

# On the Making and Provenancing of Pigments from the Early Dynastic Royal Tombs of Ur, Mesopotamia

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## Keywords

Cosmetic pigments, copper, manganese, lead, hydroxyapatite, bones, *verdigris*, lead isotopes

## Abstract

A total of 50 cosmetic pigments from the Royal Cemetery of the Sumerian city of Ur, Mesopotamia, now in the collections of the Penn Museum, Philadelphia, were investigated for their mineralogical, inorganic, organic and lead isotope composition. The aim of this study was to investigate the making of the pigments and to search for the origin of the material used. Main components of the green pigments were green secondary copper minerals mixed with white hydroxyapatite from bones. Copper acetates and formic acids were detected and the formation of *verdigris* is discussed. Black pigments mostly consist of black manganese minerals. White pigments were made of oxidized white lead minerals, while in red pigments hematite was detected. Vegetable oil or animal fats were detected in a majority of the pigment samples analyzed, and it appears that the pigments were smoothly smeared into the (shell) containers as a paste, but the modern conservation of the pigments and decomposition of the organics hinders a clear identification of the original organic components. Chemical and lead isotope analyses point to a provenance of the coloring minerals from ore deposits in Oman, on the Iranian Plateau and in southeast Anatolia.

## Introduction

In the 1920-1930s, Sir Leonard Woolley excavated thousands of gold, silver, copper, bronze and lead artifacts as well as objects of lapis lazuli, carnelian, agate, marble, limestone, and alabaster from burials dating to the late Early Dynastic, Akkadian and early Ur III periods (c. 2500-2100 BC). All these were prestige goods or other materials of high value that were acquired from various sources via the supra-regional exchange and trading system of the city of Ur. Among this multifaceted suite of finds there were also numerous shells, which were filled

with green, bluish green, gray, white, red, or black pigment. Woolley (1934, p.245) wrote: "Every woman's grave of the old cemetery seems originally to have contained cosmetics .... The ordinary receptacle is a cockle shell... In all these were found remains of the actual cosmetics used, paints or powders now reduced to a hard paste. The colors are white, red, yellow, blue, green, and black, of which green and black are the most common." Woolley (1934) quoted, that the cosmetic pigments were restricted to



Figure 1. The excavations at Ur, Mesopotamia in 1922-1930 by Sir Leonard Woolley caused a sensation worldwide. Finds of colorful pigments initiated the St. Louis Post Dispatch Sunday Magazine in 1930 to publish this picturesque illustration. This picture, however, is the only figurative presentation for a cosmetic use of pigments found in the tombs. Image courtesy of the Penn Museum, image #151273.

the “old cemetery”, that is, his late Early Dynastic cemetery, and are apparently not part of the Akkadian and later graves. Such pigments were supposedly used for cosmetic purposes, which was impressively displayed on September 28<sup>th</sup>, 1930 in the St. Louis Post Dispatch Sunday Magazine (St. Louis, Missouri) (Figure 1). The shell vessels used as containers for the pigments (taxonomic families of *Arcidae* and *Cardiidae*, Zettler and Horne, 1998, pp.143-144) are widespread marine animals in tropical and subtropical waters of the Persian Gulf, the Red Sea or the Indian Ocean. The cosmetic pigments, especially the green ones, were found in a dense but friable state. However, the pigments were most probably mixed with an organic binder that allowed it to be applied and spread smoothly. Prepared this way, the pastes were then smeared to the inside of shells, which functioned as containers. A few examples from the excavations show alternative ways to handle the cosmetics, such as the pigments being formed as a set of flat coin-sized disks (Figure 2). The storage of a black pigment powder in a small pottery vessel and a gray one in vessel with multiple receptacles has also been noted. The last mentioned type of vessel was found frequently in the late Early Dynastic Inanna Temple at Nippur (Zettler, 1984, p.50). No matter how they were prepared, almost all of them have hardened over the course of time.

Not only natural shells were used as containers, artificial shells made of gold or silver (#B16710 and B16711, Zettler and Horne, 1998, pp.135; British Museum nos. ME 121345 and ME121354) were also used for this purpose. Sample #4326/B17164 consists of fine-grained black powder stored in a small ceramic vessel. Three samples of intense rust-red pigments were analyzed, and in contrast to most of the green, white and black pigments, they were not kept in shell halves. Two of the rust-red samples are solid, coarse-grained pieces, the third sample (#4329/35-1-660) is a carefully powdered material.

This corpus of finds from the Royal Tombs of Ur represent a most interesting analogue to ancient Egyptian cosmetics, which are described and summarized by Lucas and Harris (1962, pp.338-351; Lee and Quirke, 2000). Many of these pigments were investigated using scientific methods, particularly the synthetic blue color of Egyptian blue (overview in Nicholson and Henderson, 2000; Moorey, 1994, pp.188-189). Especially Walter, et al. (1999) contributed with new ideas on synthetic production of white pigments by wet-chemical processes.

The corpus of cosmetic pigments from Ur supplements the colors used (in later periods) as wall paintings in Mesopotamia (Moorey, 1994, pp.327-329). Early investigations on the chemical composition of the cosmetic pigments from the Royal Tombs of Ur were not

systematically performed. Graham (1928) started with the first analyses, but only much later Bimson (1980) investigated some cosmetic pigments that are preserved in the Ur collection of the Department of Western Asiatic Antiquities at the British Museum in London. She applied X-ray diffraction analysis and partly also X-ray fluorescence spectrometry.

In the present paper, we provide the results of analytical investigations on the cosmetic pigment pastes, a type of find that attracted less attention in the context of pre-historic and early historic exchange of goods in southwest Asia so far. At Ur, the pigments were treated as valuable accessories to the burials in the Royal Tombs. The material characteristics of the pigment samples are the primary focus. Beyond this we considered it necessary to present a discussion about the manufacturing of the cosmetic pigments. As proved by our analyses, the pigments comprise of a mixture of various constituents, both minerals and organic materials. With the available data the origins of the inorganic raw material can be attempted.

The cosmetic pigments investigated in this study are from the inventory of the University of Pennsylvania Museum of Archaeology and Anthropology, Philadelphia. The present study is part of a joint research project of the Penn Museum, the Deutsches Bergbau-Museum and the Goethe-University Frankfurt am Main.

## Finds of cosmetic pigments in Mesopotamia and surrounding regions

Besides the examples from Ur, cosmetic pigments from other archaeological sites in the Near and Middle East were already mentioned and studied by other authors. An overview of some pigments in shells in Mesopotamia is presented by Moorey (1994, pp.138-139). He mentioned the colors of such pigments and their mineral content as determined by Graham (1928), Woolley (1934, pp.245, 248), and Bimson (1980).

