

## INVESTIGATING THE PROVENANCE OF EGYPTIAN BLUE PIGMENTS IN ANCIENT ROMAN POLYCHROMY

### AZ EGYIPTOMI KÉK FESTÉKANYAGOK SZÁRMAZÁSI HELYÉNEK VIZSGÁLATA A RÓMAI POLIKRÓM MŰVÉSZETBEN\*

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#### Abstract

*Egyptian blue is a copper-based blue pigment that was widely used across the Mediterranean from ca. 3300 BC up to late antiquity and even later. For this case study, we analyzed the provenance of Egyptian blue from a Campana relief from the collection of the Ny Carlsberg Glyptotek, Denmark. Campana reliefs are terracotta plaques, which were named after the Italian collector Gampietro Campana, who published the first collection in 1851. These mould-made plaques were used as ornaments in central Italy from ca. 60 BC to 50 AD – a time when Egyptian blue production is attested at several sites in the Bay of Naples, Italy. The provenance of copper raw materials that were used for producing this pigment could provide clues about the distribution of production centers and trade contacts. A previous investigation of the provenance of a single bulk Egyptian blue sample of this artefact by Rodler et al. (2017) indicated a possible long-distance transport of (Iberian) copper ore or mixing of distant (Iberian) and Italian copper. Our new data are based on the lead isotope analysis of four individual Egyptian blue samples. The refined sampling resolution emphasizes the Italian South-Eastern Alps as the most likely source area of copper raw materials. This copper could have been processed in local Egyptian blue production workshops or brought to the contemporary Egyptian blue production hub in the Bay of Naples and transported from there to the workshop where the artefact was painted.*

#### Kivonat

*Az “egyiptomi kék” egy réz alapú kék festék, amelyet széles körben alkalmaztak a Földközi-tenger vidékén i. e. 3300-tól a kései antikvitásig, sőt még később is. Ehhez az esettanulmányhoz egy Campana reliefen használt „egyiptomi kék” festéket vizsgáltunk a Ny Carlsberg Glyptotek (Dánia) gyűjteményéből. A Campana reliefek terrakotta plakettek, amelyeket egy olasz műgyűjtő, Gampietro Campana után neveztek el. Campana 1851-ben tette közzé első katalógusát. Ezeket a formába nyomott plaketteket dísz tárgyként használták Itália középső részén i. e. 60-tól i. sz. 50-ig – abban az időben, amikor az “egyiptomi kék” festéket több műhelyben is előállították a Nápolyi-öböl vidékén. A festék előállításához használt réz alapú nyersanyagok vizsgálata segítséget nyújthat a festéket előállító műhelyek azonosításában és a kereskedelmi kapcsolatok vizsgálatában. Egy korábbi tanulmányban Rodler et al. (2017) felvetették a távolsági kereskedelem lehetőségét, miszerint a rezet ibériai forrásokból szereztek be, vagy ibériai eredetű rezet keverték az alapanyagokhoz. Az új vizsgálatokhoz négy mintát használtunk, melyeken ólom izotóp vizsgálatokat végeztünk. A vizsgálatok szerint a réz nyersanyag nagy*

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\* How to cite this paper: RODLER, A.; MATTHYS, S.M.; BRØNS, C.; ARTIOLI, G.; SNOECK, C.; DEBAILLE, V. & GODERIS, S., (2021): Investigating the provenance of Egyptian blue pigments in ancient Roman polychromy, *Archeometriai Műhely* XVIII/2 97–108.  
doi: [10.55023/issn.1786-271X.2021-008](https://doi.org/10.55023/issn.1786-271X.2021-008)

valószínűséggel az olaszországi Délkeleti-Alpok bányáiból származik. Ezt a rezet helyi műhelyekben vagy a Nápolyi-öböl műhelyeiben dolgozhatták fel, ahonnan tovább szállították a plaketteket festő műhelyeknek.

