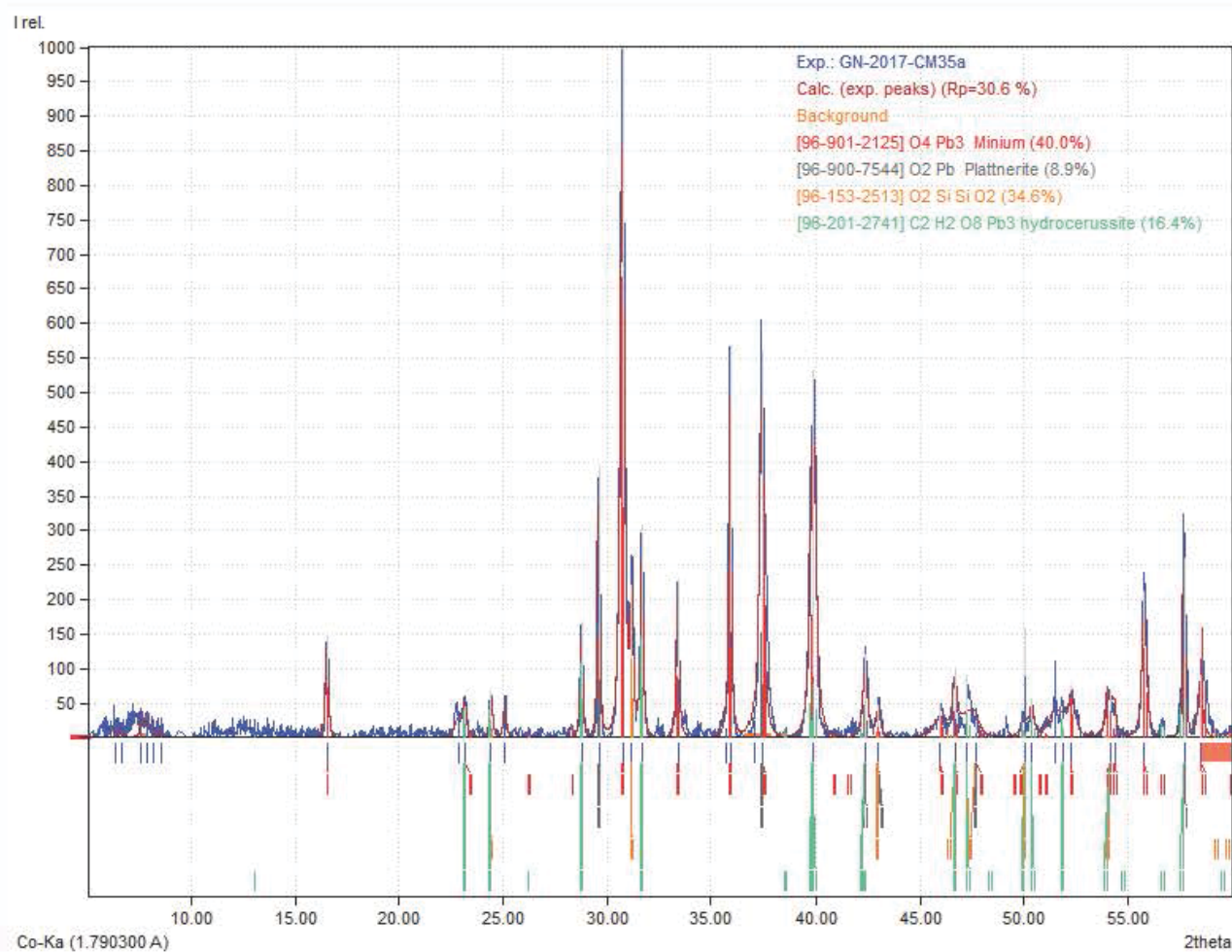
SEM-EDX

XRD

FTIR

RS

Conclusion



Suggested mineral phases

GN-2017-CM35A (image of spectra)

- Minium, Pb_3O_4 (40%)
- Plattnerite, PbO_2 (8.9%)
- Quartz, SiO_2 (34.6%)
- Hydrocerussite, $2Pb(CO_3)_2 \cdot Pb(OH)_2$ (16.4%)

GN-2017-CM35C

- Cerussite, PbO_3 (50.9%)
- Lead sulphide / Galena, PbS (49.1%)

GN-2017-CM36

Sample information

Location of sample

D17

Date of recovery (YYYY-MM-DD)

2017-09-18

Condition upon recovery

Recovered in 2107, kept in the same bag as numerous other samples from the same square

Sample description

Conical lead white ingot with alteration layer. Height 7 cm; max diam. 6.3 cm; min. diam. 3.6 cm; weight 576.4 g

Colour

The core is white, external side is gray, red and black

Storage condition

Kept dry in storage at room temperature

Cross / thin section

/

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

Yes

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

No

SEM-EDX

No

XRD

Yes

FTIR

No

RS

No

UHPLC

n/a

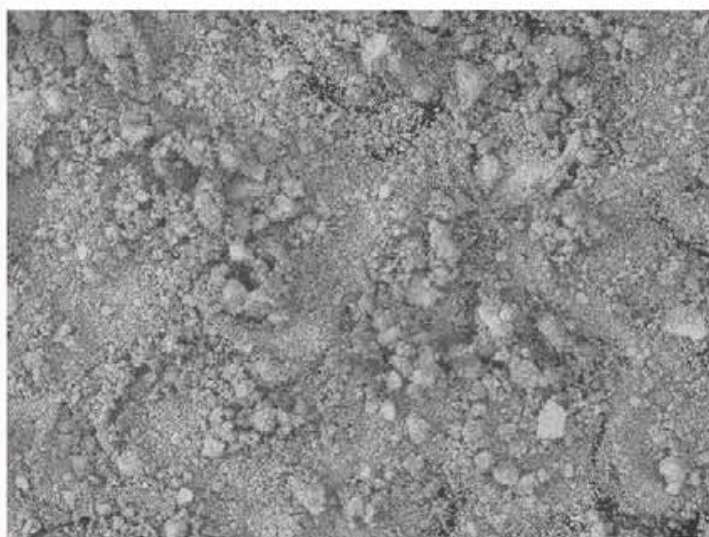
Notes

The sample was cut in half. The core was sampled for aims of SEM-EDX and XRD analyses.

To conduct in future projects

/

Microscope photo 1



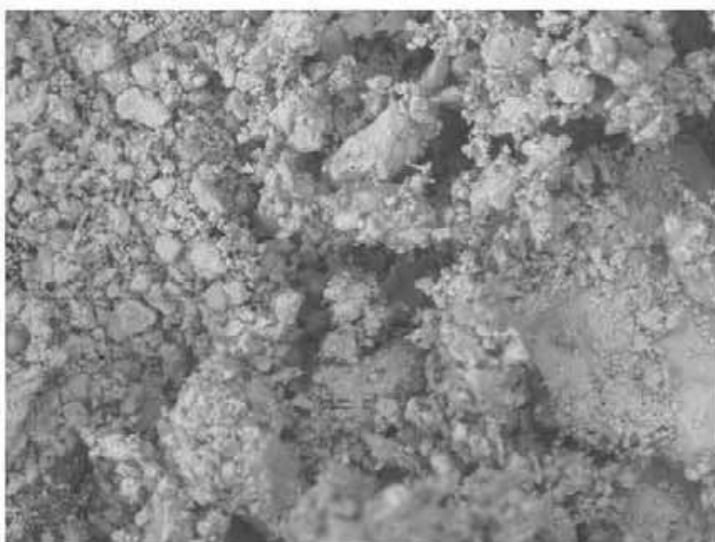
Texture description

SEM observation

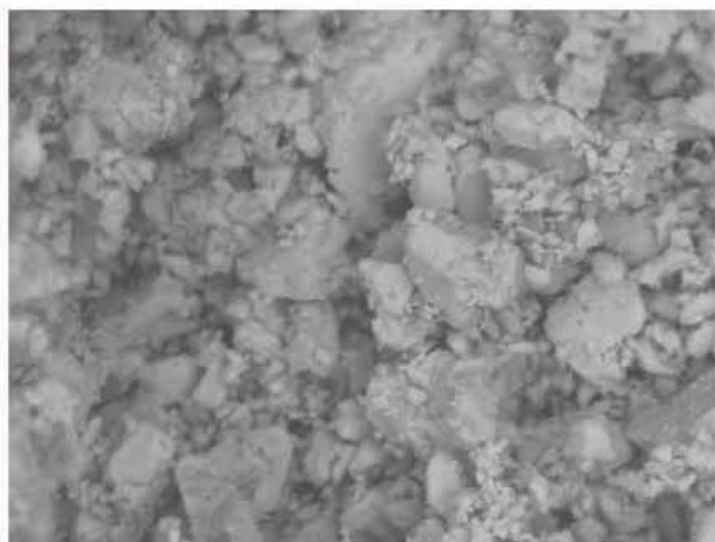
Irregular crystals of 100-200 μm and fine-grained texture.

- 1) Magnification: 100x;
- 2) Magnification: 800x;
- 3) Magnification: 2000x.

Microscope photo 2



Microscope photo 3



Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

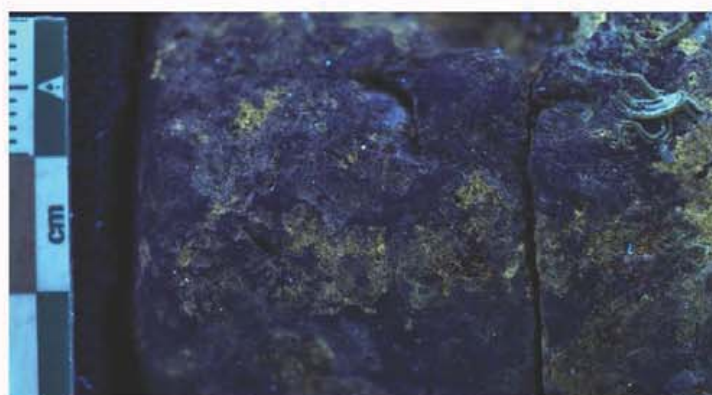
Conclusion

Visible light (VIS)



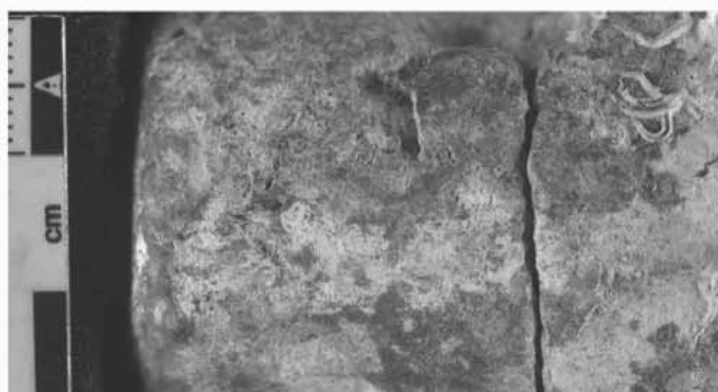
CM-36
Lumière directe

Ultraviolet light (UVL)



CM-36
Image de Fluorescence sous Ultraviolet

Infrared light (IR)



CM-36
Image dans l'infrarouge

Infrared false colour (IRfc)



