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Archaeometric analysis of raw materials for lead-based pigments from shipwreck sites in the eastern Adriatic

Katarina Batur
Research Assistant
Department of Archaeology
University of Zadar, Croatia

Vladimir Bermanec
Department of Geology
Faculty of Science
University of Zagreb, Croatia

Human beings, as creative and spiritual creatures, have always been inspired to make surrounding environments colorful 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 colors to paint objects used in everyday life. This poster focuses on maritime trade of lead-based coloring materials, and compares samples from two underwater sites in the Adriatic Sea: a Roman ship sunk at Cape Glavat on the island of Mljet (1st century), and a Venetian merchant ship sunk near the islet of Gnalić (16th century). Although there is nearly a 1500 year gap between these two sites, their existence is tangible proof that trade of coloring materials existed in Classical Antiquity, likely continued during the Middle Ages, and, in parallel with the development of Renaissance art, reached its maximum level in the 16th century.

Terminology for lead-based pigment identification

To be precise and to avoid confusion, it is important to accurately use the terminology for lead-based coloring materials. In a Croatian bibliography published recently, the terms lead carbonate, cerussite and lead white were synonymous, which is not technically correct. Lead carbonate or cerussite ($PbCO_3$) is used in the production of basic lead carbonate or lead white ($2PbCO_3 \bullet Pb(OH)_2$), a coloring material well known for its excellent covering properties.

Figs. 2 and 3: Cape Glavat - Lead oxide (minium) packed in the ovoidal three-handled, flat-bottomed ceramic vessels (photo: D. Kalogjera)

The Shipwreck of Gnalić (Gagliana grossa)

In late 1583, a Venetian merchant ship sunk near the island of Gnalić, just a few kilometers south of Biograd na Moru. Recovery operations started in 1967 and lasted until 1973, when director Ksenija Radulić decided to stop further activities due to the lack of sufficient expertise, equipment and financial resources. The excavation restarted in 2012, and continued during the following years directed by Dr. Irena Radić Rossi from the University of Zadar.

According to Venetian archival sources, the ship was transporting a rich cargo from Venice to Constantinople, including 5000 window panes intended for renovation of the old harem of sultan Murat III. Along with various types of Murano glass, parts of chandeliers, and various small objects of different provenance, the ship was transporting raw materials intended for the production of coloring materials, such as cones of lead carbonate (cerussite), iron oxide (hematite), mercury sulphide (vermilion), antimony sulphide, arsenic sulphide, lead oxide (minium) and mercury.

As the ship loaded its cargo in Venice, a city which in the 16th century built its reputation as the 'city of color', it is believed that these cargo items were acquired from shops specialized in selling coloring materials, called vendecolori. These shops probably started to separate from pharmacies in the late 15th century, and continued to grow in number due to the great demand for different grades of pigments.

The Gnalić shipwreck has provided a great amount of coloring materials, particularly lead-based materials. Conical shaped lead ingots were packed in barrels filled with straw, with height ranging from 40 to 43 cm, and head diameter ranging from 25 to 30 cm. Several barrel heads bear stamps composed of the letters S, Z and a cross, possibly indicating either the manufacturer or the vendecolori. Conical lead carbonate ingots correspond to so called 'loaves', the shape which was formed after processing and washing lead ore.

Recent analyses of the lead cones showed that they are composed of lead carbonate or cerussite ($PbCO_3$); previous analyses by Ivo Kelez have also shown the existence of basic lead carbonate or lead white ($2PbCO_3 \bullet Pb(OH)_2$). It is not known how minium (Pb_3O_4) was packed and transported; only two lumps of this material have been found and identified. Future systematic research will attempt to determine the amounts of loaded lead-based coloring materials and their disposition in the hold of the ship.

Discussion and future plans

Future analyses using both X-Ray Powder Diffraction and Scanning Electron Microscopy studies of lead based coloring materials may support conclusions about the technology of production and quality/purity. At this stage of research, only identification of the material ($PbCO_3$ and Pb_3O_4) was possible. Reports on raw materials from the Gnalić shipwreck written by Ivo Kelez in the 1970s indicated the presence of 82% basic lead carbonate or lead white ($2PbCO_3 \bullet Pb(OH)_2$) and 18% chalk in the composition of lead ingots. More recent samples have not produced the same result, indicating that the lead white ingots from Gnalić were of varying quality. It is necessary to continue research and examine more samples to confirm the composition range of the lead ingots.

During the examination of the materials, alterations at the surface of the materials were noted, particularly for samples from the Gnalić site, where the presence of sulphur at the site is causing various chemical reactions of unclear and inconsistent chemistry. In order to answer questions about the materials' natural forms and the technology of production used over different periods of time, it is necessary to cut the material to reach the inner part and take a sample that has not been altered by the sea environment.

Unfortunately, the non-systematic character of the Cape Glavat excavation does not allow strong conclusions regarding the amount of coloring materials present in the cargo, their provenance, and their disposition in the hold of the ship. However, the site shows great potential to answer crucial questions about the trade of coloring materials in Antiquity. In comparison, proper archeological, archival and analytical research of the coloring materials from the Gnalić Shipwreck provides a unique snapshot of the variety of coloring materials available in the 16th century, and is an important data source for the maritime trade of pigments in the late Renaissance.

Fig. 1: The Shipwreck of Gnalić – Area of barrels (photo: S. Govorčin)

The Shipwreck of Glavat (island of Mljet)

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. Four years of short-term excavations 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. Preliminary research on these artifacts 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.

What makes the cargo even more interesting is the existence of mineral lead carbonate or cerussite ($PbCO_3$), lead oxide or minium (Pb_3O_4), and lead sulfide or galena (PbS). Cerussite and galena were preserved in the shape of irregular white and grey cubes 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.

Fig. 4: Gnalić Islet: Orthogonal photomosaic of the state of the site at the end of 2014 excavation campaign (R. Torres, K. Yamafune, S. Govorčin)

Fig. 5: Gnalić Islet - Conically shaped ingots of lead carbonate were packed in the barrels, and immobilised with straw (photo: I. Asić)

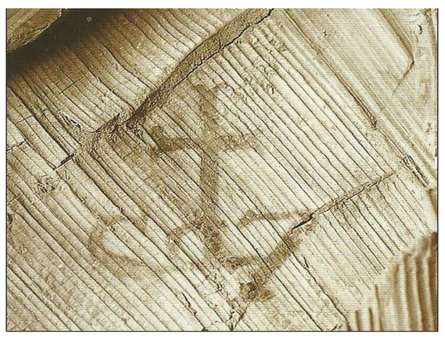

Fig. 6: Gnalić Islet - Merchant's or manufecturer's stamp on the lid of a barrel (after Mileusnic 2006, 76)

Fig. 7: Gnalić Islet - Conically shaped ingots of lead carbonate (photo: K. Batur)

Fig. 8: Gnallić Islet - The lumps of lead oxide (minium), (photo: K. Batur)

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