KEYWORDS: LEAD ISOTOPE ANALYSIS; PIGMENT PROVENANCE; TRADE IN PIGMENT RAW MATERIALS

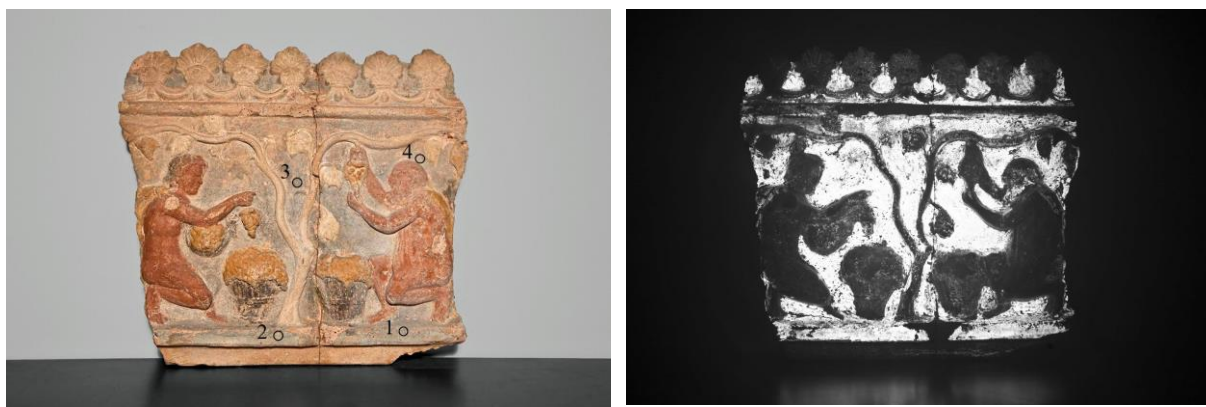
KULCSSZAVAK: ÓLOMIZOTÓP VIZSGÁLAT, FESTÉK SZÁRMAZÁSI HELY VIZSGÁLAT, FESTÉK NYERSANYAG KERESKEDELEM

## Introduction

The pigment Egyptian blue ( $\text{CaCuSi}_4\text{O}_{10}$ ) was produced in a sintering process. The coarse-textured mass of polycrystalline blue frit was obtained from fusing copper (Cu alloy or mineral), calcium (e.g., powdered limestone) and silica (e.g., silica sand), and a few percent of a flux of soda by heating in crucibles in a furnace at about 850–1050 °C (Pradell et al. 2006; Hatton et al. 2008; Grifa et al. 2016, and references therein) similar to faience and glass production (e.g., Nicholson 2012; Boschetti 2011). The blue frit was then ground to powder and used as pigment. The earliest and richest visible evidence for the use of Egyptian blue comes from Egypt (early finds from c. 3300 BC; Riederer 1997; widespread use in Egypt from the 4<sup>th</sup> Dynasty, c. 2600 BC; Berke 2002; Hatton et al. 2008), which is why the term ‘Egyptian blue’ is used for this pigment. This has also reinforced the idea that Egyptian blue was produced and exported from Egypt. However, from the 3<sup>rd</sup> millennium BC, its use became widespread in Greece and the Near East, and this pigment was also frequently used in Etruscan and Roman art (e.g., Kakoulli 2009; Piovesan et al. 2011; Ganio et al. 2015; Skovmøller et al. 2016; Brøns et al. 2016) and is even attested to Medieval art (Dariz & Schmid 2021, and references therein). Ancient texts by Pliny the Elder mention various kinds of *caeruleum* (NH 33.57; translation: Bostock 1855) – which may refer to Egyptian blue (e.g., Kakoulli 2009) – of various origins (Egypt, Scythia, Cyprus, later in the Bay of Naples and Spain). The ancient author and architect Vitruvius (c. 1<sup>st</sup> century BCE; Vitr. *De arch.* 7.11.1; translation: Morgan 1914) also mentions mass production of blue pigments first at Alexandria, later at Pozzuoli/Bay of Naples. Although only a few ancient Egyptian blue production centers in Egypt and outside of Egypt are known today, its widespread use poses the question whether local production was more common than suggested by archaeological and historical evidence.

Evaluating the potential source of copper raw materials can reconstruct ancient trade contacts. The lead (Pb) isotope approach was developed to differentiate the geological origin of ancient metal artefacts (e.g., Stos-Gale & Gale 2009) by excluding regions or mining districts that were the least likely source areas. Lead isotope analysis has recently been used for evaluating the provenance of

pigments (Shortland 2006; Nord et al. 2015; Rodler et al. 2017; Rodríguez et al. 2020; Curley et al. 2020). This can provide complementary information to constrain pigment provenance. Briefly, the abundance of one out of four Pb isotopes,  $^{204}\text{Pb}$ , has been stable since the formation of the Earth, while the other three Pb isotopes are radiogenic (*i.e.*, time dependent). The lead isotopes  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  are produced by the radioactive decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ , respectively (Faure & Mensing 2005). The variation in Pb isotope ratios of the radiogenic lead isotopes ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) to the stable lead isotope ( $^{204}\text{Pb}$ ) allows determining the geochronological age and formation history of ore minerals. It is commonly accepted that technological processes do not fractionate the Pb isotopes of the native minerals and raw materials used during archaeometallurgical production processes (e.g., Barnes et al. 1978; Stos-Gale & Gale 2009; Cui & Wu 2011). This was previously proposed for the Pb isotope composition of ancient glasses/glazes (Brill & Wampler 1967; Barnes et al. 1978; Brill et al. 1979, 1993; Wedepohl et al. 1995; Wolf et al. 2003; Henderson et al. 2005; Shortland 2006) and explained as linked to the relatively high mass of Pb isotopes and limited mass differences (Faure & Mensing 2005). However, recent research of Rademakers et al. (2020) indicates a potential Pb isotope fractionation particularly when ores with low Pb concentrations were recycled. This aspect is relevant when considering that Egyptian blue pigments may have been produced from bronze scrapings. Moreover, the available ore deposit reference data cannot be considered to fully characterize the entire spread in Pb isotope ratios of a given ore body/Pb isotope field. An interpretation of provenance thus needs to carefully consider likely variation in Pb isotope ratios within the ore body, the ancient use of ore bodies that are not known today/not included in reference databases, and potential homogenization of Pb isotopes during mixing/recycling of different alloys or minerals (e.g., Baron et al. 2014; Pearce 2016; Rademakers et al. 2020). Therefore, the use of Pb isotope ratios can only provide an exclusion of ore deposits that are unlikely source areas and thus the source discrimination has to be based on the material's cultural and archaeological background (e.g., Ling et al. 2014; Bray et al. 2016).



