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Provenancing ancient pigments: Lead isotope analyses of the copper compound of egyptian blue pigments from ancient mediterranean artefacts

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ABSTRACT

While the use of Egyptian blue (EB) as the earliest artificial pigment was common amongst ancient Mediterranean cultures throughout Egypt, Mesopotamia, Greece, and the Roman Empire, little is known about ancient production centres and the sources of raw materials. Variations in lead isotope (LI) ratios can be useful for fingerprinting the geological sources of copper metal, which has the potential to indicate local production or importation. This method is here applied to copper- and silica-rich EB pigments in order to investigate the provenance of the copper component. The investigated EB pigments were sampled from nine ancient artefacts of Egyptian, Etruscan, Canosan, and Roman origin (dating from between the 5th century BCE to the early 1st century CE) that are part of the archaeological collection of the Ny Carlsberg Glyptotek (NCG), Denmark. For the first time, copper isotope analysis was also applied to EB pigments to facilitate future studies of copper isotopes in such materials. Variations in copper isotopes hold the potential to complement lead isotope-based provenance considerations. The lead isotope data (LID) of the investigated EB pigments were compared to reference LID of copper minerals of European, Near and Middle Eastern, and North African ores that have been exploited at a time relevant for the studied EB pigments. In support of (i) a previously postulated scenario where the import of copper for producing EB dominated over the use of local resources (Shortland, 2006) and (ii) consistent with the preference for lead isotope-based exclusion of unlikely sources rather than the determination of certain provenance, copper ore deposits pertaining to Egyptian and Italian LI fields show no significant overlap with the LID of the studied EB pigments. Instead, we propose that copper sourced from various European (Aegean, Balkan, Iberian, Central European) deposits potentially supplied the production of the studied EB pigments. For example, (i) the studied Egyptian EB pigments show no overlap with Egyptian copper, but instead with Aegean sources; (ii) based on the highly variable copper provenance of the studied Etruscan EB pigments, we tentatively propose that this might argue for the importation of copper raw materials and a subsequent local production in Etruria, analogous to previously reported Etruscan glass production; (iii) we propose that Iberian copper was used for local EB production at a time when the known large-scale EB production facilities in the Bay of Naples were already active. While the testimony of ancient trade in EB is a difficult topic to unravel, the potential copper sources involved in producing EB pigments of the few investigated archaeological artefacts suggests that a few (EB) pigment workshops/production centres were highly actively trading raw materials and/or manufactured EB pigments with several different Mediterranean civilizations. Many EB pigment producing workshops and distribution sites may have existed throughout the Mediterranean facilitating a highly complex and diverse network of trade in this widely distributed ancient pigment.

1. Introduction

The vitreous blue compound Egyptian blue (EB; $CaCuSi_4O_{10}$) is the earliest known synthetically produced pigment. Its production involved a complex technique, a sintering process during which a copper (Cu) containing compound (alloy or mineral; Hatton et al., 2008; Piovesan et al., 2011), compounds containing calcium (e.g. powdered limestone) and silica (such as silica sand), and a few percent of a flux of soda were

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contained in crucibles and heated in a furnace (Grifa et al., 2016, and references therein). At temperatures of about 850–1080 °C, a blue frit would form through nucleation and growth within a liquid or glass phase (Pradell et al., 2006; Hatton et al., 2008; Grifa et al., 2016). This coarse-textured mass of polycrystalline blue frit could then be ground to a powder and used as a pigment.

The term 'Egyptian blue' is a modern construct and the reason for this particular name should be found in the fact that the earliest and the richest source of visible evidence comes from Egypt. This has reinforced the idea that the pigment was produced and exported from Egypt. Although there is evidence of earlier use of EB (c. 2900 BCE; Hatton et al., 2008), it became widespread in Egypt during the 4th Dynasty (c. 2600 BCE; Berke, 2002; Hatton et al., 2008), in Greece and the Near East from the 3rd millennium BCE, and was also frequently used in Etruria (Kakoulli, 2009; Skovmøller et al., 2016, and references therein). Further, ancient texts by Pliny mention the existence of various kinds of *caeruleum* (*NH* 33.57), which may be EB (e.g. Kakoulli, 2009), of various origins:

"*Cæruleum is a kind of sand. In former times there were three kinds of it*; *the Egyptian, which was the most esteemed of all*; *the Scythian, which is easily dissolved, and which produces four colours when pounded, one of a lighter blue and one of a darker blue, one of a thicker consistency and one comparatively thin*; *and the Cyprian, which is now preferred as a colour to the preceding. Since then, the kinds imported from Puteoli and Spain have been added to the list, this sand having of late been prepared there.*" (translation: Bostock, 1855). This illustrates that EB was likely to have been produced in Egypt, Scythia, and on Cyprus from an early period onwards, while the production at Puteoli (modern day Pozzuoli, in the Bay of Naples) and in Spain was more recent.

The mass production of synthetic blue pigments (EB) is also recorded by the ancient author and architect Vitruvius (c. 1st century BCE; Vitr. *De arch.* 7.11.1). According to him, EB was first discovered in Alexandria. He further writes that EB was later produced at Pozzuoli, introduced by a man named Vestorius. However, only a few ancient production sites for EB have been identified in Egypt and even fewer outside of Egypt. This begs the question whether EB was produced primarily in Egypt and exported to the rest of the Mediterranean region or whether local production was in fact much more common than suggested by the lack of archaeological evidence.