CM-36
Image composite Infrarouge fausse couleur

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

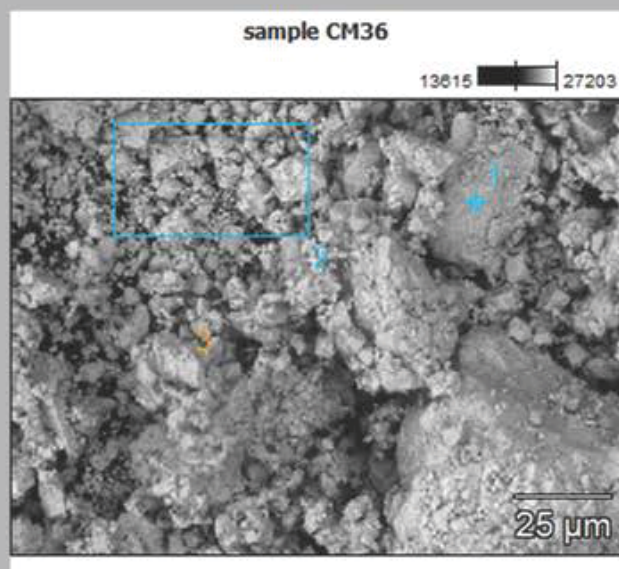
Conclusion

Pt 1: Chemical elements

Magnification: 800

Pt 1: Al, Pb, Cl, Ca / Pb

Pt 1: BSE image

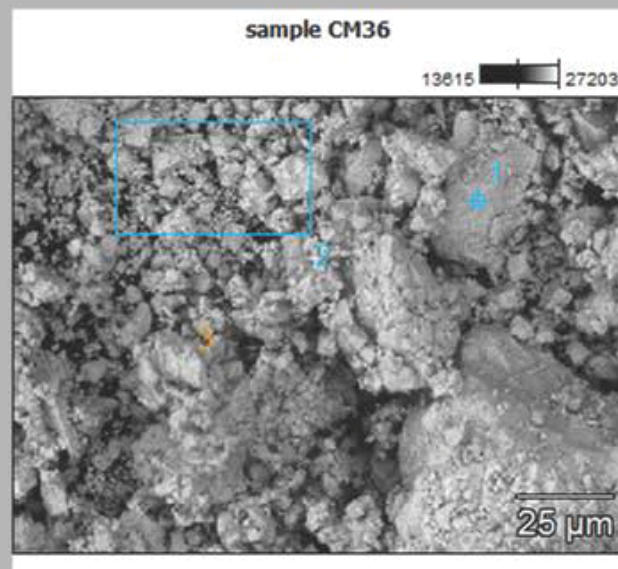


Pt 2: Chemical elements

Magnification: 800

SA 2: Mg, Al, Pb, Cl, Ca / Pb

Pt 2: BSE image

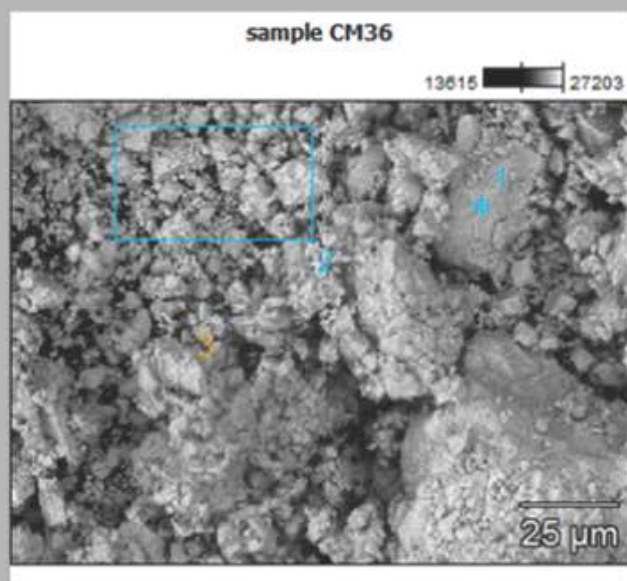


Pt 3: Chemical elements

Magnification: 800

Pt 3: Al, Pb, Cl, Ca / Pb

Pt 3: BSE image

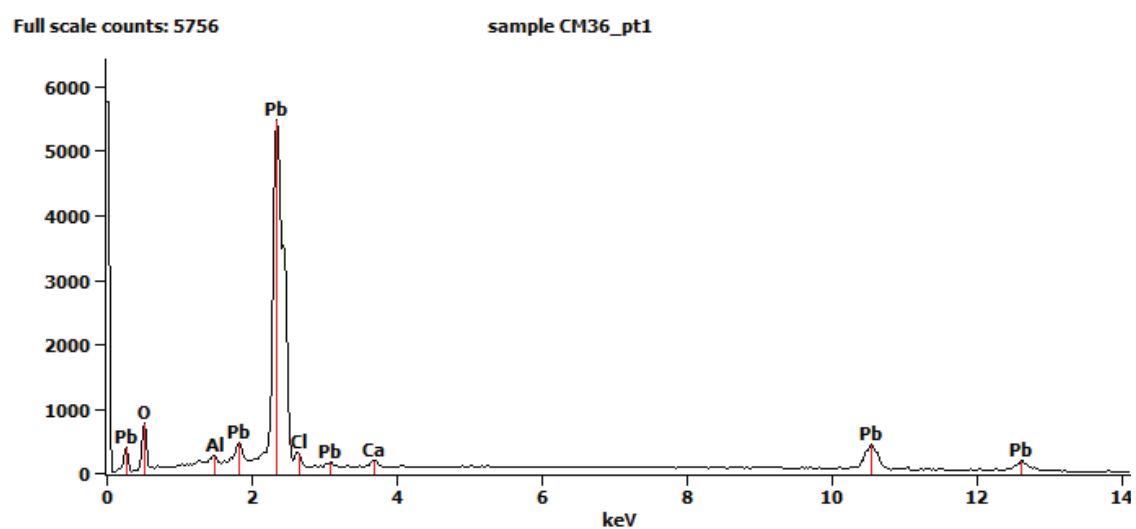


Pt 4: Chemical elements

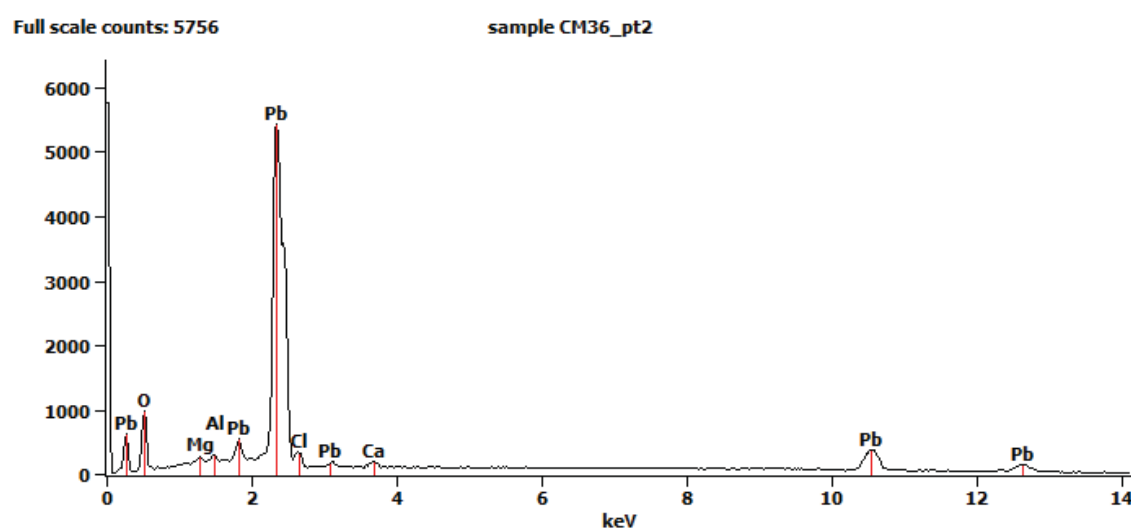
Pt 4: BSE image

GN-2017-CM36

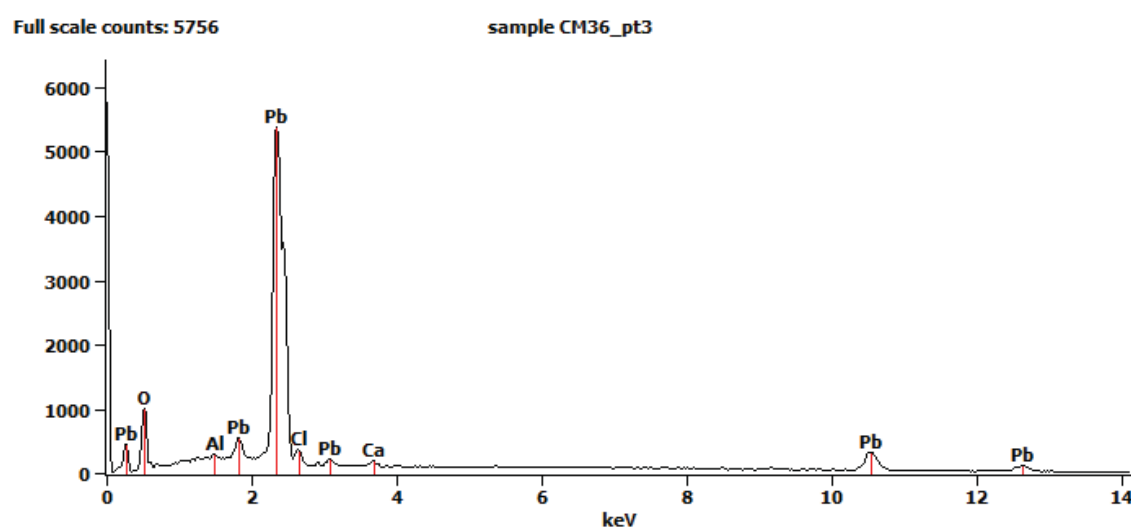
Point 1:



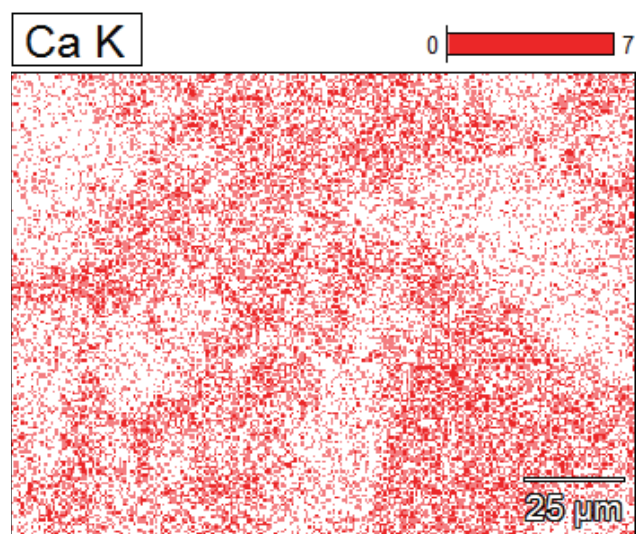
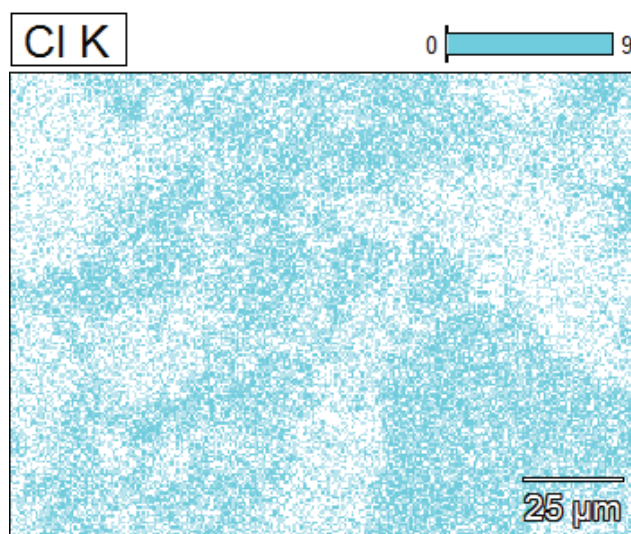
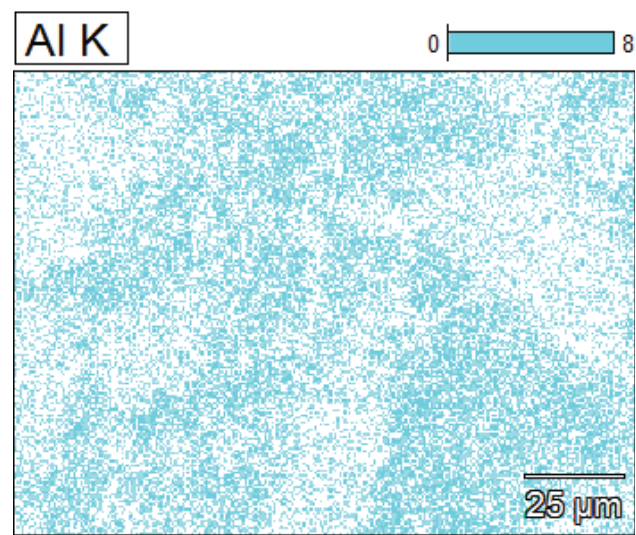
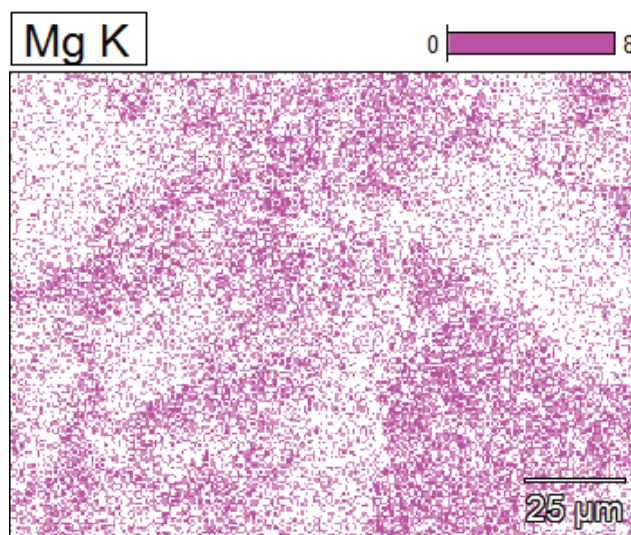
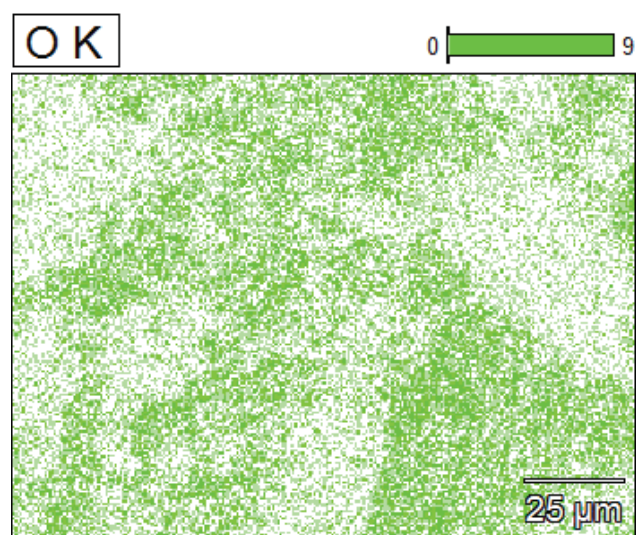
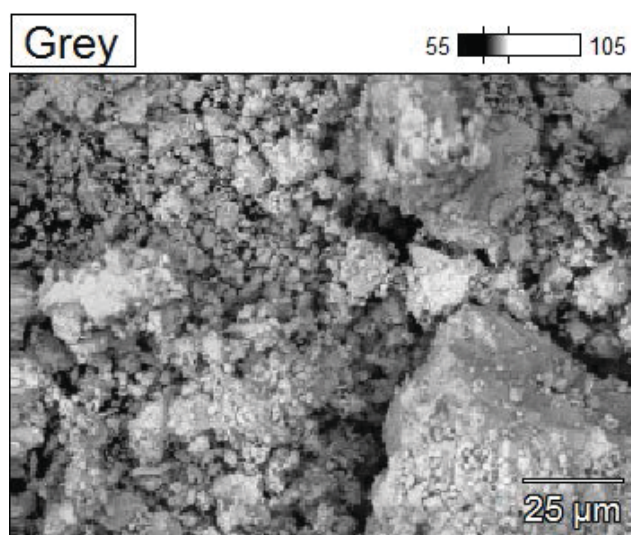
Surface area 2:



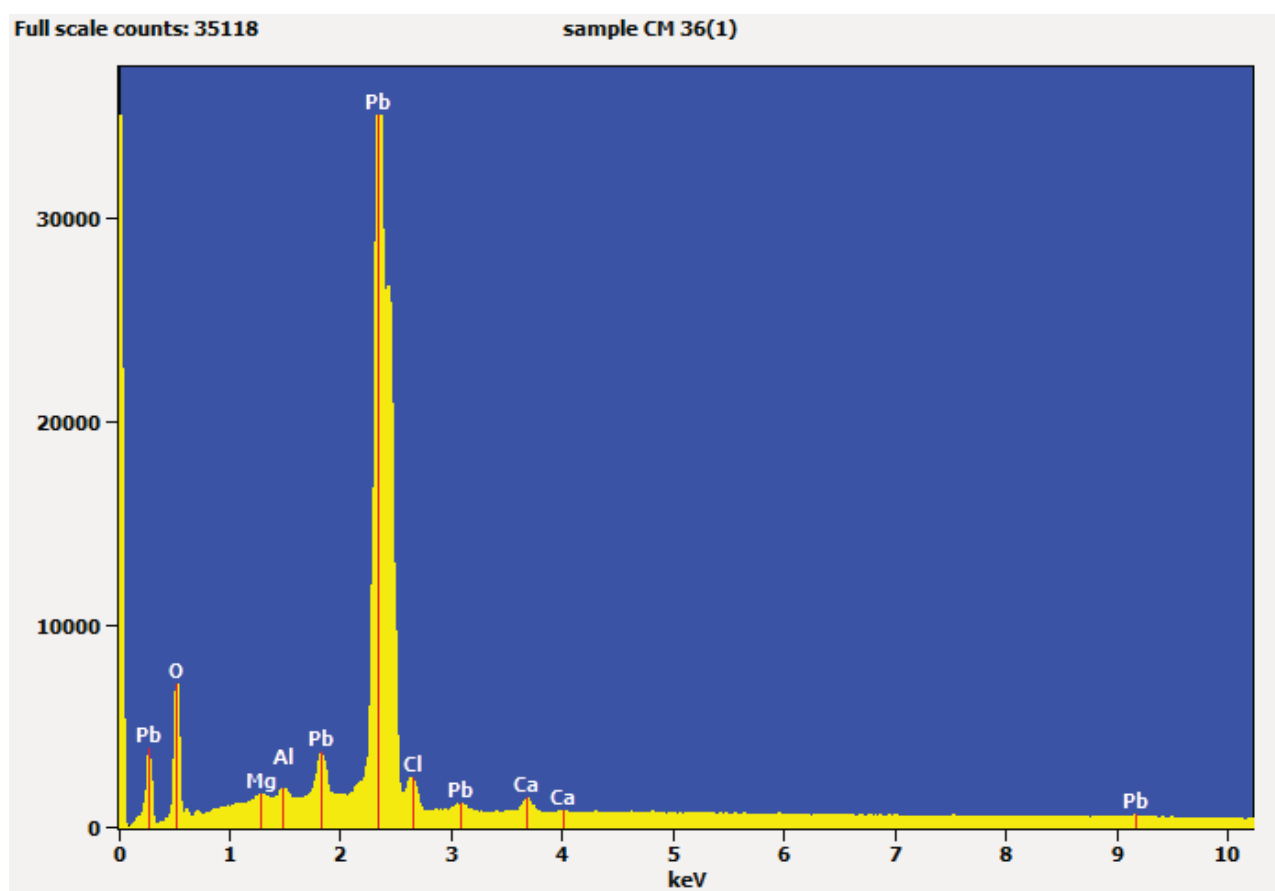
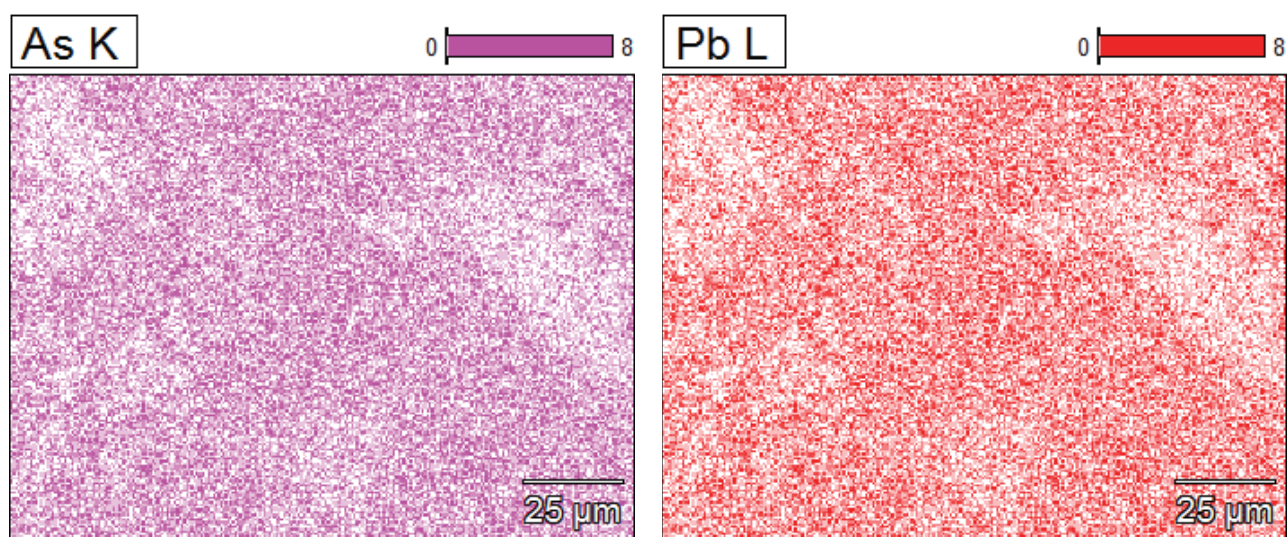
Point 3:



GN-2017-CM36



GN-2017-CM36



GN-2017-CM36

Microscope

UVL-VIS-IR-IRfc

XRF

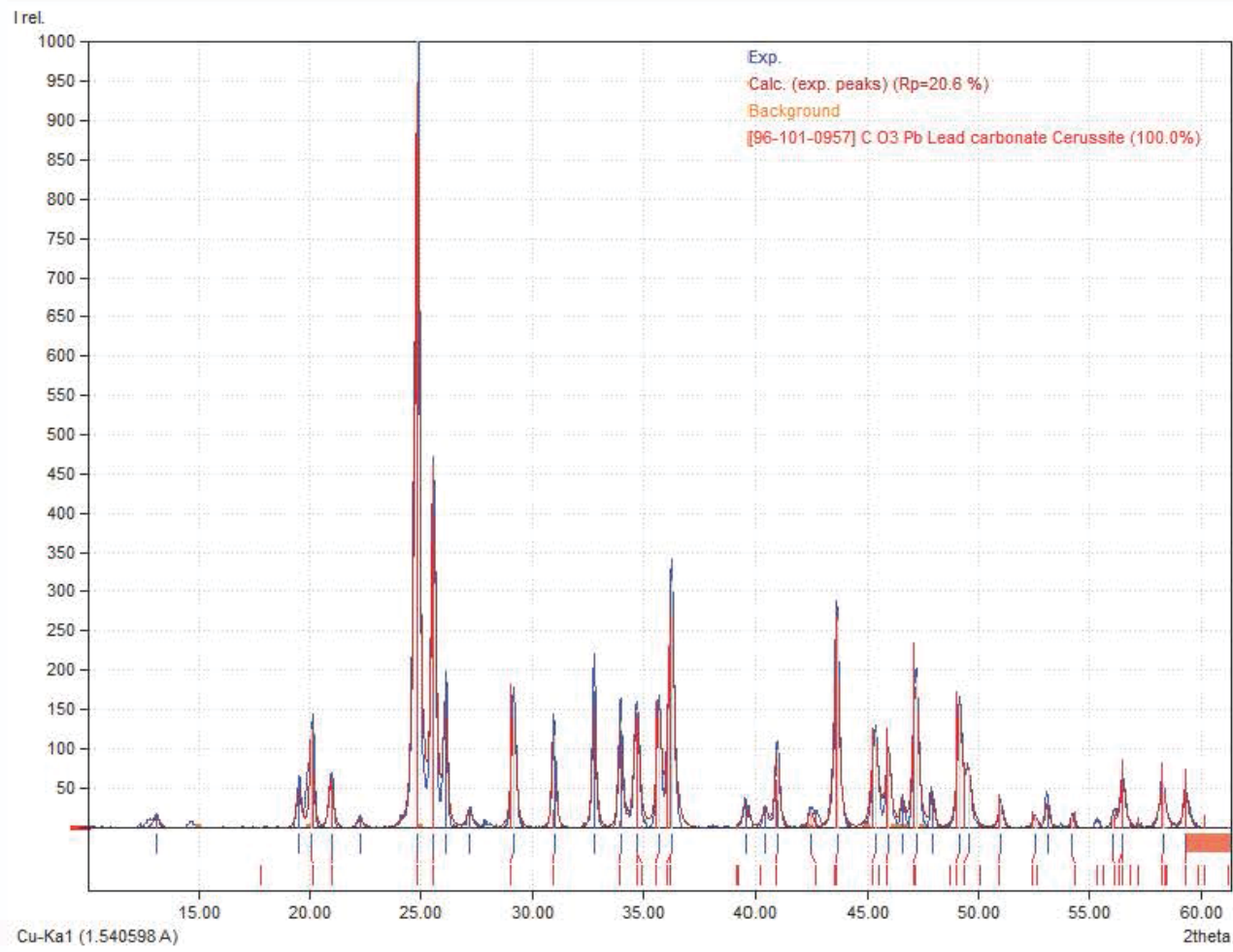
SEM-EDX

XRD

FTIR

RS

Conclusion



Suggested mineral phases

Cerussite (almost 100%)

GN-2017-CM39

Sample information

Location of sample

D18

Date of recovery (YYYY-MM-DD)

2017-09-18

Condition upon recovery

Recovered in 2107, kept in the same bag as numerous other samples from the same square

Sample description

Conical lead white ingot with alteration layer. Height 5 cm; max diam. 5.5 cm; min. diam. 2 cm; weight 256.3 g

Colour

The core is white, external side is gray, red and black

Storage condition

Kept dry in storage at room temperature

Cross / thin section

Cross section

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

Yes

RS

Yes

UHPLC

n/a

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

Yes

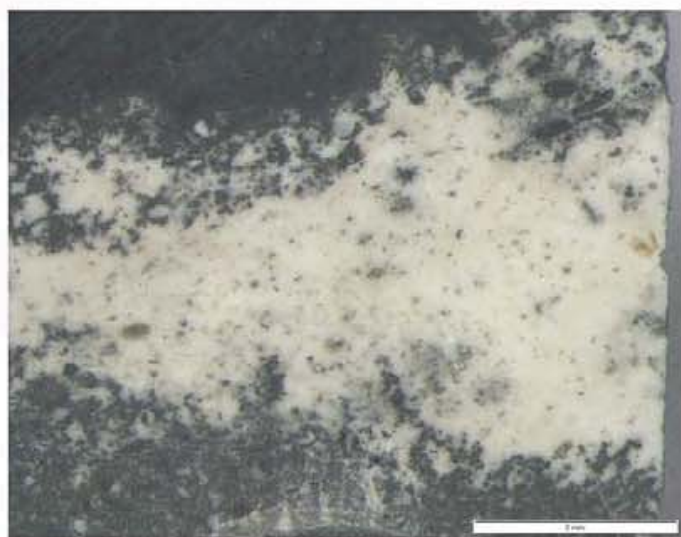
Notes

The ingot was cut in half with the aim of reaching the core. The analyses were performed on the core and alteration layer.

To conduct in future projects

/

Microscope photo 1

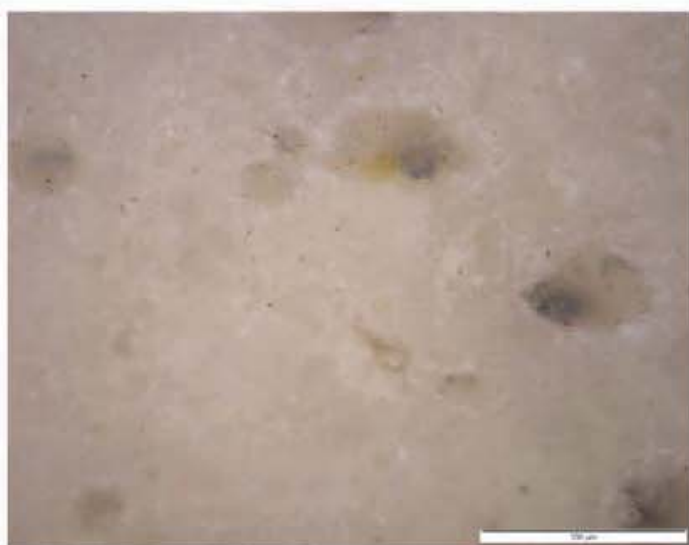


Texture description

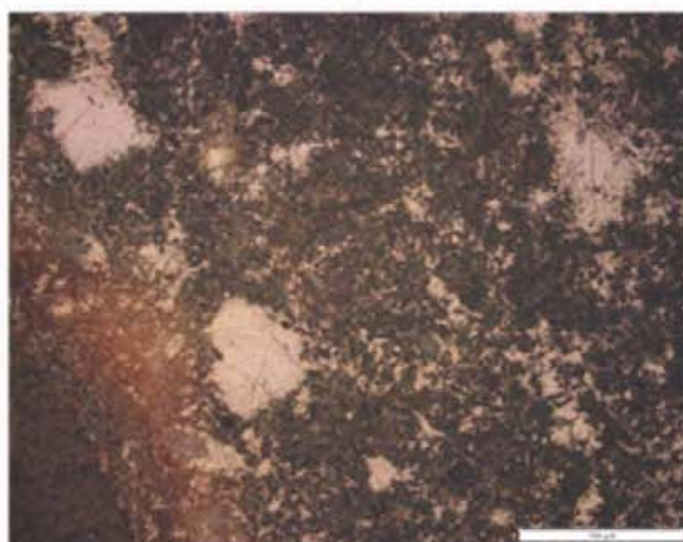
Irregular white crystals of 100-200 μm and fine-grained texture.