Beyond that overview, finds and findings of cosmetic pigments from the following localities (see Figure 3) should be noted:

Mackay (1925, pp.14-15) reports on pigments in cockle shell containers found in the graves of the cemeteries of Kish (Early Dynastic IIIB to Early Akkadian). At the time of the excavation, their colors were white, light-green, blue, red and black, of which black was the most common. One shell found in Grave 15 contained an untouched dab of green pigment on the remains of black one. He suggested that the black pigment would probably be kohl. The green pigment, which he described as being of apple-green shade, would be probably

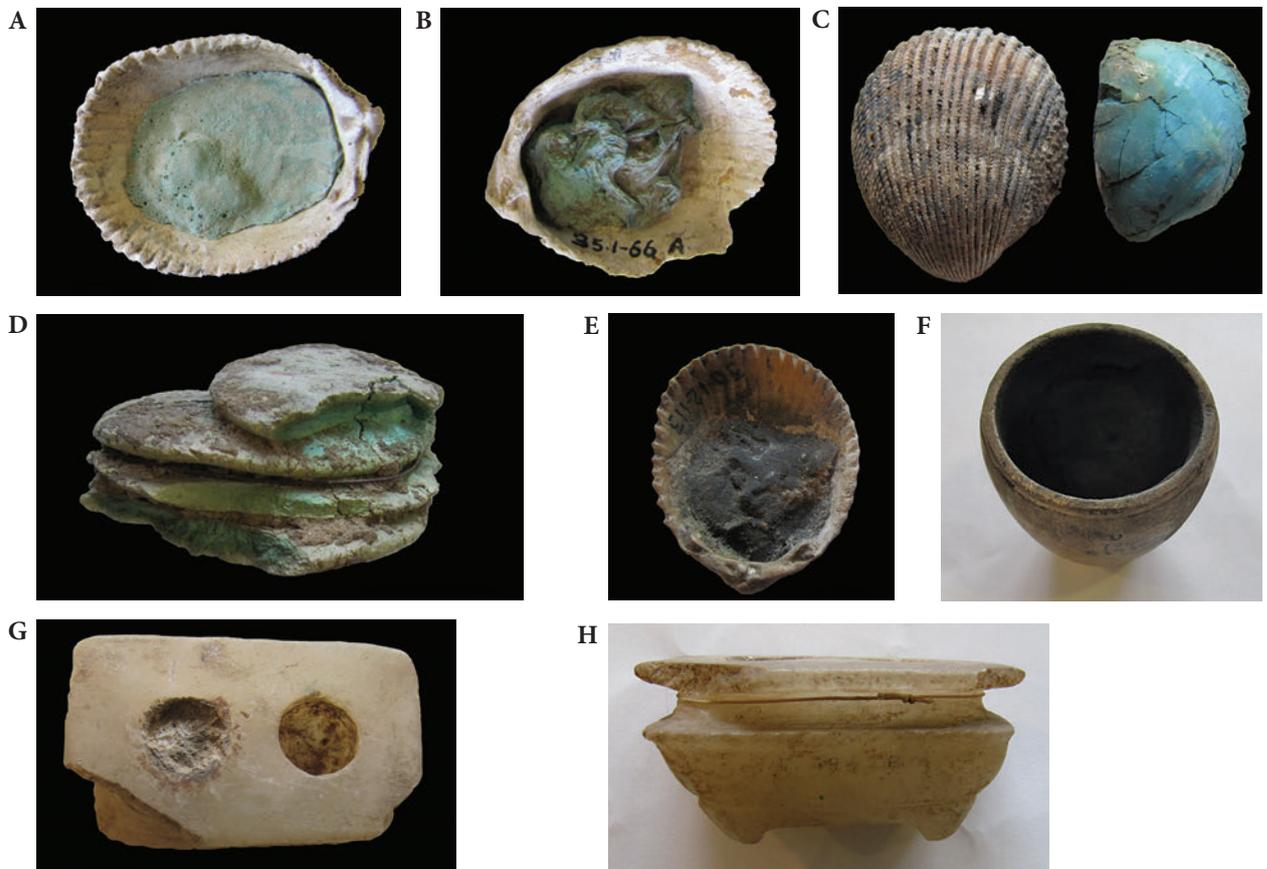


Figure 2. Cosmetic pigments in various containers found in the Royal Tombs of Ur, Mesopotamia. Three examples are of greenish (A: #4298/17025b, B: #4302/25-1-66A) and bluish (C: #4313/B17192) color were set in the shell containers in the pasty state and solidified. Note bubbles of degassing preserved in the solidified pigment in shell A. Size of the shells 5-8 cm. D: Four green discs (#4300/30-12-539) made up of paratacamite and hydroxyapatite mixed possibly with a binder containing fatty acids from an oil or fat. Size of the discs 4.5 cm. E: Black pigments in a shell container (#4317/ 30-12-113). Size of the shell 4.3 cm. F: Black powdered pigment (#4326/ B17164) in a pottery vessel. Diameter of the vessel 7.8 cm. G, H: Grayish pigment (4335/35-1-42) kept in a rectangular vessel with two receptacles. Width of the vessel 10.5 cm. Photos: A. Hauptmann, Deutsches Bergbau-Museum Bochum

malachite. Worthy of note, he comments that “whatever material it is, it appears to have been mixed with a white substance”.

In the “A” cemetery of Kish, Mackay (1925, pp.131-132) notes the finding of shells that contained kohl, a pasty white pigment, red pigment, yellow (yellow ochre) pigment and also examples of black on white pigment. In Grave 91, the two valves of an oyster (*Ostrea edulis*) were found instead of the usual cockle shell (*Cardium*). Furthermore, other finds point to cosmetics such as in burial 135, where a pair of copper saucers was found, each measuring 57 mm in length, 48 mm in width and 18 mm in depth. They are stuck together by corrosion face to face. Their contents have not yet been examined (Reg. No. 2714; Oxford). Another example, a pair of cockle shells made of copper, evidently belonging to a grave, had contained remains of a black powder. A mould of an ordinary cockle shell had clearly been taken and copied in metal (Reg. 2553; Field Museum) similar to some of the copies made in the Royal Tombs. Algaze (1983-1984) lists cosmetic shells from the contemporary “Y” ceme-

tery at Tell Ingharra (which is comparable to the site of Kish), but he lists them only by type.

Cockle shells used to hold cosmetic pigments are frequently found in burials dated to the Early Dynastic III at Tell Abu Salabikh (Martin, Moon and Postgate, 1985). The pigments are green, white, red and black, often with traces of bitumen on the outside of the shell. The black is often associated with pigments of other colors, e.g., black over white pigment, black and yellow pigment, and black over traces of red pigment. They were not analyzed.

Concerning the containers for cosmetic pigments made of stone, the Inanna temple at Nippur yielded large numbers of such containers, including square and rectangular examples with multiple receptacles, e.g., one with eleven receptacles. These stone containers are comparable to examples found at Ur (Figure 2). Only a few of them retained any trace of pigments. These cosmetic containers are all from IT Levels VIII-VIIB and date to the later half of the Early Dynastic period. Zettler (in press) suggested that the cosmetics were appropriated for the goddess Inanna.



Figure 3. Topographic map of the Near and Middle East showing sites and localities related to possible resources of cosmetic pigments excavated from the Royal Tombs of Ur. In addition, important sites mentioned in the text are plotted.

Martin (1988, p.57, 59) reports on the Diyala region where small cosmetic stone containers with paired cylindrical holes were found in the Jemdat Nasr and Early Dynastic I periods, but cockle shells containing cosmetic pigments were rather rare. Heinrich and Andrae (1931) reported about finds of pigments at Fara: “Die erhaltenen Schminkepasten sind jetzt von erdiger Beschaffenheit, etwa wie sehr weiche Pastelkreide. Es sind noch Reste von weißer, ockergelber und schwarzer Farbe vorhanden...auch hellgrüne und rosa gefärbte Pasten”. However, they do not mention shell containers. Later, Martin (1988, p.59) writes that cockle shells used to store cosmetics first appear at Fara (the ancient Shuruppak) in Early Dynastic I and gradually became more popular as the stone cosmetic pots known from Jemdat Nasr times decline in number. The change can be well seen at both Fara and in graves at Khafajah: There is a complete absence of stone cosmetic pots in the Early Dynastic II at both sites. At Fara, small stone pots were excavated that look like cosmetic pots which began to reemerge in the Early Dynastic III. The evidence points to a replacement of stone cosmetic containers by cockle shells in Early Dynastic II-III.