**Fig. 1.:** left, Color photograph of the Campana relief, NCG inv.no. IN 1708 (32 × 35 cm), with sampling spots 1 to 4 indicated by black circles; right, VIL image of artefact IN 1708 with the typical fluorescence of *Egyptian blue*.

**1. ábra:** balra, A Campana relief színes fényképe, NCG ltsz. IN 1708 (32 × 35 cm), a mintavételi pontokat 1-től 4-ig fekete körök jelölik; jobbra, a tárgy (ltsz: IN 1708) fotolumineszcens (VIL) felvétele, ami az *egyiptomi kék* festék jellegzetes fluoreszcenciáját mutatja.

Here, we re-investigate the provenance of the copper of Egyptian blue of a Roman terracotta artefact from the archaeological collection of the Ny Carlsberg Glyptotek (NCG), Denmark. Previous results of a single bulk sample pooled from various areas of this artefact (Rodler et al. 2017) indicated a potential mixing of Iberian and Italian South-Eastern Alpine copper ore. A higher sampling resolution was applied in the current case study to evaluate whether copper was indeed imported, and a mixing scenario is sustained (Rodler et al. 2017), or whether copper could have been locally sourced for Egyptian blue production in Italy. We use Pb isotope analysis to dismiss least likely copper source areas and consider the Pb isotope data within an archaeological and historical context. The overall aim is to improve our understanding of trade in copper and Egyptian blue pigments, as well as the possible distribution of ancient Egyptian blue production workshops.

### Material and methods

The studied artefact (NCG inv. no. IN 1708, **Fig. 1.**) is part of the collection of the Ny Carlsberg Glyptotek, Denmark. It was acquired at an auction in Rome in 1899 and is a typical Campana relief showing two satyrs picking grapes and an ornamental palmette frieze is placed above the figures (Østergaard 1996). Campana reliefs were mould-made in a serial production and the same motifs were often repeated. These characteristic architectural terracotta plaques were used in Rome and Central Italy for upper walls of temples, private houses, and funerary structures during the late 1<sup>st</sup> century BC and the early 1<sup>st</sup> century AD. The

artefact IN 1708 has visible traces of blue paint on the rim below the scene, on the background of the scene and between the palmettes, as well as traces of red paint on the palmettes and the skin of the satyrs, and yellow paint on their mantles and the grapes (**Fig. 1.**). Furthermore, the blue paint was identified as Egyptian blue by near-infrared (NIR) luminescence imaging (also called visible-induced luminescence, VIL, imaging; Verri 2009). The  $\text{Cu}^{2+}$  ions of Egyptian blue emit a strong luminescence band at 910 nm when excited by visible light. A camera with a filter modified for detecting only infrared light emissions can then record this luminescence. For this purpose, the internal IR-blocking filter of a Canon 40D camera was replaced with an external Schott RG830 filter (with a cut-on of 50% at 830 nm) and a LED light source (EXcled; 470–630 nm) (see also Ganio et al. 2015; Brøns et al. 2016; Skovmøller et al. 2016).

The pigment samples were collected with a scalpel from four different spots of highly luminescent areas (**Fig. 1.**); care has been taken to sample pigment layers with no signs of significant surface alteration due to later modifications and to avoid mixing of different pigment layers. These four samples were processed as individual samples instead of producing a single bulk sample (Rodler et al. 2017).

After pigment sample digestion in ~1 ml of a mixture of 14 mol l<sup>-1</sup> HNO<sub>3</sub> and 8 mol l<sup>-1</sup> HCl, Pb was separated from matrix elements by ion chromatography using a standardized HBr-HCl elution recipe on columns charged with an anion resin (AG-1 ×8 100–200 mesh, Bio Rad™) at