- 1) Binocular;
- 2) Stereo microscope;
- 3) Stereo microscope with UV illumination.

Microscope photo 2



Microscope photo 3



GN-2017-CM39

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

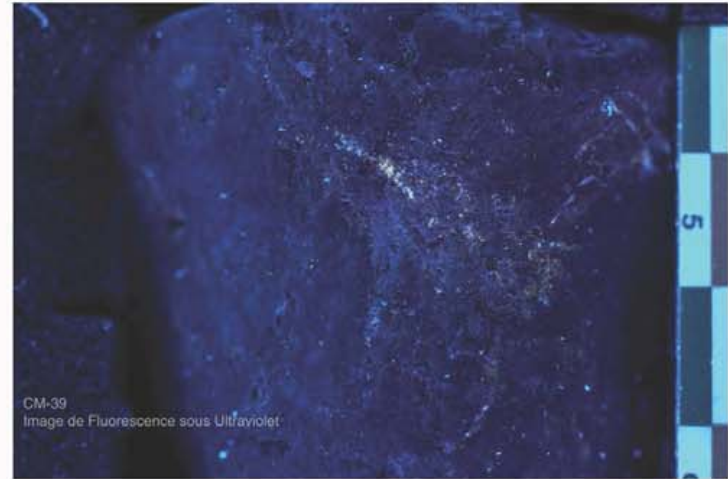
RS

Conclusion

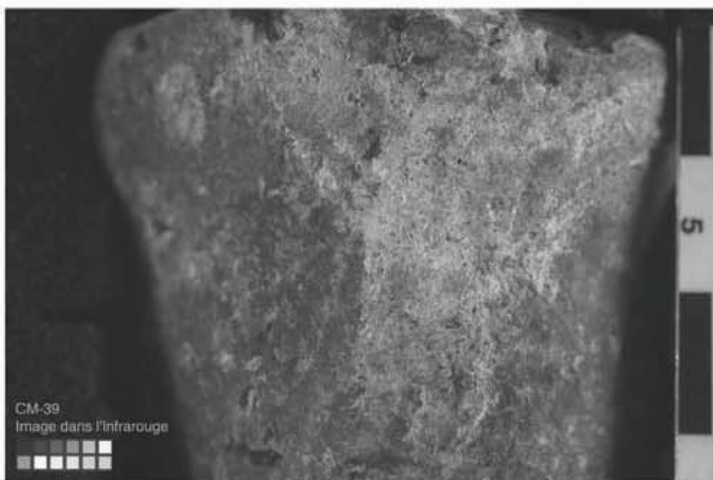
Visible light (VIS)



Ultraviolet light (UVL)

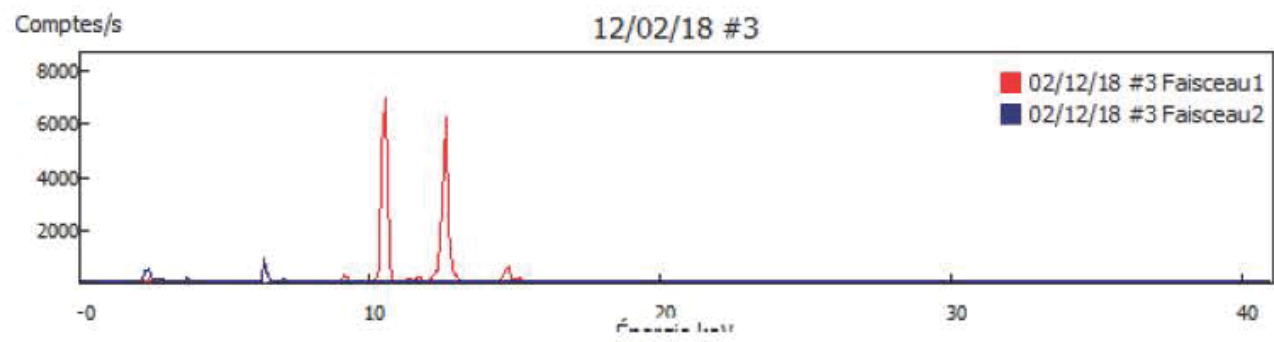


Infrared light (IR)



Infrared false colour (IRfc)





Chemical elements

Alteration layer was analyzed.

Light elements (24.97%)
Other: Pb (38.76%), S (14.02%), Fe (12.54%), As (4.21%), Ca (3.81%), Si (1.37%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

Conclusion

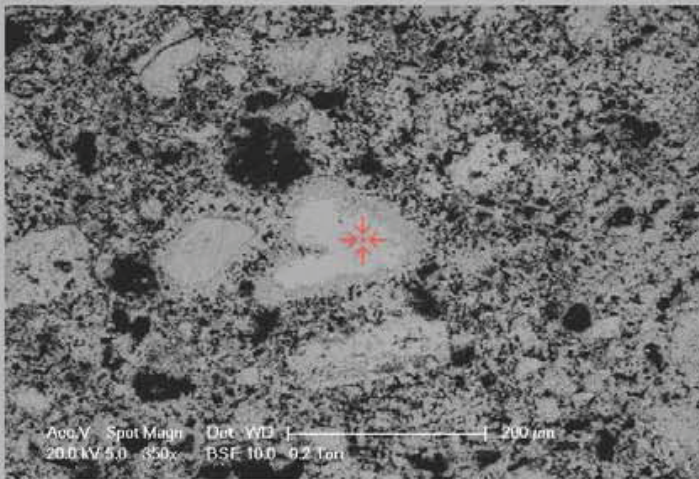
Pt 1: Chemical elements

Cross section

Magnification: 350

Pt 1: C, Fe, Pb, Ca, Fe / C, Pb

Pt 1: BSE image



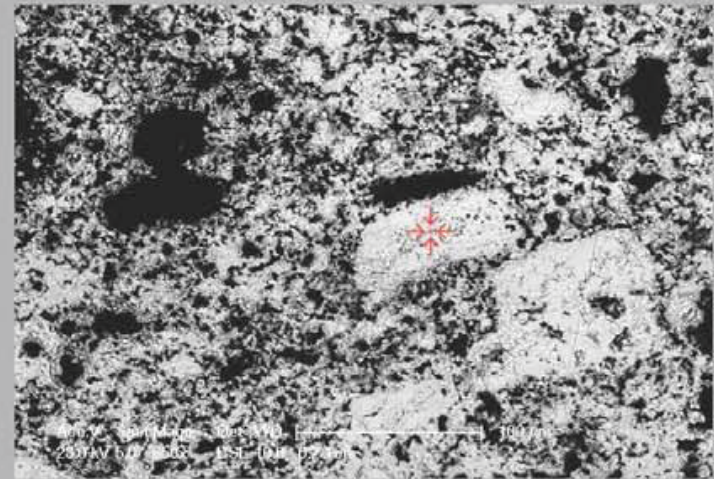
Pt 2: Chemical elements

Cross section

Magnification: 650

Pt 2: C, Fe, Pb, Ca, Fe / C, Pb

Pt 2: BSE image



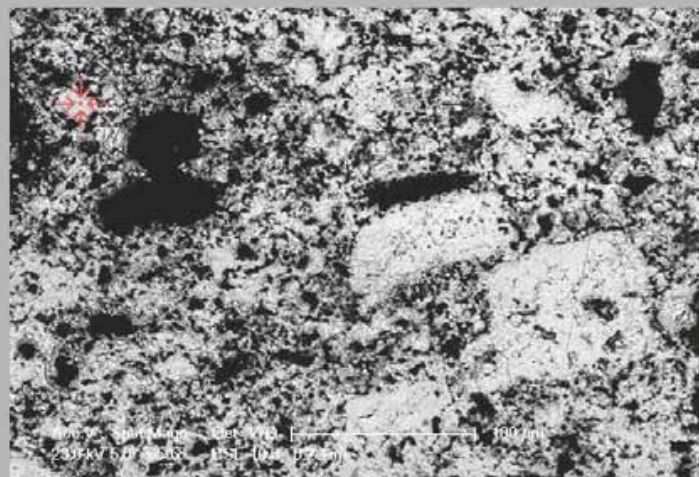
Pt 3: Chemical elements

Cross section

Magnification: 650

Pt 3: C, Fe, S/Pb, Ca / C, Pb/S

Pt 3: BSE image



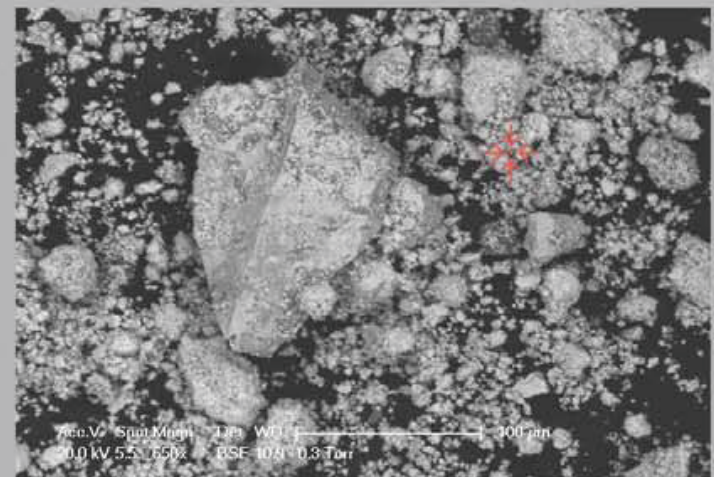
Pt 4: Chemical elements

Black alteration powder (code SP-01).

Magnification: 650

C, Na, As, Pb/S, Ca, Fe / C, Pb/S

Pt 4: BSE image

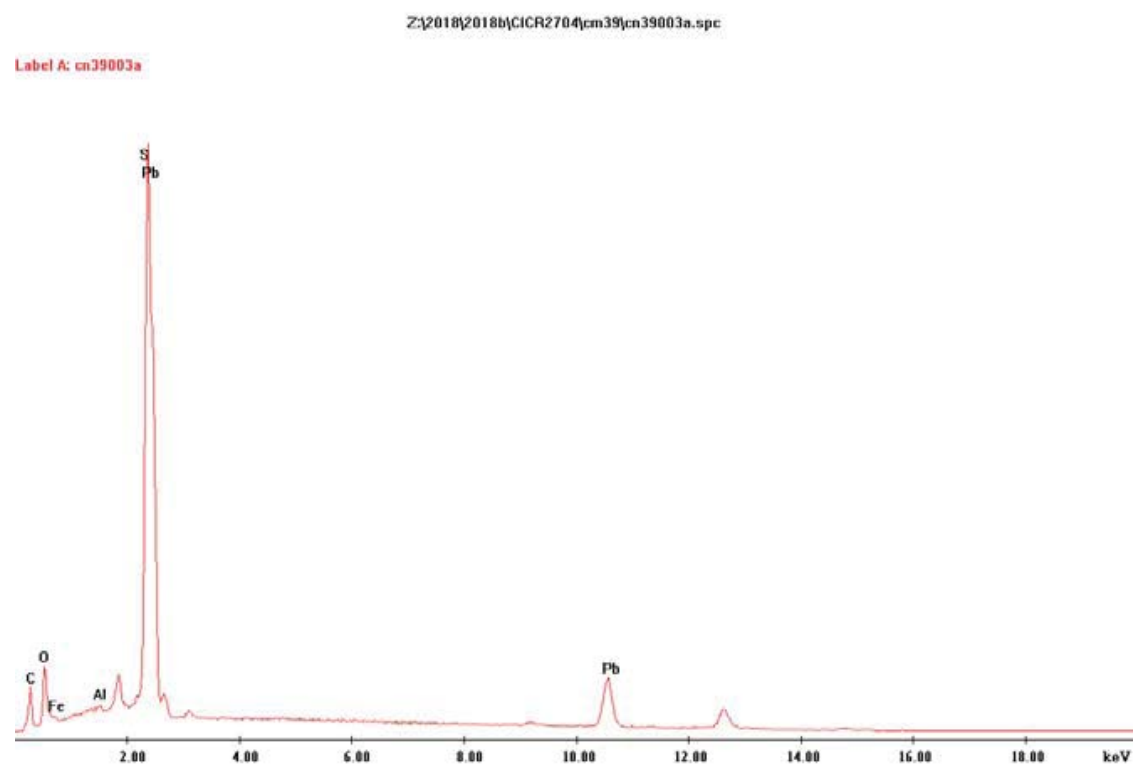


GN-2017-CM39

Point 1:



Point 2:

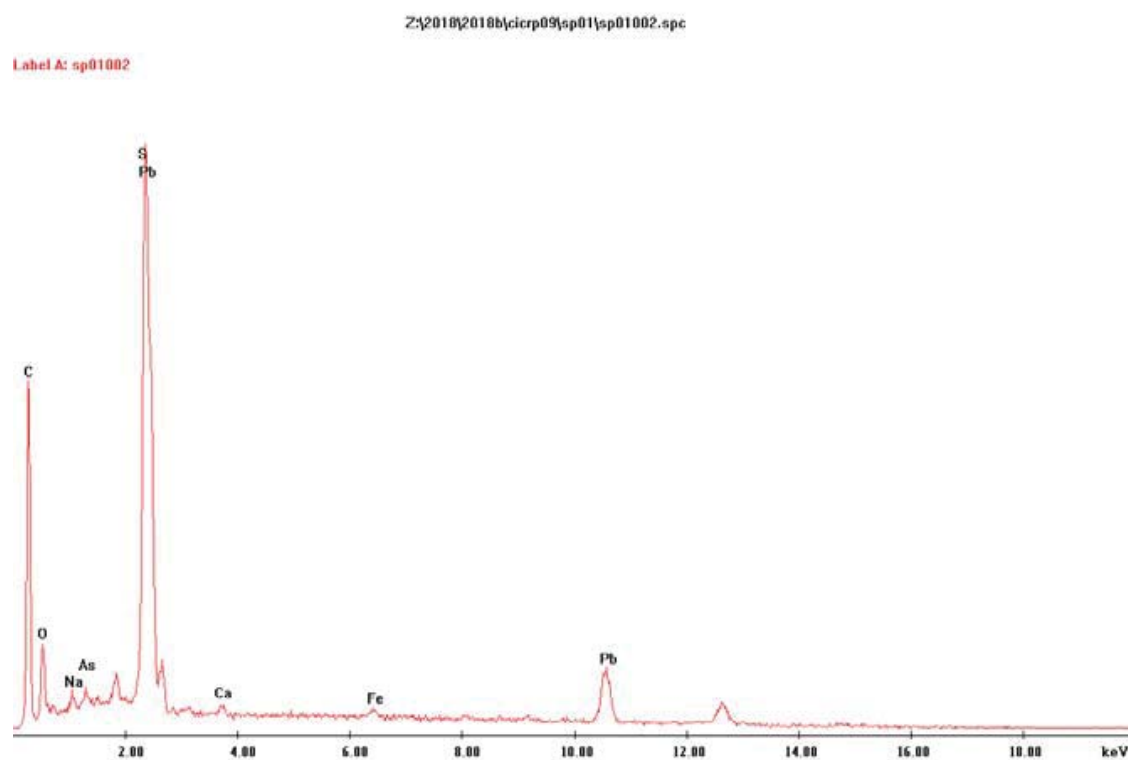


GN-2017-CM39

Point 3:



GN-2017-CM39 (SP-01)



GN-2017-CM39

Microscope

UVL-VIS-IR-IRfc

XRF

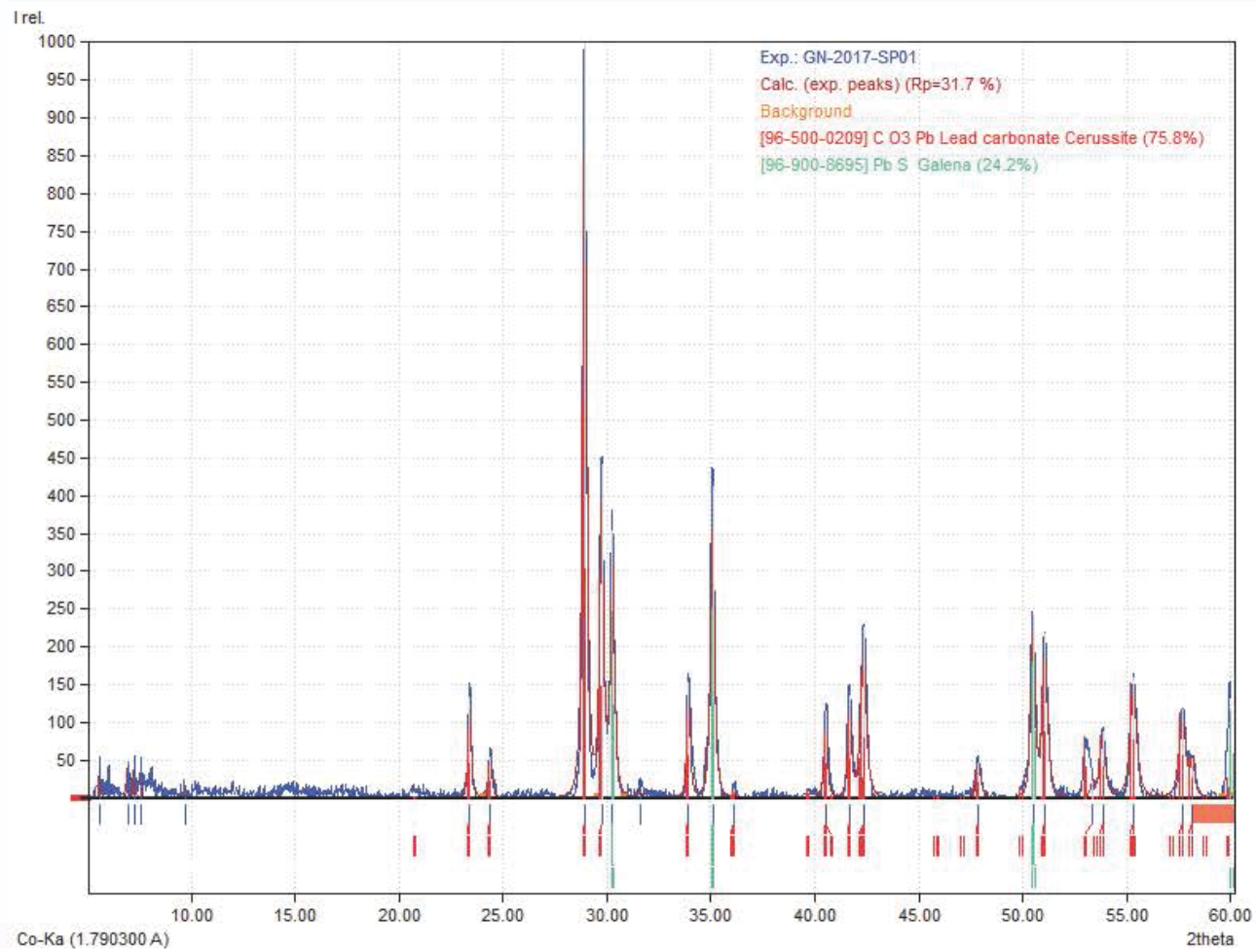
SEM-EDX

XRD

FTIR

RS

Conclusion



Suggested mineral phases

Analyses were executed on the sample of the alteration layer named GN-2017-CM39-SP1.

Cerussite: 75.8%

Galena: 24.2%

GN-2017-CM39

Microscope

UVL-VIS-IR-IRfc

XRF

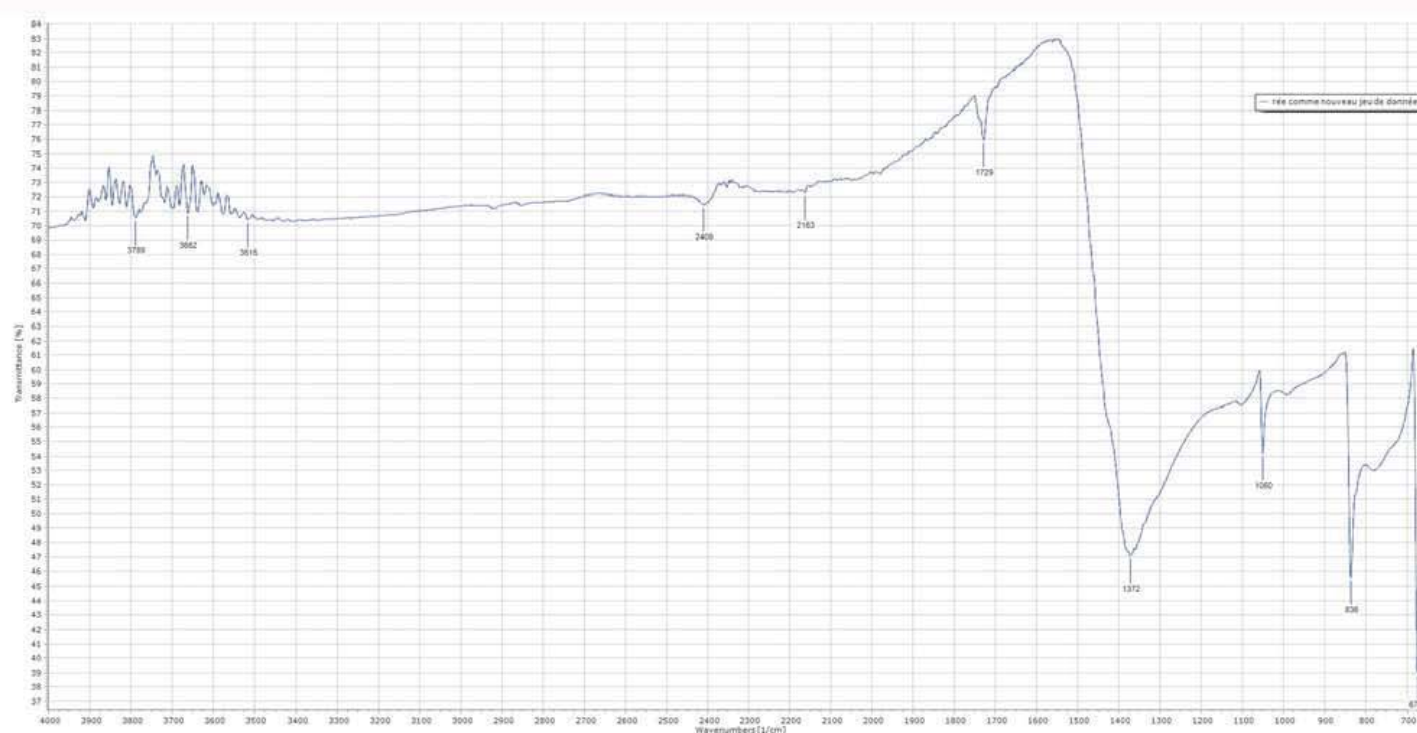
SEM-EDX

XRD

FTIR

RS

Conclusion



FTIR results

Analyses were executed on the sample of the alteration layer named GN-2017-CM39-SP1.

Absorption bands visible on: 2409 w, 2153 w, 1729 wsh, 1372 ssh, 1050 msh, 836 ssh, 675 ssh.

Corresponds to cerussite in RRUFF database (R040069-1).

(b - broad; sh - sharp; w - weak; m - medium; v - very)

GN-2017-CM39

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

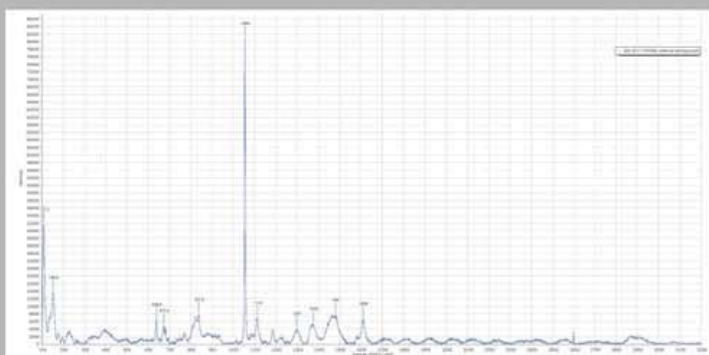
XRD

FTIR

RS

Conclusion

RS spectra 1

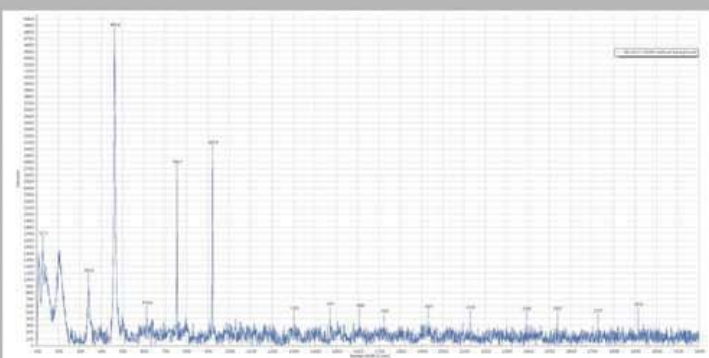


RS results 1

1) Settings: 30%, 1s, 10 acc

Peaks: 107,2 m, 152,34 m, 638 w, 672 w, 680 w, 775 w, 821 w, 837 w, 925 b, 1054 s, 1083 w, 1111 w, 1183 w, 1221 w, 1304 w, 1376 w, 1456 – 1481 wb, 1608 w.

RS spectra 2

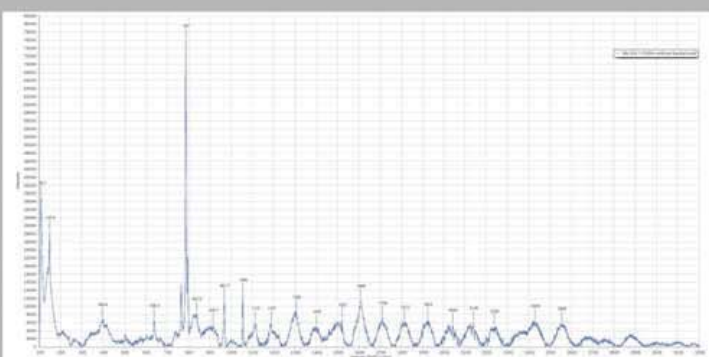


RS results 2

2) Settings: 30%, 1s, 10 acc

Peaks: 112 m, 127,1 m, 194 m, 340 m, 463 s, 614 w, 755 s, 920 s, 1303 w, 1471 w, 1608 w, 1723 w, 1931 w.

RS spectra 3



RS results 3

3) Settings: 30%, 1s, 10 acc

Peaks: 108,1 m, 143 m, 206 w, 394,8 b&w, 638 w, 741 w, 767 m, 787 s, 795 m, 824-836 w, 913 w, 971 m, 1055 m, 1111 w, 1189 w, 1306 w, 1399, 1508 w, 1608 w, 1706 w, 1815 w, 1923 w, 2019 w, 2140 w, 2240 w, 2429 w, 2555 w, 2671 w, 2760 w, 2881 w.

Summary

1) cerussite (RRUFF R040069), calcite (RRUFF X050035);
 2) quartz: 112m, 127,1 m, 194 m, 340 m, 466s. ? Galena (RRUFF 060187). Unknown: 340,9 m, 463,9 vs, 614,5 w, 755,7 vs, 920 vs;
 3) cerussite (RRUFF R040069), calcite (RRUFF X050035).

Unknown: 787 vs.