Delougaz, et al. (1967, pp.58-142) mentioned stone and cockle shell cosmetic containers in graves of the Diyala region containing green, black, white, and reddish

pigments, but except for a few sentences they do not discuss them further.

A black pigment identified as manganese oxide was found in an Early Bronze Age bottle-shaped vessel at Müslümantepe at the bank of the Tigris River in Southeast Anatolia (Ay, Kibaroglu and Berthold, 2014). Haarmann (2005) noted that the basic black color was produced by the mixing of soot, galena, manganese minerals, or the iron oxide mineral magnetite with a paste of bees wax or suet.

Cosmetic pigments in shells were also recovered from localities that date to the second half of the 2<sup>nd</sup> millennium BC at Sharm, Fujairah, close to the road of Hormuz in Oman, ten bivalve shell halves and two fragments were found in the tombs, which contained traces of green material adhering to their inside (Masia, 2000). In a bivalve shell (*Marcia hiantina*) from an Iron Age I context (c. 1300 - 1000 BC) at Tell Abraq, also near the road of Hormuz (Thomas and Potts, 1996), the copper mineral atacamite (copper hydroxy chloride) was identified as the coloring pigment. Shells with black pigments were found during excavations in Ras al-Jinz, along the coast of Oman in circa 2300 BC (locality RJ-2 in Cleuziou and Tosi, 2007, p.175). The coloring substance in this shell was identified as the manganese mineral pyrolusite (MnO<sub>2</sub>), and lime was identified as an additional com-

ponent. The shells themselves were identified as *Anadara Ehrenbergi*, which belongs to the family of *Arcidae*. They are therefore similar to the cosmetic shells from Ur.

The variety of colors predominantly represented by the jewelry of Ur in the first place was clearly surpassed and augmented by the various colors of the pigments: While in the jewelry blue (lapis lazuli), gold (metal), silver (metal), red (carnelian beads) and white (agate, shells) predominate, the pigments contributed green, pale blue, yellow, brown and black.

## Potential raw material sources and their trading to Mesopotamia

Southern Mesopotamia is devoid of many resources particularly of mineral resources. Therefore, not only metals, but many types of stones, timber, fish and oil, and also materials for making the cosmetic pigments had to be imported from elsewhere. Potential geographical and geological surroundings rich in metal sources include Anatolia, northern Mesopotamia, Oman, Iran, Pakistan, Northwest India, i.e., the cultural regions of Akkad-*Dilmun-Magan-Meluhha* and Afghanistan, Uzbekistan and Tadjikistan, i.e., the Bactria-Margiana archaeological complex (BMAC). Egypt, the Levant, the Caucasus and Central Asia have to be taken into consideration as suppliers of metal, ore or pigments.<sup>1</sup> These regions are shown in Figure 3, in which also important archaeological sites and ore deposits are plotted. Ore deposits and mines represented in this figure are those from which lead isotope analyses were previously published or alternatively were analyzed recently in preparation of this paper. In addition, localities where there are indications of ancient ore exploitation are known solely through the existence of archaeological or archaeometallurgical finds and are taken into account. A review of ore deposits is compiled in the master thesis of Köster (2008).

### Copper

The large mountain range in the southeastern part of the Arabian Peninsula, in **Oman**, is extraordinarily rich in copper resources: More than 150 copper ore deposits and occurrences, partly gold containing, are located over a distance of some 400 km (Coleman, et al., 1979; Hauptmann, 1985, p.16), the largest of them in the region of Suhar (see Figure 3). Oman was identified as the ancient Sumerian *Magan* (Heimpel, 1987; Weisgerber, 1980; 1981). Therefore, in the development of the gulf trade in the second half of the third millennium,

the Oman peninsula took supremacy among the metal suppliers in the context of the regions *Magan*, *Dilmun* and *Meluhha* (Potts, 1990). It was known to be a valuable trading partner for copper in the city states of Mesopotamia (Begemann and Schmitt-Strecker, 2009; Begemann, et al., 2010; Heimpel, 1987; Weisgerber, 1981). The ore deposits were exploited as early as in the Hafit period (c. 3200 - 2600 BC, Weisgerber, 1981). The blooming period concerning the export of copper from *Magan* was in the Umm an-Nar period c. 2600 - 2000 BC, when copper was traded in large quantities to Ur and other localities in Mesopotamia (Begemann and Schmitt-Strecker, 2009; Begemann et al. 2010; Weisgerber, 1980; 1981). Cleuziou and Tosi (2007, p.184) report that next to copper, at least in the late 3<sup>rd</sup> millennium BC, Oman obviously sent also commodities such as black, hard and soft stones, wood and marine products to Mesopotamia.

Cambrian sedimentary copper-manganese deposits occur in the Wadi Arabah in the **southern Levant** (Hauptmann, 2007, p.78). It was mentioned earlier (Hauptmann, 2007, pp.147, 150-151) that there is evidence that mines of Faynan may have had the most extensive copper production of the Near East during the later Early Bronze Age, whereas at Timna there is no clear evidence for mining and metal production for this period (Hauptmann, 2007, p.285, 293). The two major copper deposits of the Wadi Arabah are genetically of the same ore genesis and their geochemical and isotopic signature is thus identical. The possibility of the Wadi Arabah as the provenance of copper metal of Ur is discussed by Begemann and Schmitt-Strecker (2009). The striking secondary copper minerals and the associated black manganese minerals of Faynan were exploited since the pre-pottery Neolithic period. There is little archaeological evidence of trade relations between Mesopotamia and the southern Levant and Egypt in the 3<sup>rd</sup> millennium, although the commercial metropolis of Ebla must have played a significant role in the overland trade in this region (Schmidt, 2005, p.94-95). Lapis lazuli was delivered to the southern Levant (Nahal Mishmar: see Bar Yosef Mayer, 2008; Bar Yosef Mayer, Porat and Davidovich, 2014) and to Egypt from the north, which definitely came from northeastern Afghanistan. Why, then, should we exclude the metal-rich ore deposits in the Wadi Arabah, namely Faynan and Timna, as possible suppliers of raw materials for Ur?

Very little is known about copper deposits in the **Arabian Peninsula** and its cultural relation to Mesopotamia in the 3<sup>rd</sup> millennium. However, Kisnawi, et al. (1983) reports of copper (and Roman-Islamic gold) deposits in the western part of Saudi Arabia and traces of early copper production in the Hijaz at Shim at-Tasa,

Imsayea and Az-Zuwaydiyah at Al-Disa. They indicate ancient mining and smelting of small sedimentary ore deposits in sandstone (see also Hauptmann, 2007, p.63). Some metallurgical remains from Qurayyah and Tayma were published by Liu, et al. (2015).