Laboratoire G-Time, Université Libre de Bruxelles, Belgium. After separating Pb from matrix elements, the samples were diluted in 2% HNO<sub>3</sub> to a Pb concentration of approximately 500 ppb for subsequent Pb isotope analysis with a Nu Instruments Multi-Collector Inductively-coupled-Plasma Mass Spectrometer (MC-ICP-MS) Nu-Plasma II at the Laboratoire G-Time. The sample solutions were doped with a thallium standard solution (Alpha ICP standard) with a known <sup>205</sup>Tl/<sup>203</sup>Tl isotope ratio of 2.3871. Monitoring the Tl isotope ratio while analyzing the Pb isotope ratios was used to correct for instrumental mass bias. Isobaric interference on mass 204 (<sup>204</sup>Hg) was monitored during acquisition using mass 202. The sample-standard-bracketing (SSB) procedure was used to correct for mass fractionation; sample Pb concentrations were determined during Pb isotope analysis. The procedural Pb blank (< 50 pg ml<sup>-1</sup>) was significantly lower than the Pb concentrations of the purified Pb samples (1.53–140 ppm). The certified reference material NIST SRM 981 was analyzed along with the sample materials to correct the results and to assess accuracy and reproducibility. The routine analysis of NIST SRM 981 achieved a long-term external reproducibility of ±0.006 % (2σ) for the <sup>206</sup>Pb/<sup>204</sup>Pb ratio (18.234, n >312), ±0.005 % (2σ) for the <sup>207</sup>Pb/<sup>204</sup>Pb ratio (15.624, n >291), ±0.015 % (2σ) for the <sup>208</sup>Pb/<sup>204</sup>Pb ratio (38.274, n >378), ±0.0003 % (2σ) for the <sup>208</sup>Pb/<sup>206</sup>Pb ratio (2.0990, n >143), and ±0.0001 % (2σ) for the <sup>207</sup>Pb/<sup>206</sup>Pb ratio (0.8569, n >113). However, following a conservative approach to our

external reproducibility and the error propagation reported by other authors (e.g., Stos-Gale & Gale 2009; Ling et al. 2014), we use an uncertainty of ± 0.1% for Pb isotope ratios including <sup>204</sup>Pb for provenance evaluations.

## Results

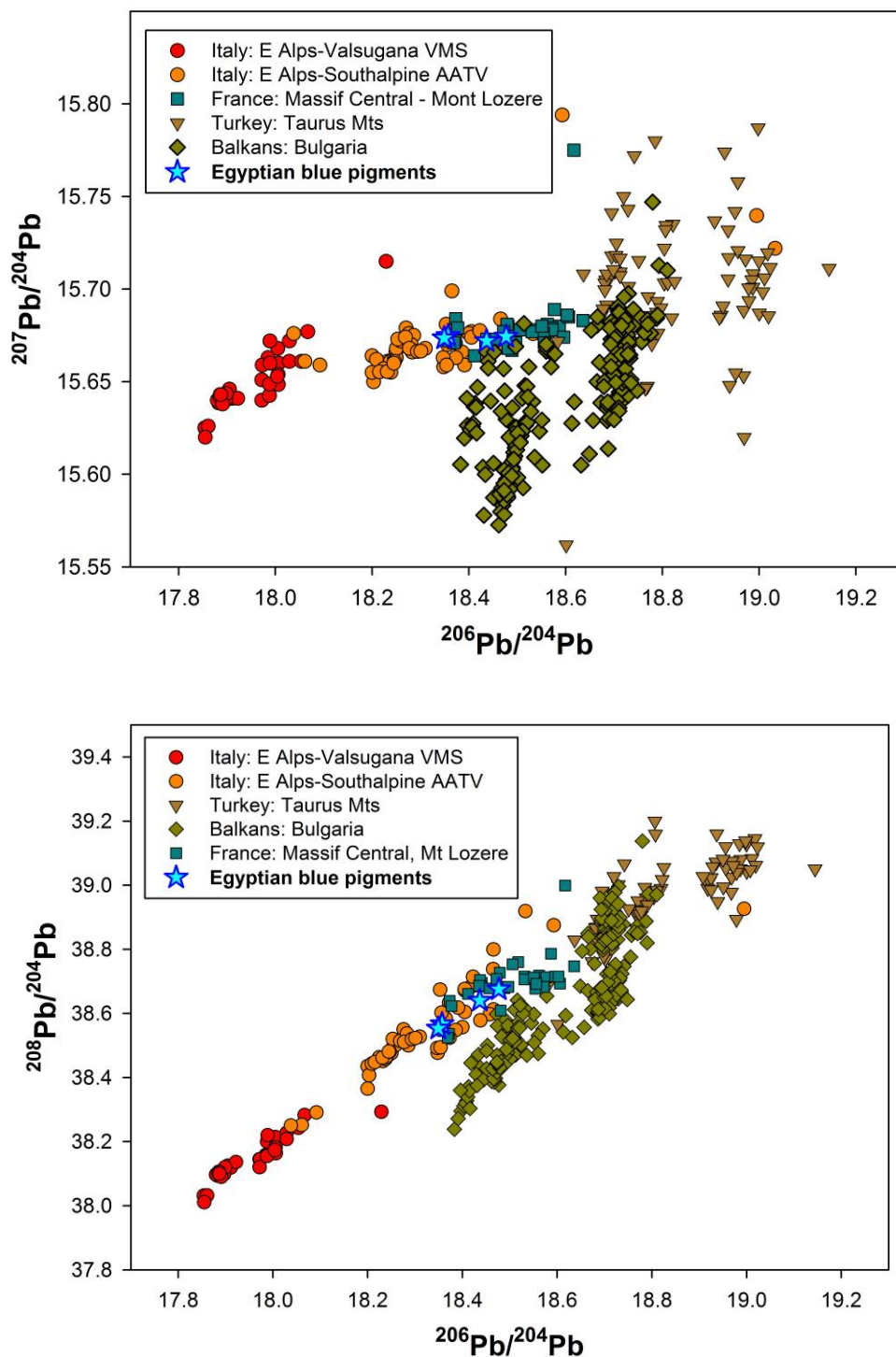
The Pb concentrations and Pb isotope data of all samples are listed in **Table 1**. The four Egyptian blue samples display a narrow range in all analyzed Pb isotope ratios with <sup>208</sup>Pb/<sup>204</sup>Pb between 38.552 and 38.676, <sup>207</sup>Pb/<sup>204</sup>Pb between 15.672 and 15.675, <sup>206</sup>Pb/<sup>204</sup>Pb between 18.349 and 18.477, <sup>208</sup>Pb/<sup>206</sup>Pb between 2.093 and 2.101, and <sup>207</sup>Pb/<sup>206</sup>Pb between 0.8483 and 0.8542. While we report all analyzed Pb isotope ratios, for the purpose of provenance evaluation in comparison with copper ore deposits, we will focus on the three Pb isotope ratios over <sup>204</sup>Pb. Here, all four samples have comparable <sup>207</sup>Pb/<sup>204</sup>Pb ratios, while there is a slightly more pronounced difference in <sup>208</sup>Pb/<sup>204</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb between the two samples from the rim (CampEB-1 and -2) and from the background at the top of the scene (CampEB-3 and -4). Furthermore, the samples from the background have significantly lower Pb concentrations compared to the rim (3.75 to 1.53 ppm and 62.0 to 140 ppm, respectively). The sample Pb concentrations are calculated from the signal during Pb isotope analysis and have a relative standard deviation of 10%.