GN-2017-CM42

Sample information

Location of sample

B19

Date of recovery (YYYY-MM-DD)

2017-09-18

Condition upon recovery

Recovered in 2107, kept in the same bag as numerous other samples from the same square

Sample description

Conical lead white ingot with alteration layer. Height 4 cm; max diam. 4.8 cm; min. diam. 2 cm; weight 184.7 g

Colour

The core is white, external side is gray and black

Storage condition

Kept dry in storage at room temperature

Cross / thin section

Thin section

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

No

SEM-EDX

No

XRD

No

FTIR

No

RS

No

UHPLC

n/a

Photo documentation

Photography of underwater location



Sample condition

GN-2017-CM42



Photogrammetry

Yes

Notes

/

To conduct in future projects

/

Microscope photo 1

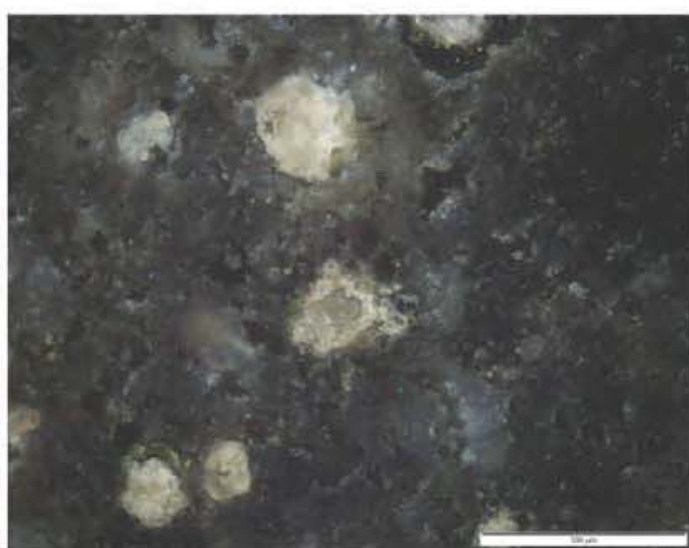


Texture description

Irregular crystals of 100-200 μm and fine-grained texture. Around 5% consists of irregular white opaque crystals of 10-50 μm

- 1) Stereo microscope with UV illumination - cerussite;
- 2) Stereo microscope - galena and cerussite crystals;
- 3) Stereo microscope - cerussite crystal.

Microscope photo 2



Microscope photo 3



GN-2017-CM42

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

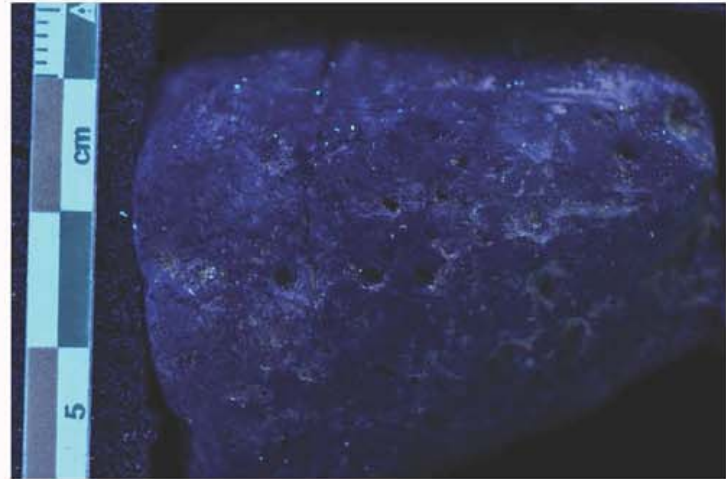
RS

Conclusion

Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



GN-2017-CM42

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

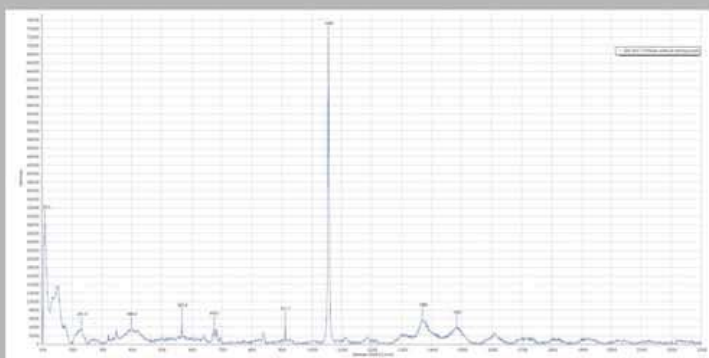
XRD

FTIR

RS

Conclusion

RS spectra 1

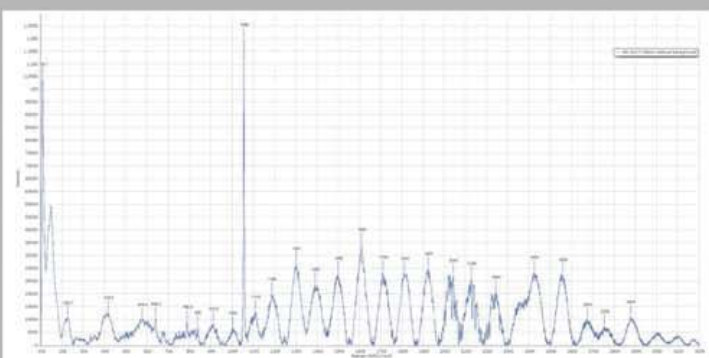


RS results 1

1) Settings: 30%, 1s, 10 acc

Peaks: 108,3 m, 149,05 wb, 224 w, 365-454 b (399), 567,5 w, 675 w, 683w, 840 w, 911,7 w, 1055 vs, 1369 vb, 1482 vb, 108 vb, 1714 vb, 1806 vb, 1914 vb.

RS spectra 2



RS results 2

2) Settings: 30%, 1s, 10 acc

Peaks: 108,7 s, 149,7 m, 227 w, 418 w&b, 484 – 657 (640) w&b, 786,9 w&b, 910 w&b, 1000 w&b, 1055 s, 1107 w&b, 1187 w, 1301 m, 1398 m, 1496 m, 1611 m, 1706 m, 1803 m, 1920 m, 2043 m&n, 2124 m&n, 2248 m&n, 2424 m&b, 2558 m, 2672 w, 2759 w, 2878 w, 3004 w, 3009 w

RS spectra 3

RS results 3

Summary

1) cerussite (RRUFF R040069), calcite (RRUFF X050035);
2) cerussite (RRUFF R040069), calcite (RRUFF X050035).

GN-2017-CM52

Sample information

Location of sample

Southern part of Z17

Date of recovery (YYYY-MM-DD)

2014-08 (unknown date)

Condition upon recovery

Recovered in plastic bag, soaked in tap water

Sample description

Irregular lump, with metallic luster and bladed particles

Colour

Gray / silver

Storage condition

Soaked in tap water and stored in glass jar

Cross / thin section

/

Photo documentation

Photography of underwater location



Sample condition



Photogrammetry

n/a

Analyses done

Microscope

Yes

UVL-VIS-IR-IRfc

Yes

XRF

Yes

SEM-EDX

Yes

XRD

Yes

FTIR

No

RS

No

UHPLC

n/a

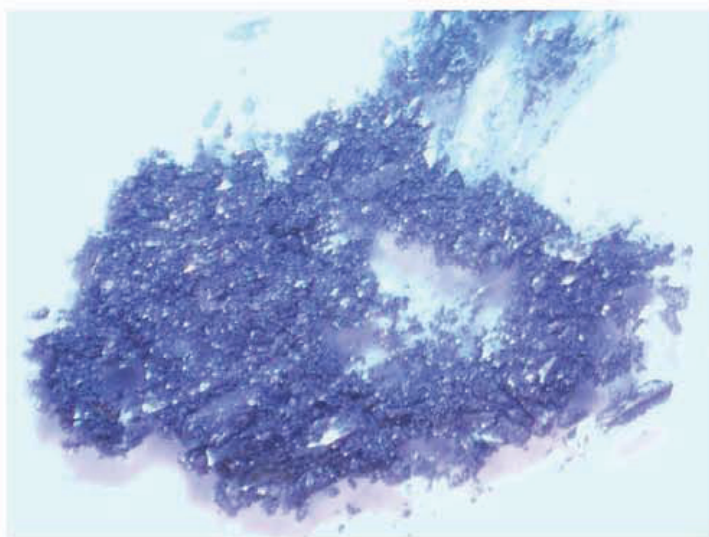
Notes

/

To conduct in future projects

FTIR, RS, Microscope

Microscope photo 1



Texture description

Bladed gray crystals of various sizes 10-100 μ m.

- 1) Binocular, magnification 0.8x;
- 2) SEM, magnification 500x.

Microscope photo 2



Microscope photo 3

GN-2017-CM52

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

Conclusion

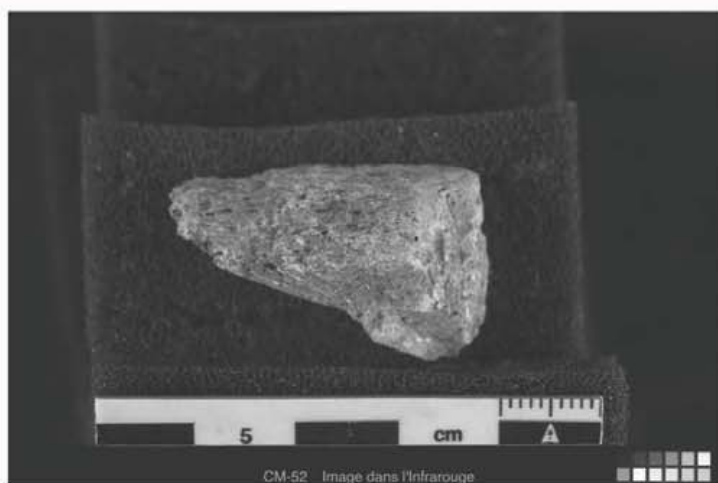
Visible light (VIS)



Ultraviolet light (UVL)



Infrared light (IR)



Infrared false colour (IRfc)



GN-2017-CM52

Microscope

UVL-VIS-IR-IRfc

XRF

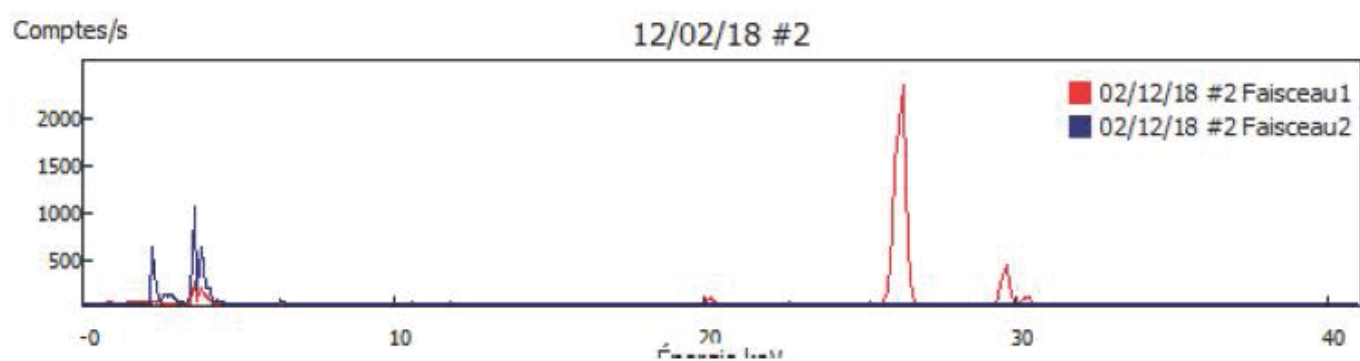
SEM-EDX

XRD

FTIR

RS

Conclusion



Chemical elements

Light elements (10.13%)
Other: Sb (51.31%), Ca (22.35%), S (13.43%), Fe (0.92%)