Many ophiolite bound copper deposits occur also in the **Zagros Mountains in Iran** (overview in Ghorbani, 2013) and on **Cyprus**. Unfortunately, no geochemical data are accessible from the deposits in Iran, so that a comparison with these ores is not possible. Cyprus as a raw material supplier is mentioned in the cuneiform texts of Mesopotamia in the middle of the 18<sup>th</sup> century BC (Potts, 1997, p.168) just when the provision of copper from the Arabian Peninsula, according to textual evidence, ended. The field evidence does not provide surprising results: On the island itself there is only one small smelting site for the production of copper in the 3<sup>rd</sup> millennium BC (Belgiorno, 2000).

Many copper ore deposits are known in the modern-day Afghanistan-Pakistan-Iran triangle, in the regions of **Makran**, **Baluchistan**, and **Seistan**. These are ores from the deposits of Chechel Kureh and from the giant porphyry copper deposit of Reqo Dik in the Chagai porphyry copper belt of western Pakistan (unpubl. data, DBM/Frankfurt a. M.; Perello, et al., 2008) where also prehistoric copper slags are reported from the Gardan Reg (Dales, 1992; Tosi, 1977). Third millennium BC copper production, possibly from local sources, is reported from the settlement of Shahr-i Sokhta (Hauptmann, Rehren and Schmitt-Strecker, 2003), Shahdad and from the Gardan Reg (Dales, 1992, p.23; Fairservis, 1961; 74; Tosi, 1977, p.60). According to the similar composition of lead isotope ratios we would not exclude that the Chechel Kureh or Reqo Dik copper deposits were also raw sources for the copper production at the settlement of Shahr-i Sokhta in a distance of only 150-200 km. Its metallurgical finds (copper ore, slags, copper) predominantly date to the Early Bronze Age (first half of the 3<sup>rd</sup> millennium BC), and therefore contemporary with Ur. All these localities are situated on connecting trade routes between Mesopotamia and northeastern Afghanistan (Kenoyer and Miller, 1999; Kohl and Lyonnet, 2008), namely by the sea route through the Persian Gulf via the Indus and on the overland route Kerman-Sistan-Afghanistan (Potts, 1994, p.43).

Wide spread overland trade routes from northeastern **Afghanistan** to the southwest, e.g., to the workshops for making beads in Shahr-i Sokhta (Tosi and Piperno, 1973), Shahdad, Tal-i Malyan and further to other markets such as Susa and Ur in Mesopotamia are recorded by many finds of the rare and semi-precious lapis lazuli (overview in Casanova, 2013). Schmidt (2005, p.57) dis-

cussed a trade route (including tin, gold and lapis lazuli) of eastern Afghanistan across to the Indus, which describes the ancient region of *Meluhha* (Kohl and Lyonnet, 2008), but he also argued for the possibility of an overland route from the Hindu Kush to the southwest by way of the Iranian Plateau to Mesopotamia. Considering the intercultural connections within the BMAC, between the western Early Bronze Age cities and the Harappan culture in the East, it is hard to believe that the ancient people would have overlooked or ignored the potential of raw sources of these geographically relatively close copper ore deposits in ancient times.

We know very little about the metal supply from Afghanistan. Copper deposits clearly exist, for example the district of Mes Aynak, which is very large and economically important up to today. Geographically, it is located southeast of the capital city of modern Afghanistan, Kabul. Mes Aynak was already exploited in ancient times (Wolfart and Wittekind, 1980; personal comm. G. Toubakis, University of Aachen, Germany and J. Thomalsky, Deutsches Archäologisches Institut Berlin, August 2014). Today, extensive old, but so far undated mining traces and meter-thick “ancient” slag layers were excavated by archaeologists from Afghanistan. On the way to the southwest there are also productive gold placers, which potentially were also already exploited in ancient times. The potential provenance of the gold metal used for gold artifacts from Ur from this occurrence is under investigation.

## Manganese

Massive sedimentary manganese-rich deposits occur with low hydrothermal input, which are frequently associated with sea-floor mineralizations of massive sulfide copper deposits of the Late Cretaceous ophiolite belt of Southwest Asia (Moghadam and Stern, 2011), e.g., the Samail ophiolite of **Oman** (Wilson, 1997) and **Cyprus** (Kindermann, 2005). Wilson (1997, p.20ff.) reports about 19 metalliferous Mn-rich sediment deposits in the north of Oman that are predominantly associated with Cu-mineralizations. Glennie (2006, p.228), in addition, reports about one from near Ras al-Hadd, southeast of Sur, far outside of the ophiolite complex (see above for finds of cosmetic pigments from Ras al-Jinz).

The manganese ores of **Cyprus** are associated with the copper ores in the “devil’s mud” or “umber”. However, they were used presumably not before the Late Bronze Age period, i.e., much later than the Royal Tombs of Ur are dated. Manganese ore from Cyprus was proven to be used as a fluxing agent in the smelting charge to improve

the smelting of copper ore to metal (Bachmann, 1982). The application of manganese-rich minerals from these deposits for cosmetic pigments is not known.

Across the **Iranian Plateau** around 100 manganese mineralizations and deposits are known (Ghorbani, 2013 and personal communication Nezafati August 2014), but, as it is the case with copper minerals, no geochemical data are available to us, and nothing is known to date about the use of manganese ores in (pre-) historic times.

## Lead

Since the Uruk expansion in the 4<sup>th</sup> / 3<sup>rd</sup> millennium (Al-gaze, 2005), Mesopotamia had commercial relationship to southeast **Anatolia**. Lead ores from the Taurus Mountains in Anatolia, approximately 2,000 kilometers to the northwest, were obviously delivered to Ur. According to cuneiform texts it is believed that in addition to lead, silver, and gold also resin, bitumen, and honey were imported from Anatolia to Mesopotamia (Potts, 1997).

Lead isotope ratios indicate that the litharge cakes from Habuba Kabira on the upper Euphrates river were made by metallurgical processes from silver-rich Taurus lead ores which were exported to this settlement for silver extraction (Pernicka, Rehren and Schmitt-Strecker, 1998). Habuba Kabira is an Early Bronze Age settlement, which is located at the upper Euphrates river banks. Its location is not far from the lead deposits in the Taurus Mountains, and it is chronologically related to Ur. Interaction between Taurus and Mesopotamia, thus potentially also for Ur, is known for the 3<sup>rd</sup> millennium (Yener, 2000, p.67). Litharge finds were also discovered at 4<sup>th</sup> / 3<sup>rd</sup> millennium BC Fatmali Kalecik in the Keban region (DBM, unpublished data).

Iran could possibly be a potential supplier due to its richness of lead-zinc-silver deposits, which occur in high number and which were possibly exploited almost everywhere in Iran in ancient time (Vatandoust, 2004). Of special importance are the two localities of **Arisman** and **Nakhlak** in the middle of the Iranian Plateau. The settlement of Arisman dates from the 4<sup>th</sup> / 3<sup>rd</sup> millennium BC. The litharge cakes from Arisman are suggested to be produced from ore of the large lead-silver-zinc deposit of Nakhlak (Pernicka, et al., 2011). The huge mineralizations of Nakhlak had major importance since ancient times (Stöllner, et al., 2004).

Oman /*Magan*, though an important supplier of copper and manganese, does not seem to play a major role as a source for lead minerals, because only one small occurrence of lead ores and one smelting site are known (Hauptmann, 1985; Begemann, et al., 2010). In addition,

no remains of mining and metallurgy earlier than the Islamic times are known from these localities.