Identifying the source of raw materials, such as a potential copper source candidate, can contribute to the reconstruction of ancient trade routes and can help to better understand economic aspects of ancient civilizations. The lead (Pb) isotope approach was developed to differentiate the geological origin of ancient metal artefacts (e.g. Stos-Gale and Gale, 2009), which can subsequently lead to potential geographic regions or mining districts that may have supplied sources. In archaeometry, lead isotope analysis (LIA) is a widely used method to determine e.g. the potential sources of raw materials of various inorganic artefacts (e.g. Sayre et al., 2001; Niederschlag et al., 2003; Wolf et al., 2003; Shortland, 2006; Ling et al., 2014; Artioli et al., 2016; for an overview see also the lead isotope inventory by Cattin et al., 2009) as well as the environmental contamination related to ancient industrial activities (e.g. Véron et al., 2006; Delile et al., 2014; Fagel et al., 2016). Furthermore, the combination of Pb and Cu isotope analyses represents a powerful tool for provenance and characterization studies of the ores mngf (e.g. Gale et al., 1999; Klein et al., 2010; Asael et al., 2012; Jansen et al., 2017).

Briefly, three out of four stable Pb isotopes are radiogenic (i.e. time dependent), ^{206}Pb, ^{207}Pb and ^{208}Pb, these are produced by the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively (Faure and Mensing, 2005). The fourth lead isotope, ^{204}Pb, is not a radiogenic nuclide and its abundance has been stable since the formation of the Earth. The natural abundances of these isotopes are approximately 52.4%, 22.1%, 24.1% and 1.4% for ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb respectively. The variations in Pb isotope compositions of the radiogenic lead isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) to the stable lead isotope (^{204}Pb) allow determining the geochronological age of ore minerals. Thus, the lead isotope (hereafter also written as LI) variation leads to ore deposits that were formed during particular geological events. Based on this, world-wide occurrences of ore deposits can be tracked as potential candidates for a particular LI ratio combination. This can provide complementary information to constrain the potential provenance of the copper ore used for manufacturing an artefact. Additionally, variations in stable Cu isotopes may further constrain the provenance of a potential copper source candidate. The two stable copper isotopes ^{63}Cu and ^{65}Cu (natural abundance: 69.2% and 30.8%, respectively) show a significant natural variability in copper deposits (Albarède, 2004). Copper isotopes fractionate by redox reactions, for example, during the evolution of ore fluids, by leaching and weathering of primary sulphides, and re-deposition in secondary ores (Asael et al., 2012; Klein et al., 2010, and references therein). Hence, the combination of variations in the radiogenic ^{206}Pb, ^{207}Pb and ^{208}Pb to the stable ^{204}Pb, with variations of the two stable copper isotopes ^{63}Cu and ^{65}Cu, holds the potential for determining the ore deposit field and the type of ore minerals (e.g. primary vs secondary) used for manufacturing an artefact, respectively.

Importantly, it is commonly accepted within archaeometallurgy that technological processes are not expected to fractionate the Pb isotopes of the native minerals (e.g. Barnes et al., 1978; Gale et al., 1999; Stos-Gale and Gale, 2009, and references therein; Cui and Wu, 2011). This is due to the relatively high mass of their heavy isotopes and low internal mass differences (Faure and Mensing, 2005). Previously, a similarity in the lead isotopic composition of ancient glasses/glazes and nearby, hence most likely used, lead occurrences was reported by Brill and Wampler (1967). Their work thus postulates that Pb isotopes of the native minerals will remain nearly identical to that of the raw materials used during processes related to glass/glaze production. This reasoning was also employed by others studying glasses/glazes by using LIA (Brill et al., 1979; Brill et al., 1993; Wedepohl et al., 1995; Wolf et al., 2003; Henderson et al., 2005, and references therein) and was experimentally tested for lead-based pigments produced from galena (Barnes et al., 1978). Due to the similarity in the production (i.e. process parameters) of glass/glaze and of EB pigments, this hypothesis of inferred identical lead isotopic characteristics between copper raw materials and finished EB pigments was also employed by Shortland (2006). However, while the Cu isotope composition of ancient glass has been investigated (Lobo et al., 2014), the potential for Cu isotope fractionation during processes related to glass/glaze/pigment production has yet to be evaluated.

Although LIA is a powerful tool for investigating the provenance of metal artefacts, available ore deposit reference data cannot be considered to fully characterize the entire LI distribution of a given ore body/LI field. Challenges with interpreting LID for provenance considerations are due to, for example, variations in LI ratios within the ore body itself (e.g. due to a complex geological history), the use of yet unknown ore bodies by ancient metalworkers, and potential homogenization of lead isotopes during mixing/recycling of different alloys or minerals (see e.g. Baron et al., 2014; Pearce, 2016). Hence, even precise LIA and a careful assessment of similarities between sample and reference LID can only be considered to provide indications of a potential match between a given artefact and a LI field. More precisely, the application of LIA can lead to the exclusion of ore deposits that are not significant. Therefore, it is crucial to consider the potential LI-based provenance of raw materials in an archaeological context with source discrimination based on the material's cultural and political-historical background (e.g. Ling et al., 2014; Bray et al., 2016).

In the current study, we set out to investigate the provenance of the copper compound of ancient EB pigments. We test whether this compound was locally sourced or imported by comparing EB pigments from artefacts originating from the two different geographical regions where EB was produced as reported by the ancient literary sources (in Egypt and the Bay of Naples). The aim was to investigate whether there is any indication for the production of EB in Italy earlier than the 1st century