Microscope

UVL-VIS-IR-IRfc

XRF

SEM-EDX

XRD

FTIR

RS

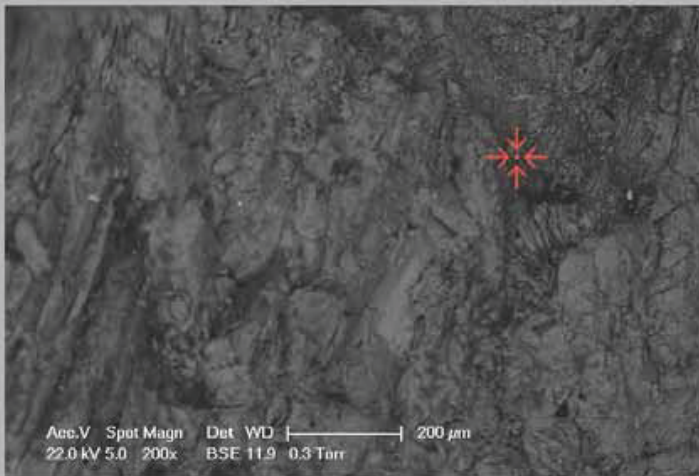
Conclusion

Pt 1: Chemical elements

Magnification: 200

Pt 1: C, O, Al, Si, S, Sb, Fe / S, Sb

Pt 1: BSE image

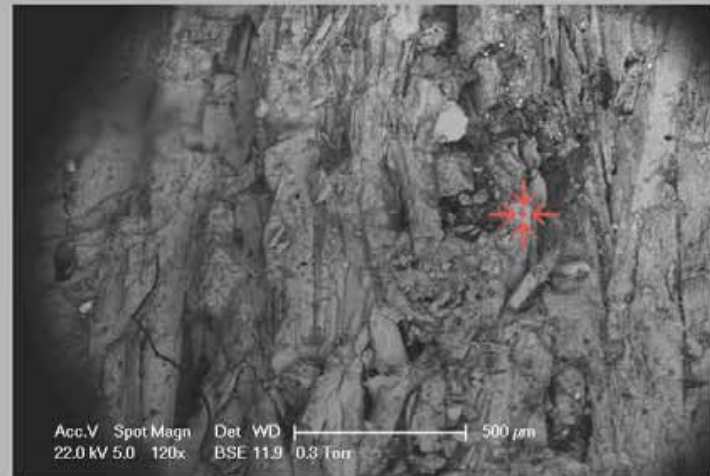


Pt 2: Chemical elements

Magnification: 200

Pt 2: C, O, Al, Si, S, Sb, Fe / S, Sb

Pt 2: BSE image



Pt 3: Chemical elements

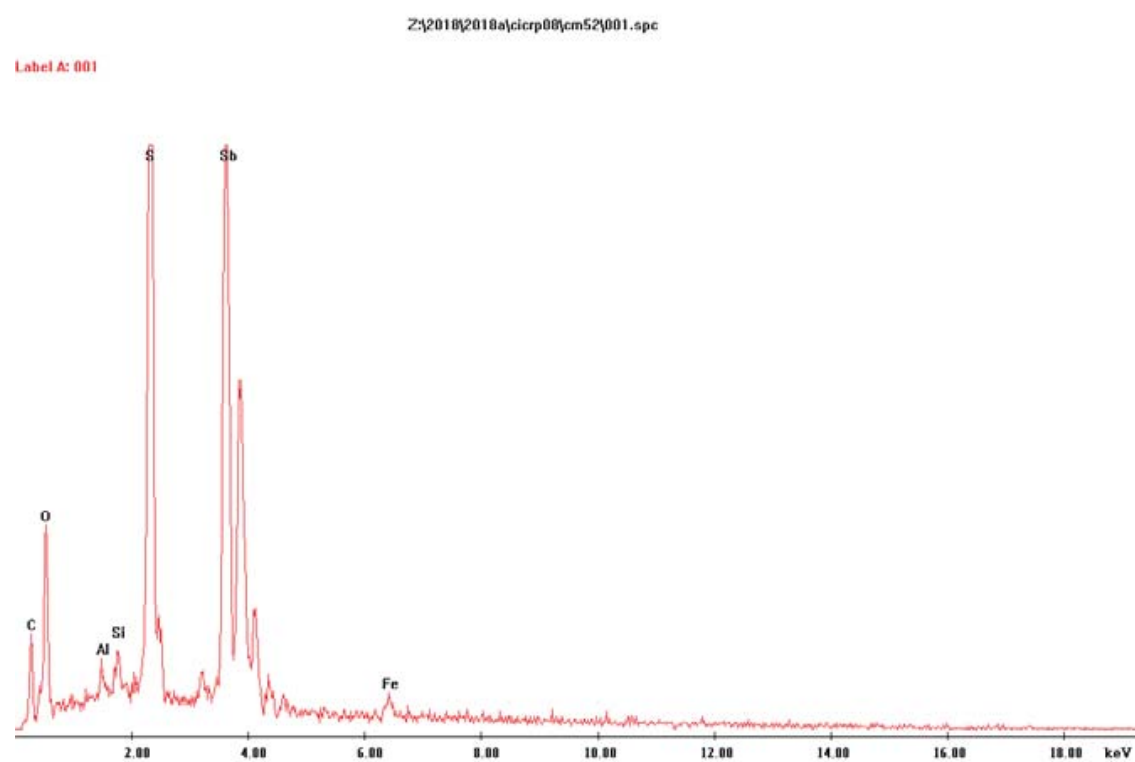
Pt 3: BSE image

Pt 4: Chemical elements

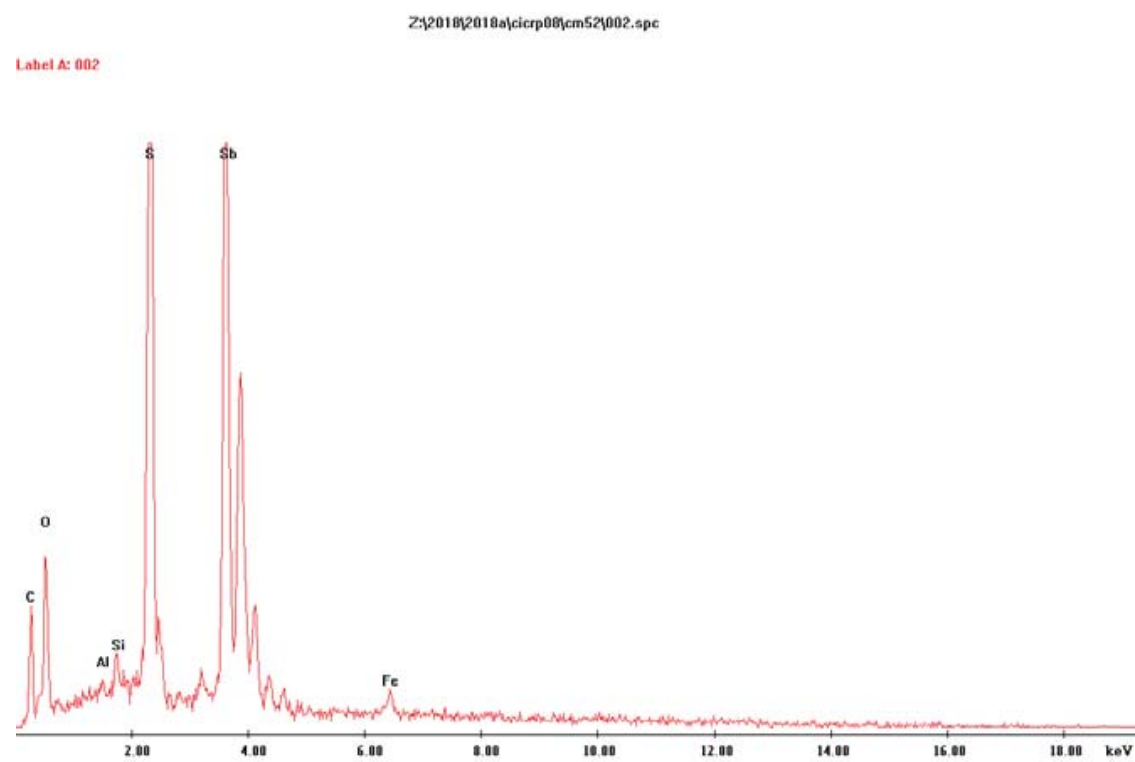
Pt 4: BSE image

GN-2017-CM52

Point 1:



Point 2:



GN-2017-CM52

Microscope

UVL-VIS-IR-IRfc

XRF

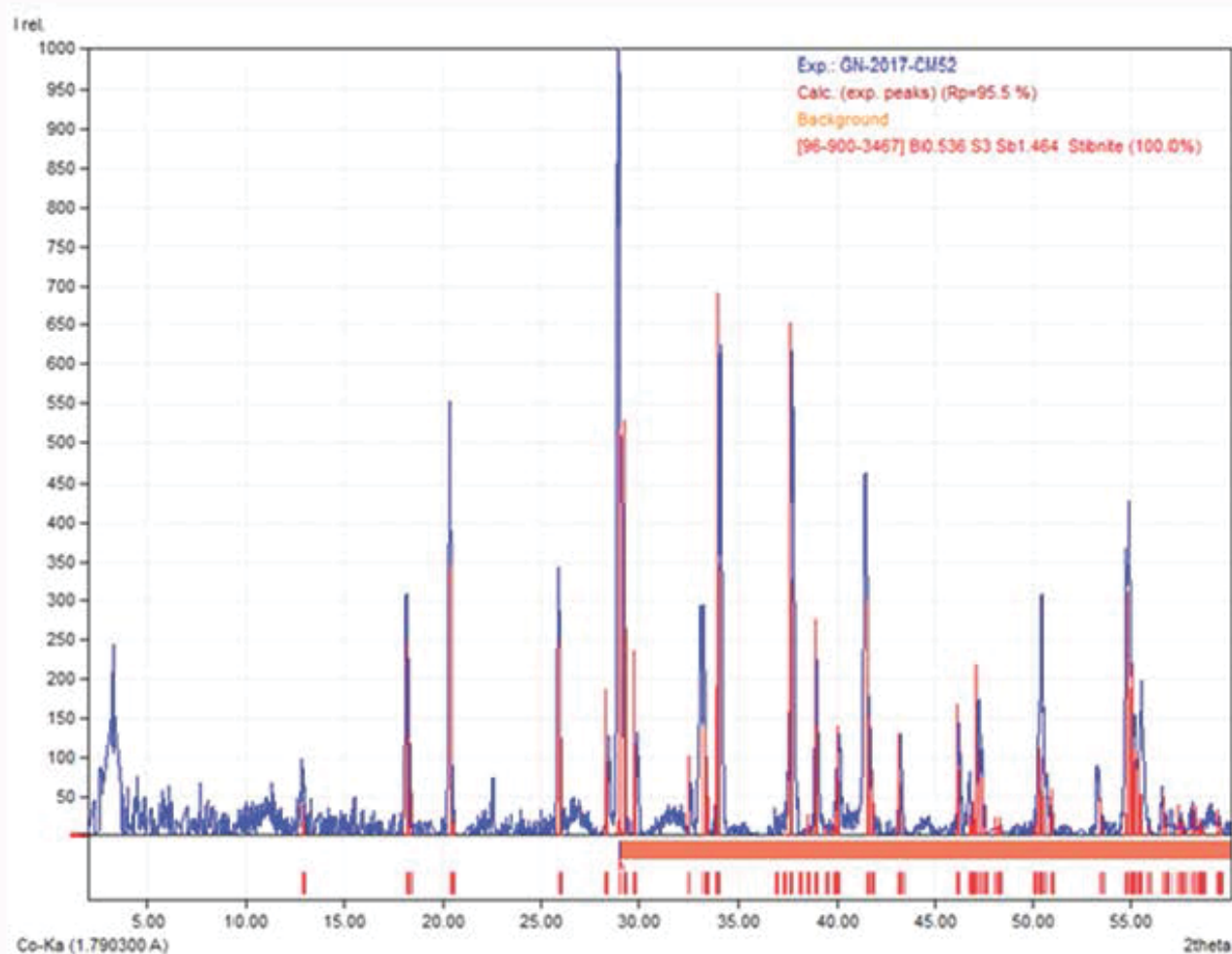
SEM-EDX

XRD

FTIR

RS

Conclusion

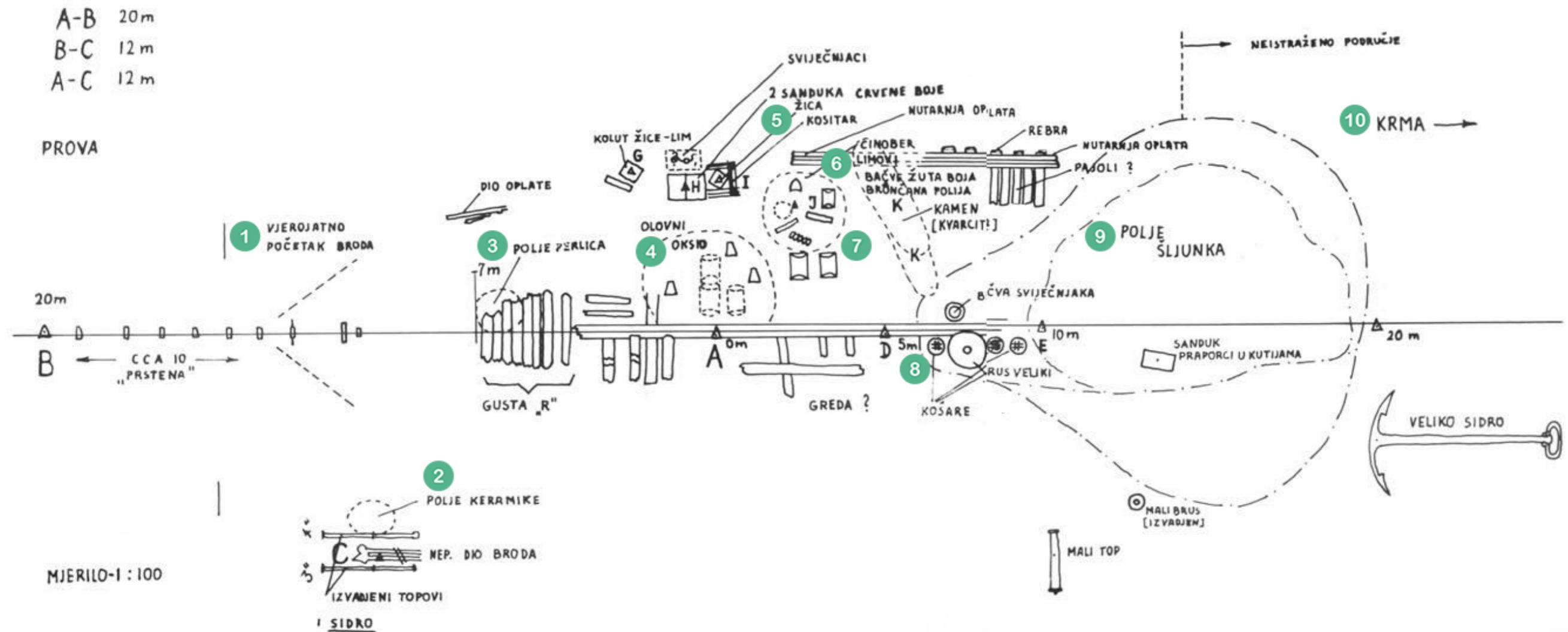


Suggested mineral phases

The main phase is the antimony (III) sulphide, stibnite type (almost 100%).

Other phase is present in the minority, but it was not possible to identify at the moment (2theta 3.26, 11.01, 22.62, 26.89, 31.47).