## Materials and analytical methods

In all, 50 samples of pigments were analyzed. They are compiled in Table 1 including detailed information about archaeological context and color. Most of the pigments were still present as compact material within the shell, but four of them (#4300/30-12-539; 4327/B14989; 4329/35-1-660; 4328/35-1-661) were preserved as powders.

In order to present a standardized terminology for the pigment's colors, they were defined using the systematics of Munsell (Soil Color Charts). The Munsell color system (Munsell Color Chart, 1998) was originally set up for soils, but we found it suitable for the pigments, too. It relates the colors in shades of red, yellow, green, blue, and purple. The value notation indicates its lightness, and the chroma notation indicates the strength of the color. The eleven charts in the collection contain 399 different standard color chips that were systematically arranged according to their Munsell notations.

Mineralogical / phase identification was carried out by polarized microscopy, X-ray diffraction (Panalytical X'pert Pro), and scanning electron microscopy (SEM) with an energy dispersive system (Zeiss Supra 40 VP) in Bochum.

The chemical composition of the inorganic components (main, minor, and trace elements) was determined at the laboratory of the material science research department at the Deutsches Bergbau-Museum Bochum using a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS / Element XR, Thermo Scientific). Bulk chemical compositions are presented in Table 2a and trace elements in Table 2b. Cu-acetates and formic acids in 17 samples were analyzed by ion exclusion chromatography in Bochum. The results are compiled in Table 3. Measurements were performed using a Dionex Ionchromatographic System ICS-1600 equipped with an analytical column IonPac ICE-AS6.

Lead isotope measurements of 46 samples were performed at the Goethe-University Frankfurt am Main Institute of Geosciences using a multicollector ICP-MS (Neptune, Thermo Scientific). For extracting the lead, a standard column separation procedure for lead isotope analysis in archaeological samples preceded the measurements. This procedure is described in detail by Klein, et al. (2004). The results are presented in Table 4.

Organic components of five pigment samples from Ur were analyzed at Munich (Table 5). The binding me-

Table 1. List of pigment samples and dating of the finds (after Pollack, 1985 and Woolley, 1934 (in brackets)) classified by color (Munsell). The inventory numbers: DBM, Penn Museum and field numbers. Abbreviations of minerals/phases in table 1A.

DBM	Penn	Field	Grave	Dating	Munsell	Color	Description	Mineralogy
<b>Green pigments</b>								
4296_13	B16998a	-	-		no material left	light green		Fap, Mus, Mal
4298_13	B17025b	U.9723	PG 681	MAkk (EDIII)	no material left	light green-whitish	pasty, gas bubbles	Hxap, Atac, Mal
4299_13	B17186	U.10966	PG 800	EDIIIa		light green, bluish tint	crumbly	Fap, Azu
4300_13	30-12-539	U.11564	near PG 1068		no material left	green,	shaped discs	Fap, Parac
4301_13	31-17-93	-	-		no material left	light green, whitish	pasty	Fap, Atac, Clap
4302_13	35-1-66A	-	-		no material left	green,	pasty	Fap, Azu, Parac
4304_13	98-9-118	-	-		GLE1 6_1 5GY	greenish gray	crumbling	Parac, Atac, Cup, Qtz
4305_13	B16993a	-	-		GLE2 6_1 5B	greenish gray	2 layers; top: greenish blue	Azu, Parac, Cc
4308_13	30-12-118B	-	-		no material left	light	several shells, light pigment	Hxap, Qtz, Cc, Atac
4309_13	30-12-188E	-	-		no material left	green	pigment in shell	Qtz, Parac, Gyps, Fap, Cc, Ab, Micr
4313_13	B17192	-	-		no material left	greenish blue	pigment in shell	Fap, Azu, Parac
4314_13	B17025	U.9723	PG 681	MAkk (EDIII)	GLE1 7_1 5GY	greenish blue, brown crust	pigment in shell	Atac, Hm, Hal, Magh, Qtz
4315_13	B17040a	U.8192	PG 143	MAkk (EDIII)	GLE1 7_1 5GY	light greenish gray	pigment in shell	Hxap, Parac
4320_13	30-12-117O	-	-	EDIII*	GLE1 6_1 5GY	greenish gray	pigment in shell	Mal, Atac
4321_13	30-12-117H	-	-	EDIII*	no material left	green	shell length; 5.5 cm	Fap, Parac
4322_13	30-12-117	-	-	EDIII*	GLE1 7_1 5GY	light greenish gray	pigment in shell	Hxap, Parac
4323_13	30-12-117D	-	-	EDIII*	no material left	green	pigment in shell	Azu, Cc, Gyps, Fap
4324_13	35-1-67	-	-	Possibly ED III*	GLE2 6_1 10BG	Egyptian Blue	small solid lump	Qtz, Cupriv
4333_13	30-12-111i	-	-		no material left	green	dense, adhered to shell	Hxap, Azu, Cc
4336_13	31-16-541B	-	-		GLE1 7_1 10Y	light greenish gray	pigment in shell	Hxap, Az, Parac
4341_13	17192	-	-		GLE1 7_1 5GY	light greenish gray	pigment in shell	Hxap, Parac, Dol
4342_13	30-12-118A	-	-		no material left	greenish blue	pigment, dense, in shell	Fap, Azu, Parac
4343_13	30-12-117J	-	-	EDIII*	no material left	green	pigment in shell	Hxap, Bass
4344_13	30-12-112	-	-		GLE1 6_1 5G	greenish gray	pasty pigment in shell	Hxap, Azu, Parac
4345_13	B17189	U.8345	PG193	MAkk (EDIII)	no material left	green	pigment crust in shell	Hxap, Azu, Parac