**Table 1:** Lead isotope ratios

**1. táblázat:** Ólomizotóparányok

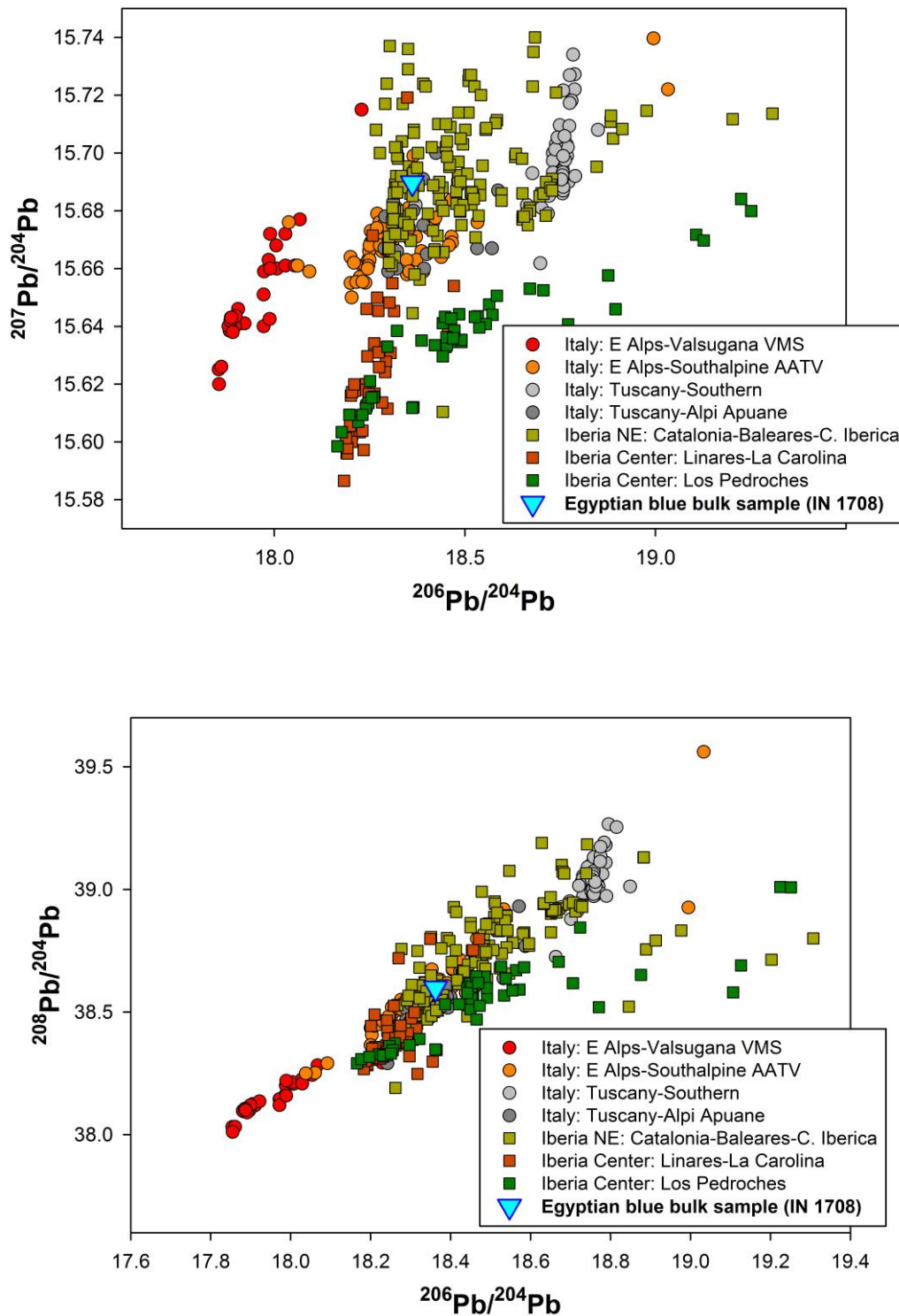
Sample ID	<sup>208</sup> Pb/ <sup>204</sup> Pb ± SE	<sup>207</sup> Pb/ <sup>204</sup> Pb ± SE	<sup>206</sup> Pb/ <sup>204</sup> Pb ± SE	<sup>208</sup> Pb/ <sup>206</sup> Pb ± SE	<sup>207</sup> Pb/ <sup>206</sup> Pb ± SE	Pb (ppm)
CampEB-1	38.567 ± 0.002	15.675 ± 0.001	18.357 ± 0.001	2.1009 ± 0.0000	0.8539 ± 0.0000	62.0
CampEB-2	38.553 ± 0.002	15.674 ± 0.001	18.349 ± 0.001	2.1012 ± 0.0000	0.8542 ± 0.0000	140
CampEB-3	38.675 ± 0.002	15.674 ± 0.001	18.477 ± 0.001	2.0931 ± 0.0000	0.8483 ± 0.0000	3.75
CampEB-4	38.640 ± 0.002	15.672 ± 0.001	18.437 ± 0.001	2.0958 ± 0.0000	0.8500 ± 0.0000	1.53
IN 1708 bulk <sup>1</sup>	38.597 ± 0.039	15.690 ± 0.013	18.362 ± 0.012	2.1020 ± 0.0012	0.8545 ± 0.0002	n.a.