MAPS



The drawing is based on the data from excavation reports from the 1960s and 1970s written by Ksenija Radulić, coupled with the personal observations of Zdenko Brusić and the team involved in the project in the summer of 1996 (Zdenko Brusić, 1996). Explanation of the numbers:

- | | |
|---|---|
| <ul style="list-style-type: none"> 1. Assumed beginning of the ship's construction – bow (in reality the stern); 2. The field of pottery; 3. The field of the glass beads; 4. 'Lead oxide' (in reality the cones of lead white – cerussite and hydrocerussite); 5. Description from top to bottom: chandeliers, two chests of red colour (not identified), wire (probably brass), tin (probably rods, in the chest); | <ul style="list-style-type: none"> 6. Bells of mercury sulphide, brass foil; 7. Barrels of yellow colour; 8. Baskets, large grinding stone and the barrel filled with chandeliers; 9. The field of pebbles; 10. Assumed end of the ship's construction – stern (in reality the bow). |
|---|---|



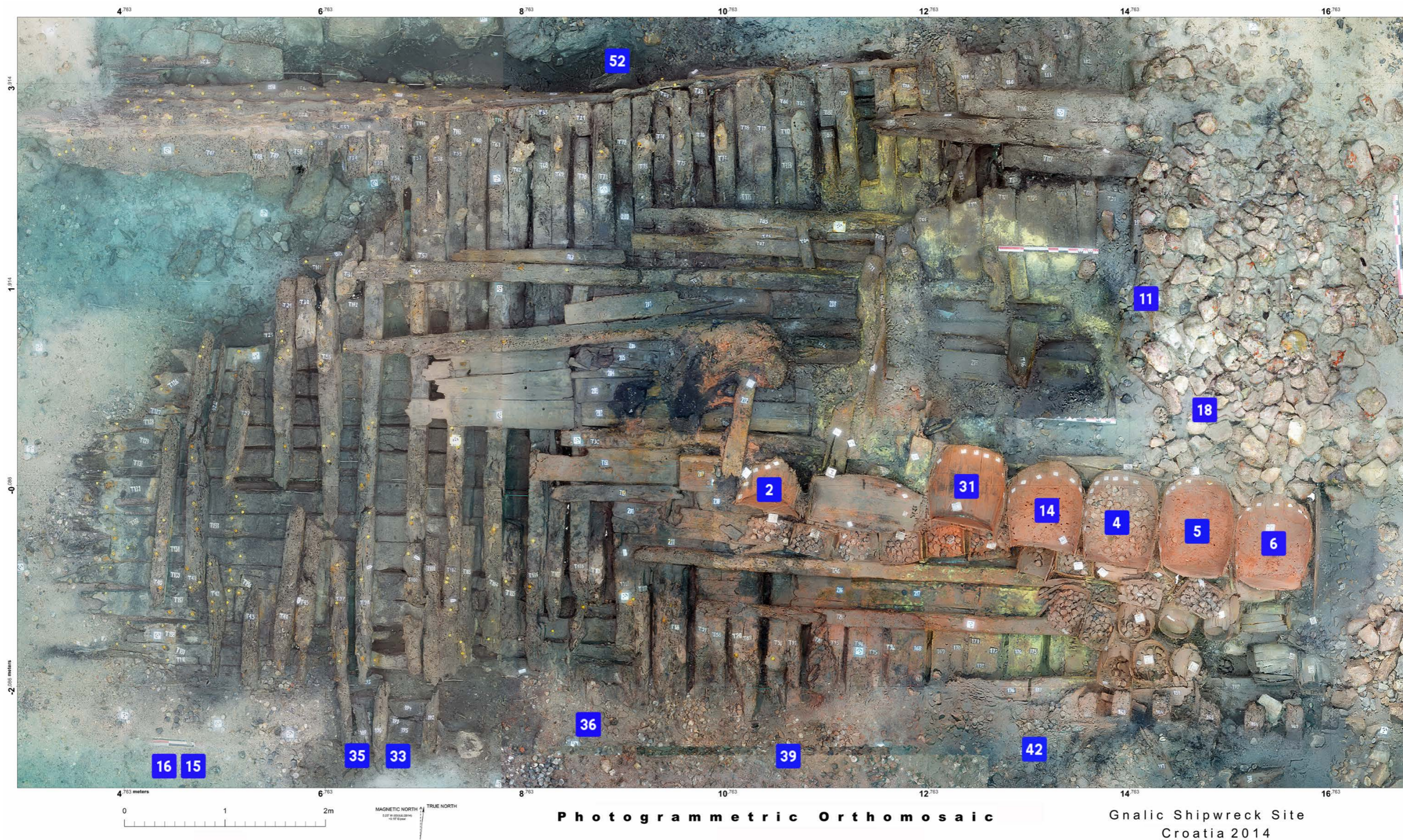
Arrangement of barrels in excavation season of 2013 (author: J. L. Casaban)



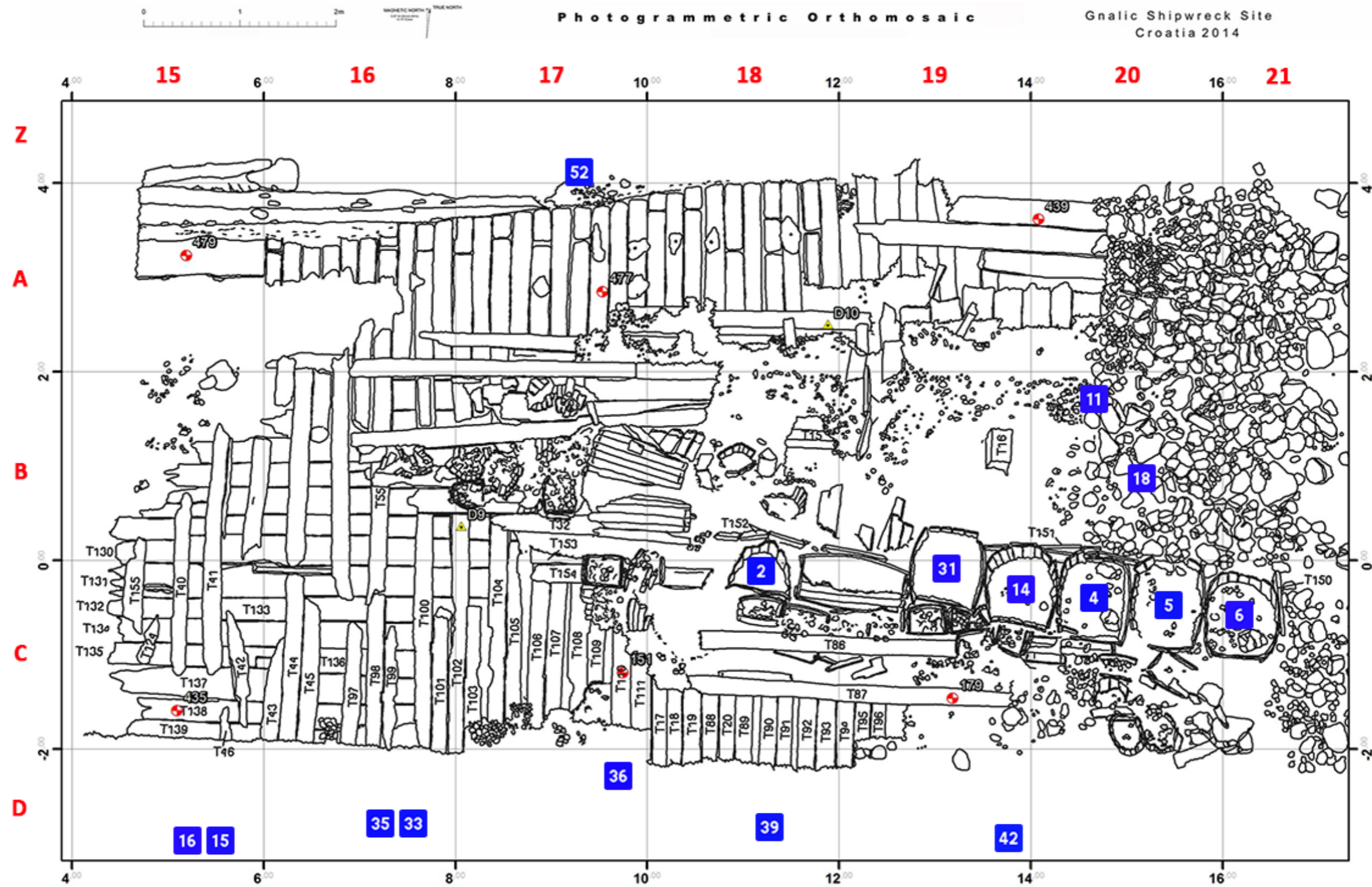
Arrangement of the casks and barrels in the excavation season of 2013 (author: J. L. Casaban).



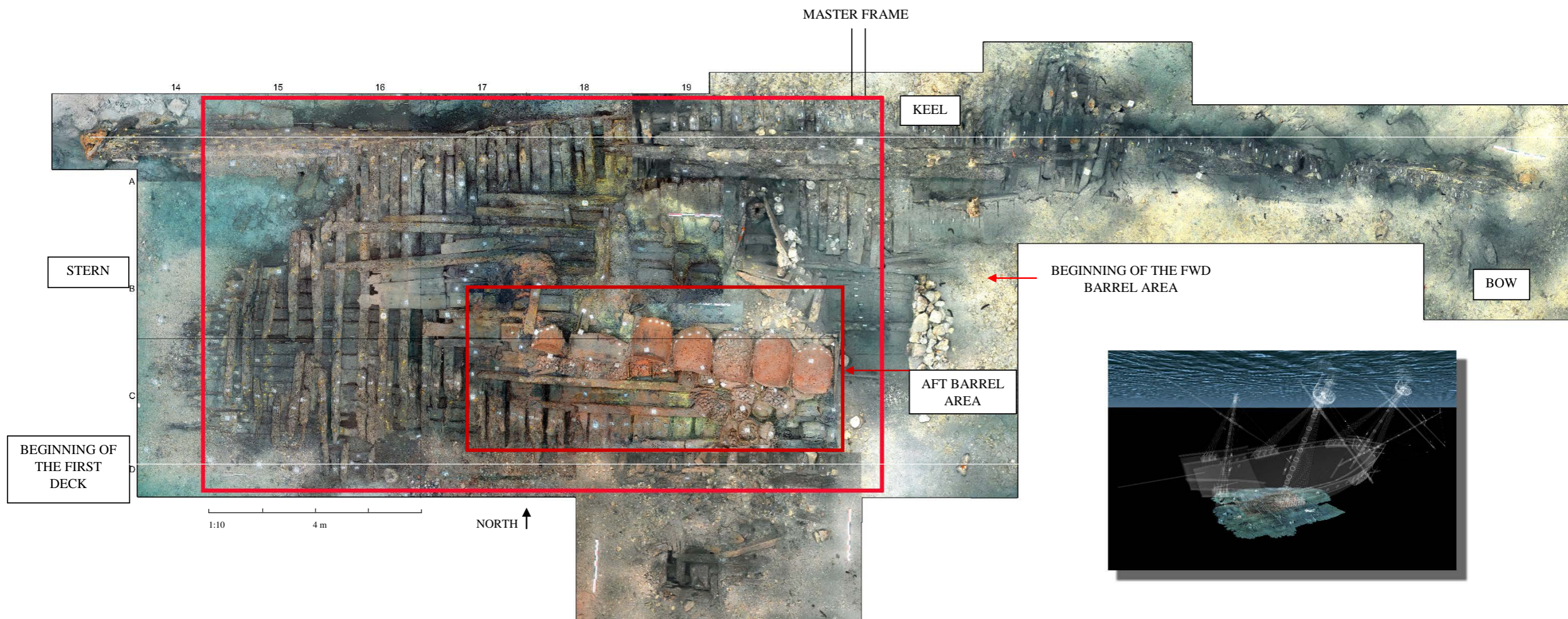
The barrel area in excavation season of 2014 (orthophoto: R. Torres, K. Yamafune & S. Govorčin).



Orthophotography of the Gnalic shipwreck site from excavation season 2014. The description on the map avoided excessive details so the samples are marked with the plain number, without the entire code (authors: K. Yamafune, R. Torres, S. Govorčin).



Orthophotography of the Gnalčić shipwreck site from excavation season 2014. Numbers are marking the position of sampling performed in 2017. The description on the map avoided excessive details so the samples are marked with the plain number, without the entire code (drawing: R. Torres).



Composite orthophotography of the Gnalić shipwreck site from excavation season of 2016. Rectangle is marking the aft of the ship and the area of sampling in 2017. The rectangle surface area is represented in Map 2 (authors: K. Yamafune, R. Torres, S. Govorčin).

BIOGRAPHY

Katarina Batur was born on October 16th, 1991 in Zadar, Croatia. From the beginning of her undergraduate studies in the Archaeology Programme at the University of Zadar, her activities have been focused on maritime archaeology and the preservation of traditional Adriatic maritime heritage. She has gained ample terrestrial and underwater fieldwork experience throughout Croatia. Shortly after master's graduation in 2015, she enrolled in the PhD program Archaeology of the Eastern Adriatic at the University of Zadar.

Shortly after graduation in 2015, Katarina was a visiting scholar at Anthropology Department, Texas A&M University in College Station, USA. In the *J. Richard Steffy Ship Reconstruction Laboratory* and *Conservation Research Laboratory* she learned to draft the ship lines, and to apply the photogrammetry recording for documentation and presentation purposes.

From late 2016 Katarina has been employed at the University of Zadar Archaeology Department through the Croatian Science Foundation project *Young Researchers' Career Development Project – Training of New Doctoral Students*. From 2016 until 2019 she was a team member of the project *AdriaS – Archaeology of Adriatic Shipbuilding and Seafaring in the Eastern Adriatic* (HRZZ-IP-2014-09-8211), also supported by the Croatian Science Foundation. Her research interests are focused on the development of shipbuilding and seafaring in the Adriatic Sea, and on trade with colouring materials in the 16th century. During the PhD studies, Katarina delivered eleven talks on the international and local conferences, ten public talks and published six papers.

In 2015 Katarina earned the award of organization *Women Divers Hall of Fame* and Connelly family, as well as Rector's Award for outstanding accomplishments at the University of Zadar. In 2020 she was again awarded by the Women Divers Hall of Fame for the project *Discovering colours in the cargo of Gagliana grossa*, which aims to improve the methodology of detecting metal-based colouring materials in underwater environments.