DBM	Penn	Field	Grave	Dating	Munsell	Color	Description	Mineralogy
<b>Brown_black pigments</b>								
4297_13	B 16998b	-	-		no material left	brown-black	pigment in shell	Azu, Paratac, Cc
4303_13	35-1-66B	-	-		no material left	black-brown	pigment in shell	Qtz, Pylu, Crypt, Mnox
4306_13	B16993b	-	-		HUE 10YR 4_2	dark grayish brown	2 layers; bottom: brown	Cc, Mnt, Qtz
4306_13	B16993b	-	-		no material left	brown	2 layers; bottom: brown	Cc, Mnt, Qtz
4312_13	B16999? (y)	U.10584	PG 789	EDIIIa	no material left	black	pigment in shell	Cerss, Gyss, Laur, CrCl
4316_13	B17040b	U.8192	PG 143	MAkk (EDIII)	no material left	black	spot on B17040b	Cc, Mnt, Gyss, Qtz, Crypt
4317_13	30-12-113	-	-		no material left	black	pigment in shell	Mnt, Qtz, Pyr, Cc, Crypt
4319_13	B16998	-	-		HUE 2.5Y 4_2	dark grayish brown	pigment in shell	Gyss, Qtz, Cc, Mnt
4325_13	35-1-66B	-	-		HUE 7.5YR 3_1	dark brown	pigment in shell	Qtz, Mnt, Crypt
4326_13	B17164	U.7996	PG 55	EDIII	no material left	black	pigment in lithic pot	Mnox, Crypt, Gyss, Mnt, Qtz
4331_13	30-12-111hh	-	-		no material left	black	pigment in shell	Crypt, Qtz, Cc, Hal, Mnt, Phlog
4332_13	30-12-111dd	-	-		HUE 7.5YR 2.5_1	Munsell: black	pigment in shell	Pyr, Gyss, Qtz, Crypt, Mnt, Cc
4334_13	B16946	U.9585	PG 652	Akk	no material left	black	pigment in shell	Qtz, Hm, Hxap, Crypt, Cc
4339_13	31-16-542M	-	-		no material left	black	pigment crust in shell	Mnt, Qtz, Gyss, Cc, Frankl
4346_13	B16999	U.10584	PG 789	EDIIIa	no material left	black, white efflorescence	pigment in shell	Gyss, Mnt, Cc, Qtz, Hsm
4347_13	30-12-111h	-	-		no material left	black	crust, in shell	Mnt, Qtz, Pylu, Cc, Crypt
<b>White and gray pigments</b>								
4310_13	30-12-188 (x)	-	-		no material left	white	pigment in shell	Hxap, Ank, Cc, Qtz
4311_13	B16999? (x)	U.10584	PG 789	EDIIIa	no material left	white	pigment in shell	Cerss, Gyss, Laur, CrCl
4318_13	30-12-115	-	-		no material left	white	pigment in shell	Hxap, Cc, Qtz
4330_13	30-12-111no. no.	-	-		no material left	white	leavings in shell	Cerss, Gyss, Micr
4335_13	35-1-42	U.19428			HUE 10YR 6_2	gray	lithic tray with two pits	Crcl, Gyss, Qtz, Cc
4338_13	98-9-150	-	-		no material left	white	"Removed from Ur exhibition in 1998"	Hxap, Ank, Cc
<b>Red pigments</b>								
4327_13	B14989	-	-		HUE 10R 4_6	red	coarse grained fragment	Gyss, Qtz, Hm, Hal, Anhydr
4328_13	35-1-661	-	-		HUE 10R 4_6	red	coarse grained fragment	Gyss, Qtz, Anhydr, Hm
4329_13	35-1-660	-	-		HUE 10R 4_8	red	powder	Qtz, Hm, Micr, Ab

Key: DBM = Deutsches Bergbau-Museum; \* = Dating according to databank Penn Museum; ED = Early Dynastic; M = Middle; Akk = Akkadic; \*\* removed from Ur exhibition. The inventory numbers of the Deutsches Bergbau-Museum (DBM) give additionally the year when the samples were analyzed (e.g., 4310\_13). For a better overview this year number is neglected in the text.

Table 1a. Explanation of abbreviations and chemical composition of minerals mentioned in Table 1.

<b>Ab</b>	Albite	Na[AlSi <sub>3</sub> O <sub>8</sub> ]	<b>Hal</b>	Halite	NaCl
<b>Anhydr</b>	Anhydrite	CaSO <sub>4</sub>	<b>Hm</b>	Hematite	Fe <sub>2</sub> O <sub>3</sub>
<b>Ank</b>	Ankerite	FeCO <sub>3</sub>	<b>Hsm</b>	Hausmannite	Mn <sup>2+</sup> Mn <sub>2</sub> <sup>3+</sup> O <sub>4</sub>
<b>Atac</b>	Atacamite	Cu <sub>2</sub> (OH) <sub>3</sub> Cl	<b>Hxap</b>	Hydroxyapatite	Ca <sub>5</sub> [OH](PO <sub>4</sub> ) <sub>3</sub>
<b>Azu</b>	Azurite	Cu <sub>3</sub> (OH)CO <sub>3</sub>	<b>Laur</b>	Laurionite	PbOHCl
<b>Bass</b>	Bassanite	Cu[SO <sub>4</sub> ].0.5 H <sub>2</sub> O	<b>Magh</b>	Maghemite	γ-Fe <sub>2</sub> O <sub>3</sub>
<b>Cc</b>	Calcite	CaCO <sub>3</sub>	<b>Mal</b>	Malachite	Cu <sub>2</sub> [(OH) <sub>2</sub> ](CO <sub>3</sub> )
<b>CrCl</b>	Caracolite	Na <sub>3</sub> Pb <sub>2</sub> (SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub>	<b>Micr</b>	Microcline	K[AlSi <sub>3</sub> O <sub>8</sub> ]
<b>Cerss</b>	Cerussite	PbCO <sub>3</sub>	<b>Mnox</b>	Manganese-Oxide	general
<b>Clap</b>	Chloro-Apatite	Ca <sub>5</sub> [Cl](PO <sub>4</sub> ) <sub>3</sub>	<b>Mnt</b>	Manganite	γ-MnOOH
<b>Crypt</b>	Cryptomelane	KMn <sup>4+</sup> 2 <sup>+</sup> <sub>8</sub> O <sub>16</sub>	<b>Musc</b>	Muscovite	KAl <sub>2</sub> [(OH,F) <sub>2</sub> ](AlSi <sub>3</sub> O <sub>10</sub> )
<b>Cupriv</b>	Cuprorivaite	CaCuSi <sub>4</sub> O <sub>16</sub>	<b>Parac</b>	Paratacamite	Cu <sub>2</sub> (OH) <sub>3</sub> Cl
<b>Dol</b>	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	<b>Pylu</b>	Pyrolusite	β-Mn <sup>4+</sup> O <sub>2</sub>
<b>Fap</b>	Fluorapatite	Ca <sub>5</sub> [F](PO <sub>4</sub> ) <sub>3</sub>	<b>Qtz</b>	Quartz	SiO <sub>2</sub>
<b>Gyps</b>	Gypsum	Ca[SO <sub>4</sub> ].H <sub>2</sub> O			

Table 2a. Composition (main and minor components) of the cosmetic pigments from Ur determined by HR-ICP-MS. Values are given in weight percent.