**Note:** The sample IDs CampEB-1 to CampEB-4 correspond to the sampling spots (1 to 4) high-lighted in Fig. 1; variation of Pb concentration, relative standard deviation, 1RSD, is 10%; n.a. = not analyzed; 1 IN 1708 bulk sample was previously analyzed by Rodler et al. (2017).



**Fig. 2.:** Lead isotope biplots (top:  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  and bottom:  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$ ; uncertainty of  $\pm 0.1\%$  for provenance evaluations) of the analyzed Egyptian blue samples (blue stars) compared to the Pb isotope fields of Italian (VMS = Volcanogenic Massive Sulphide ore deposits; AATV = Alto-Adige-Trentino and Veneto field), Turkish, Balkan, and French copper ore deposits.

**2. ábra:** Ólomizotóp megoszlás (fent:  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  és lent:  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$ ;  $\pm 0.1\%$  bizonytalanság mellett) a vizsgált egyiptomi kék festékmintákban (kék csillagok) az olasz (VMS = vulkanogén masszív szulfid érctelepek; AATV = Alto-Adige-Trentino és Veneto vidék), török, balkáni és francia rézérc lelőhelyek adataihoz hasonlítva.



**Fig. 3.:** Lead isotope biplots (top:  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  and bottom:  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$ ; uncertainty of  $\pm 0.1\%$  for provenance evaluations) of one Egyptian blue bulk sample (blue triangle) compared to the Pb isotope fields of Italian and Iberian copper ore deposits, modified after Rodler et al. 2017.

**3. ábra:** Ólomizotóp megoszlás (fent:  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  és lent:  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$ ;  $\pm 0.1\%$  bizonytalanság mellett) az egyiptomi kék festékmintában (kék háromszög) az olasz és az ibériai rézérc lelőhelyek adataihoz hasonlítva, Rodler et al. 2017. adatainak felhasználásával

The sample Pb isotope ratios were compared to reference Pb isotope data of the AAcP Pb isotope database (Artioli et al. 2016), considering ore deposits that were available to the Romans. Based on a statistical data evaluation, Pb isotope fields that closely match our samples include copper ores from France, Bulgaria, Turkey, and Italy. To evaluate patterns of distribution, sample Pb isotope ratios and these potentially matching Pb isotope fields were also plotted in an uranogenic ( $^{206}\text{Pb}/^{204}\text{Pb}$  vs  $^{207}\text{Pb}/^{204}\text{Pb}$ ) and thorogenic ( $^{206}\text{Pb}/^{204}\text{Pb}$  vs  $^{208}\text{Pb}/^{204}\text{Pb}$ ) scatter diagram (Fig. 2.). Due to limitations typical to reference datasets (e.g., the entire range of Pb isotope distribution of an ore body/Pb isotope field cannot be fully characterized), the Pb isotope-based provenance evaluation of pigments (and other archaeological artefacts) can only provide indications of a potential match between samples and ore deposits. However, the previous interpretation of a long-distance importation of copper or a mixing scenario, as proposed by Rodler et al. (2017) for a bulk sample from the same artefact, was refined by analyzing several individual samples. The Pb isotope ratios of the single bulk sample are similar to our new data (Table 1). However, the refined sampling resolution allowed for better statistical data evaluation and evaluation of data alignment compared to reference Pb isotope data. The four samples plot within the Pb isotope field of the French Massif Central as well as of the Italian South-Eastern Alps (Fig. 2.). The latter was already indicated by a previous provenance evaluation of a single bulk sample (Fig. 3.).

## Discussion

Lead isotope analysis as a potentially useful approach for evaluating the provenance of artefacts (e.g., Stos-Gale & Gale, 2009; Artioli et al. 2008, 2016) has a long history in archaeological sciences. Its application, potential and pitfalls were recently reviewed by Killick et al. (2020) and Artioli et al. (2020). Before discussing provenance and trade scenarios of copper used for producing Egyptian blue pigments, we must consider several challenges inherent to the Pb isotope approach. The Pb isotope composition of an ore deposit is controlled by the local geological history (see e.g., Baron et al. 2014), which is why this information can be interesting for tracing the provenance of archaeological artefacts. However, the geological history of an ore deposit can be complex (e.g., due to different ore sequences during the time span of deposition, various origins of mineralized fluids and metals within) and there can be a potentially significant natural spread of Pb isotope ratios within individual deposits. Also, Mediterranean ore deposits show overlapping isotopic signatures between different ores/regions. Moreover, even

though large Pb isotope databases of ore deposits that were worked during antiquity are available as reference (Killick et al. 2020), there is still a potential lack of comparable Pb isotope data (e.g., Klein et al. 2010). All these aspects are relevant when evaluating the quality and information gained through Pb isotope analysis. Additional information for provenance evaluation can be gained through major and trace element analysis as well as mineralogical phase characterization. These analyses were not available for the current work due to the available sample size. Our work is thus based on the interpretation of Pb isotope data compared to a large Pb isotope database (AAcP; Artioli et al. 2016), Pb isotope biplots and the artefact's archaeological context.

When interpreting Pb isotope data, we must keep the complexity of ore bodies and the limitations of reference databases in mind, and we must also consider various contamination scenarios. Even though care was taken during sample processing and collecting, contamination could have occurred at several stages during the life cycle of Egyptian blue pigments. Contamination during laboratory sample preparation, processing and analysis was routinely evaluated with reference materials and blank samples and did not have a significant influence on our results. All four samples were collected by an experienced conservator and from a paint layer that was identified as consisting predominately of Egyptian blue (Fig. 1., VII image). The samples were stored individually to avoid mixing of sample materials. All sampled material appeared homogenous; however, due to the lack of a chemical and mineralogical characterization of the analyzed samples, we cannot rule out that other layers of the artefact's polychromy were collected as well.

For the application of Egyptian blue pigments to the artefact, high-Pb pigments such as lead white [ $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ ] may have been added (Skovmøller et al. 2016) for achieving a specific hue such as a brighter blue. However, a lead white layer underneath the Egyptian blue paint was not visible and the sample Pb concentrations (1.53 to 140 ppm; Tab. 1) are relatively low. These Pb concentrations could therefore reflect the Pb concentration of copper ores rather than deliberate addition of Pb during Egyptian blue application to the artefact (i.e., mixing with high-Pb pigments) or during pigment production (i.e., production using bronze scrapings). Nevertheless, without a chemical and mineralogical characterization of the analyzed samples, it is equally likely that their Pb contents represent a trace composite of a mixture of various raw materials used to produce copper ingots or bronze and other (low-Pb) pigments.

Moreover, various copper materials might have been used for Egyptian blue production and we

cannot be certain whether raw copper ore, refined copper metal from ingots, copper alloys or bronze was added as metal fillings during pigment production (see e.g., Jaksch et al. 1983; Piovesan et al. 2011). The typically low Pb concentrations of copper ores render copper-based materials susceptible to contamination with Pb isotope signatures of other lead sources (Rademakers et al. 2020); this might also apply to Egyptian blue pigments. Mixing of different alloys, additives during smelting or metal recycling could contribute to the overall Pb budget and homogenize the original Pb isotope signature of different materials. If significant mixing between various raw materials had occurred, the pigment Pb isotope ratios might plot on mixing lines between various Pb isotope fields. All four samples have similar Pb isotope ratios, even though the samples of the rim and the background of the scene group in two sets that exhibit differences in Pb concentrations and isotope ratios. This indicates that they were produced from copper sources or copper mixtures with similar Pb isotope ratios and not from batches of copper from distinctly different ore deposits. Furthermore, all four samples match and align well within the overlapping Pb isotope fields of the Italian South-Eastern Alps and the French Massif Central (**Fig. 2.**).