DBM	Penn Museum	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MnO	Fe <sub>2</sub> O <sub>3</sub>	Cu	K <sub>2</sub> O	BaO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
<b>Green pigments</b>													
4296_13	B 16998a	1.07	0.43	0.30	0.59	43.7	0.004	0.33	3.91	0.24	0.07	36.4	1.22
4298_13	B 17025b	0.89	0.59	0.36	<0.11	38.9	0.04	0.24	8.71	0.22	0.25	32.4	<0.06
4299_13	B 17186	0.57	0.37	0.19	0.15	36.0	0.001	0.26	13.3	0.06	0.03	28.1	<0.06
4300_13	B 30-12-539	1.43	0.62	0.29	20.4	20.4	0.03	0.66	22.0	0.25	0.27	15.4	0.07
4301_13	31-17-93	0.72	0.52	0.42	7.98	32.4	0.16	0.30	11.4	0.24	0.07	25.9	<0.06
4302_13	35-1-66a	1.04	0.47	0.42	2.64	29.6	0.05	0.42	17.2	0.20	0.09	23.8	0.08
4304_13	98-9-118	0.37	0.53	0.47	12.0	1.43	0.01	0.30	51.6	0.01	0.004	0.09	2.14
4305_13	B16993 a	0.73	0.60	0.22	9.36	5.93	0.06	0.24	40.9	<0.0005	0.02	2.95	1.51
4308_13	30-12-118b	1.46	1.51	1.95	12.2	32.3	0.13	1.00	4.50	0.01	0.002	2.20	<0.06
4309_13	30-12-188e	1.37	1.44	2.12	23.4	15.8	0.27	0.99	7.08	0.32	0.07	9.3	4.79
4313_13	B17192	0.42	0.55	0.19	16.2	10.2	0.01	0.22	19.8	<0.0005	0.004	8.49	0.64
4314_13	B17025	1.21	0.89	1.10	9.60	3.82	1.02	59.5	8.14	0.22	0.10	0.73	0.81
4315_13	B17040a	0.57	0.77	0.22	24.6	25.6	0.15	0.41	9.74	<0.0005	0.01	18.7	0.45
4320_13	30-12-117O	0.64	0.62	0.18	1.76	3.12	0.08	0.31	52.5	<0.0005	0.01	1.41	1.02
4321_13	30-12-117H	0.80	0.52	0.12	5.86	25.0	0.02	0.31	21.2	0.31	0.01	29.3	3.80
4322_13	30-12-117	1.34	0.82	0.32	9.30	34.3	0.04	0.28	7.91	0.11	0.01	34.0	0.87
4323_13	30-12-117D	0.61	0.71	0.27	23.6	29.9	0.07	0.23	13.8	0.22	0.004	3.10	1.88
4324_13	35-1-67	0.93	0.50	0.26	73.5	11.8	0.08	0.95	6.72	0.05	0.01	0.33	0.57
4333_13	30-12-111i	0.52	0.95	0.28	12.6	23.7	0.22	0.26	26.5	0.37	0.15	16.4	0.82
4336_13	31-16-541B	0.75	0.66	0.29	0.74	42.4	0.04	0.22	4.82	<0.0005	0.01	36.1	0.69
4341_13	17192	0.98	1.18	0.23	26.0	25.2	0.08	0.19	7.08	<0.0005	0.01	22.9	1.09
4342_13	30-12-118A	0.79	0.58	0.21	25.0	19.4	0.12	0.72	28.7	0.27	0.01	15.8	0.67
4343_13	30-12-117J	1.00	0.66	0.44	6.12	46.2	0.01	0.32	3.88	0.28	0.02	35.0	3.97
4344_13	30-12-112	0.91	0.69	0.25	13.5	28.4	0.02	0.25	20.8	0.28	0.01	22.7	1.09
4345_13	B17189	0.53	0.59	0.23	15.1	29.2	0.08	0.22	11.3	0.12	0.01	26.8	1.17

DBM	Penn Museum	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MnO	Fe <sub>2</sub> O <sub>3</sub>	Cu	K <sub>2</sub> O	BaO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
<b>Brown_black pigments</b>													
4297_13	B 16998b	0.58	0.60	0.23	8.58	7.73	3.58	0.76	33.7	0.16	0.15	2.27	<0.06
4303_13	35-1-66b	0.68	2.55	4.33	27.2	9.17	12.8	2.23	0.05	1.35	0.38	1.09	4.79
4306_13	B16993 b	0.28	0.84	0.56	3.76	15.5	49.3	4.22	1.20	0.01	0.93	0.48	2.74
4312_13	B16999? (y)	0.28	0.32	0.13	1.43	8.11	2.14	0.25	0.12	0.14	0.09	1.00	13.7
4316_13	B17040b	0.15	0.52	0.51	12.8	15.3	50.1	0.32	1.05	0.26	0.34	2.19	5.23
4317_13	30-12-113	0.32	0.35	0.76	9.52	7.11	68.0	0.42	0.77	0.67	0.33	1.57	1.13
4319_13	B16998	0.24	0.51	0.14	7.43	21.1	11.0	0.84	0.17	0.01	0.37	1.33	31.7
4325_13	35-1-66B	0.34	0.44	1.12	13.2	2.67	66.6	1.09	0.98	1.34	0.34	0.88	0.41
4326_13	B17164	0.33	0.32	0.98	14.4	1.53	64.2	0.65	0.18	3.07	0.70	0.33	0.92
4331_13	30-12-111hh	0.41	0.35	0.77	9.20	6.28	54.7	1.44	0.62	2.52	0.66	1.50	3.46
4332_13	30-12-111dd	0.25	0.49	0.93	5.98	9.30	66.6	0.45	0.22	2.11	0.63	1.39	4.36
4334_13	B16946	0.65	0.96	1.90	25.6	10.3	26.4	16.7	0.37	1.28	0.18	5.11	2.28
4339_13	31-16-542M	0.22	0.70	0.50	4.19	8.76	66.7	0.81	0.25	<0.0005	0.22	0.25	3.04
4346_13	B16999	0.34	0.80	0.37	5.00	27.6	18.9	1.14	0.42	<0.0005	0.43	2.05	30.2
4347_13	30-12-111h	0.01	0.47	30.4	37.8	1.60	7.02	0.26	0.07	5.70	8.25	1.51	2.56
<b>White and gray pigments</b>													
4310_13	30-12-188(x)	0.87	1.17	0.21	7.97	40.6	0.02	0.28	5.17	0.31	0.01	28.7	1.20
4311_13	B16999? (x)	0.19	0.12	0.02	1.39	18.1	0.15	0.05	0.07	0.12	0.04	0.83	27.9
4318_13	30-12-115	3.65	0.96	1.63	3.01	42.6	1.47	0.53	0.06	0.93	0.16	34.9	1.25
4330_13	30-12-111no. no.	0.16	0.14	0.16	3.50	10.5	0.42	0.43	0.12	0.14	0.12	0.63	19.2
4335_13	35-1-42	1.12	2.62	3.79	21.4	23.1	0.17	2.52	0.04	0.76	0.01	7.7	8.69
4338_13	98-9-150	0.77	0.98	0.39	4.66	47.6	0.03	0.26	1.65	0.01	0.01	41.7	1.31
<b>Red pigments</b>													
4327_13	B14989	0.82	0.27	1.84	30.6	20.2	0.11	9.05	0.02	0.40	0.02	0.39	35.6
4328_13	35-1-661	0.82	0.54	0.93	26.8	24.6	0.07	5.26	0.01	0.74	0.04	0.30	33.7
4329_13	35-1-660	0.39	0.28	2.75	49.7	0.30	0.07	42.7	0.004	0.40	0.04	1.45	<0.06

Table 2b. Composition (trace elements) of the cosmetic pigments from Ur analyzed by HR-ICP-MS. Values are given in parts per million, values in weight percent are separately indicated

DBM	Museum	Ag	Sn	Sb	Te	Au	Bi	U	Pb	Co	Ni	Zn	As	Se
<b>Green pigments</b>														
4296_13	B16998a	40	10	25	3	65	10	1	470	1	30	70	2660	230
4298_13	B17025b	30	20	15	8	85	8	2	1310	1	15	70	2200	25
4299_13	B17186	7	35	60	2	25	3	1	2.36 (%)	3	210	25	745	6
4300_13	30-12-539	2	20	10	1	40	3	10	185	2	60	20	425	6
4301_13	31-17-93	80	20	10	4	230	10	2	695	4	65	65	205	7
4302_13	35-1-66a	155	15	30	5	50	10	1	410	5	135	65	1350	6
4304_13	98-9-118	250	30	70	10	3	5	4	340	20	620	35	2370	20
4305_13	B16993 a	27	15	40	3	3	7	1	510	20	510	70	990	8
4308_13	30-12-118b	27	10	70	5	<2	5	1	1825	8	100	145	210	5
4309_13	30-12-188e	105	70	60	15	10	10	<0,001	3.65 (%)	15	330	290	3360	<4