Due to such overlap and the diversity of raw materials used for manufacturing Egyptian blue, a provenance and/or trade interpretation can be complicated. However, based on the archaeological context of the artefact, we tentatively propose a potential provenance of copper used for the studied Egyptian blue pigments. The previously reported minor overlap for South-Eastern Alpine copper sources for a single bulk sample (Rodler et al. 2017) is supported by our new data. This area is closer to where the artefact was produced and is therefore more likely than Iberian sources (**Fig. 3.**; Rodler et al. 2017) or copper sources from the French Massif Central.

Exploitation of copper ores and production of copper metals have been attested in the Southern Alps during Roman times (Artioli et al. 2015, and references therein; Addis et al. 2016). Copper from the peripheral Roman provinces might have been used at presently unknown local Egyptian blue production workshops or might have been traded to known centers of pigment production. The metallurgical processes attested to the Southern Alps during Roman times could have been utilized for other types of pyrotechnology (Fenn 2015), such as glass/glaze/faience (Nicholson 2012) and pigment production. Local Egyptian blue production would have required highly skilled, specialized workers. Egyptian blue was widely used in settlements in the peripheral Roman provinces of the South-Eastern Alps (e.g., Kenner 1985; Dörfler

2009; Tober 2015). Egyptian blue pellets were also found at several sites in the Southern Alps (Delamare & Repoux 2018; recent excavations at Aguntum Municipium/East Tyrol, p.c. M. Auer) as well as pigment processing vessels of what might have been a pigment workshop (Jaschek 1993). However, the identification of pigment workshops is challenging (Kostomitsopoulou Marketou et al. 2020) and not confirmed at any of these sites.

The Campana relief dates from a time during the Roman period when Egyptian blue production was attested in the Bay of Naples (Lazzarini & Verità 2015; Grifa et al. 2016). Contemporaneous to the Egyptian blue production at Memphis, Egypt (Nicholson 2003, 2013; Hatton et al. 2008), several sites in the Bay of Naples (presently Pozzuoli, Cuma and Literno) were producing Egyptian blue pellets in the 1<sup>st</sup> century BC. The harbor of Pozzuoli was the main port of the Roman Republic before Ostia was created. Transport by ships, as attested by Roman cargo ships that carried Egyptian blue pellets (e.g., Boschetti 2011), as well as by land would have facilitated the importation of copper and other constituents. In turn, local production sites in the Bay of Naples may have exported the finished pigments for artistic uses of Egyptian blue in Rome and across Italy (Grifa et al. 2016).

## Conclusions

In this work, we analyzed the provenance of four samples of Egyptian blue from a Campana relief from the collection of the Ny Carlsberg Glyptotek, Denmark. The Pb concentration of these samples is relatively low, which might imply the use of copper minerals instead of bronze scraps as main copper source. Although there is a slight difference in Pb isotope data for the Egyptian blue samples of the background and the rim, this difference does not necessarily imply that copper ores from different source areas were used. All four samples plot in a narrow range and match well with several identified Pb isotope fields. As the formation history of Mediterranean copper ore deposits falls within narrow age-windows, significant overlaps can be expected. However, using the archaeological context, the most probable source area of copper used for manufacturing the studied Egyptian blue pigments corresponds to ore deposits of the Italian South-Eastern Alps. The proximity of these deposits over those from the French Massif Central, which also overlap with the analyzed Egyptian blue pigments, favors a copper source from the South-Eastern Alps. The previously proposed scenario of an Iberian source and/or mixing between different ore deposits (Rodler et al. 2017) therefore appears more convoluted. Thus, copper from local Italian deposits was likely used to manufacture the Egyptian blue of the studied Roman-age Campana relief at local production centers, perhaps within the Bay of Naples.



## Acknowledgements

Thanks to Signe Buccarella Hedegaard and to Henrietta Havsteen-Mikkelsen, Ny Carlsberg Glyptotek, Denmark, for taking photographs, VIL images and for careful sampling. Thanks to Wendy Debouge and Jeroen de Jong, Université Libre de Bruxelles, for help with ion chromatography and Pb isotope analysis, respectively. We are grateful to the Carlsberg Foundation for funding the research project *Transmission and Transformation. Ancient Polychromy in an Architectural Context* of which this research is part. Thanks are also due to the NCG for their generous support and the permission to obtain the necessary samples for this project. VD thanks the FRS-FNRS for support. ASR, SG and VD acknowledge support from the EoS program "ET-HoME". Moreover, we thank M. Mödlinger, A. Kairiss, E. Godfrey and A. Traviglia, who organized Session #262 for EAA2020, where our work was presented and solicited for submitting to this journal, as well as Hedvig Györy and an anonymous reviewer for their constructive comments that improved this work.

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