DBM	Museum	Ag	Sn	Sb	Te	Au	Bi	U	Pb	Co	Ni	Zn	As	Se
4313_13	B17192	10	15	45	3	<2	7	3	1100	4	410	25	780	6
4314_13	B17025	20	20	305	7	<2	20	4	1030	220	290	300	5840	<4
4315_13	B17040a	3	10	10	3	<2	10	10	5580	5	90	60	240	<4
4320_13	30-12-117O	7	6	100	3	<2	10	<0,001	7300	10	660	40	2880	<4
4321_13	30-12-117H	3	130	50	10	<2	10	0.2	910	30	380	80	2950	10
4322_13	30-12-117	10	15	35	5	<2	8	<0,001	1070	10	440	60	440	<4
4323_13	30-12-117D	7	20	80	5	<2	7	30	2.87 (%)	4	150	45	8370	30
4324_13	35-1-67	8	200	35	1	<2	2	1	5670	200	540	95	470	<4
4333_13	30-12-111i	160	22	15	2	2	5	4	530	5	60	35	420	<4
4336_13	31-16-541B	30	70	15	5	2	2	<0,001	2560	4	230	50	380	12
4341_13	17192	30	50	15	3	2	4	14	1080	2	50	85	30	<4
4342_13	30-12-118A	10	45	15	5	<2	20	17	680	20	280	90	370	8
4343_13	30-12-117J	35	70	12	10	<2	10	1	1370	3	50	70	105	<4
4344_13	30-12-112	6	20	25	5	<2	5	3	760	5	150	50	340	<4
4345_13	B17189	15	35	30	6	<2	10	8	7650	10	300	70	750	6
<b>Brown_black pigments</b>														
4297_13	B16998b	3	4	20	1	40	4	3	395	35	270	20	590	<4
4303_13	35-1-66b	4	2	2	<1	10	0.3	1	30	10	70	40	15	3
4306_13	B16993 b	11	4	25	2	<2	1	10	2490	400	260	90	540	5
4312_13	B16999? (y)	120	<2	65	<1	<2	7	2	59.7 (%)	35	<15	25	75	15
4316_13	B17040b	6	4	55	35	<2	8	10	1.52 (%)	340	45	90	250	5
4317_13	30-12-113	6	2	25	<1	<2	1	4	1.72 (%)	140	40	60	145	5
4319_13	B16998	55	3	30	<1	<2	1	1	3.37 (%)	210	80	90	160	7
4325_13	35-1-66B	<2	8	5	2	<2	1	4	7960	240	75	75	335	7
4326_13	B17164	5	6	7	2	<2	<0.2	5	1270	135	50	80	150	7
4331_13	30-12-111hh	1670	2240	230	305	950	20	0.1	1.11 (%)	220	65	150	470	5
4332_13	30-12-111dd	160	90	15	20	15	1	5	4660	160	75	90	115	15
4334_13	B16946	310	250	30	5	20	1	2	8960	20	75	85	440	<4
4339_13	31-16-542M	50	15	53	5	50	10	25	4310	440	480	150	135	8
4346_13	B16999	135	7	95	1	8	2	2	85	220	90	120	190	10
4347_13	30-12-111h	5160	120	130	25	35	6	85	6560	230	210	480	750	<4
<b>White and gray pigments</b>														
4310_13	30-12-188(x)	20	15	12	1	3	4	1	680	2	50	65	145	<4
4311_13	B16999? (x)	95	<2	20	<1	<2	5	<0,001	38,6 (%)	5	<15	15	55	15
4318_13	30-12-115	10	25	25	2	<2	40	<0,001	5,21 (%)	25	40	40	340	<4
4330_13	30-12-111no. no.	45	<2	110	<1	<2	6	<0,001	46,8 (%)	3	<15	20	120	<4
4335_13	35-1-42	5	2	6	<1	<2	1	1	3,98 (%)	10	95	60	1150	25
4338_13	98-9-150	30	40	15	4	<2	4	1	1340	2	65	60	100	<4
<b>Red pigments</b>														
4327_13	B14989	3	5	3	<1	<2	<0.2	<0,001	105	10	120	25	30	<4
4328_13	35-1-661	<2	3	<2	<1	<2	<0.2	0.3	75	7	45	20	20	<4
4329_13	35-1-660	<2	<2	<2	<1	<2	<0.2	1	60	4	15	30	25	<4

Table 3. Copper acetates and formic acids in some pigments from Ur. Values are given in parts per million (ppm).

DBM	Penn Museum	Cu-acetates	Formic acids
<b>Green pigments</b>			
4304_13 A	98-9-118	215	1045
4304_13 B	98-9-118	285	1060
4305_13	B 16993 a	1270	2565
4315_13 A	B17040a	7655	9175
4315_13 B	B17040a	7630	9015
4320_13	30-12-117O	2650	2160
4321_13 A	30-12-117H	2390	4750
4321_13 B	30-12-117H	2330	4460
4324_13	35-1-67	990	290
4333_13	30-12-111i	8040	11055
4341_13	17192	1175	2755
4342_13	30-12-118 a	7255	4365
4343_13	30-12-117 J	235	1360
4344_13	30-12-112	3665	2780
<b>Brown_black pigments</b>			
4317_13	30-12-113	465	115
4319_13	B 16998	855	250
4325_13	35-1-66B	295	215

Table 4. Lead isotope abundance ratios of the cosmetic pigments from Ur.

DBM	Penn	<sup>208</sup> Pb/ <sup>206</sup> Pb	<sup>207</sup> Pb/ <sup>206</sup> Pb	<sup>204</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
<b>Green pigments</b>							
4298_13	B17025b	2.0741	0.8360	0.05332	18.755	15.679	38.900
4299_13	B17186	2.0655	0.8291	0.05286	18.919	15.686	39.077
4300_13	30-12-539	2.0769	0.8378	0.05343	18.717	15.680	38.873
4301_13	31-17-93	2.1072	0.8622	0.05504	18.168	15.665	38.280
4302_13	35-1-66a	2.0825	0.8408	0.05368	18.629	15.664	38.795
4304_13	98-9-118	2.0917	0.8499	0.05422	18.443	15.674	38.577
4305_13	B16993a	2.0810	0.8414	0.05366	18.637	15.681	38.784
4308_13	30-12-118b	2.0872	0.8463	0.05406	18.499	15.656	38.612
4309_13	30-12-188e	2.0864	0.8400	0.05358	18.663	15.677	38.938
4313_13	B17192	2.0779	0.8375	0.05340	18.728	15.685	38.914
4314_13	B17025b	2.0818	0.8413	0.05382	18.582	15.633	38.684
4315_13	B17040a	2.0718	0.8351	0.05323	18.786	15.688	38.921
4320_13	30-12-117O	2.0855	0.8401	0.05359	18.661	15.677	38.917
4321_13	30-12-117H	2.0849	0.8435	0.05387	18.561	15.656	38.700
4322_13	30-12-117	2.0740	0.8516	0.05328	18.769	15.676	38.928
4323_13	30-12-117D	2.0861	0.8398	0.05358	18.665	15.674	38.937
4324_13	35-1-67	2.0916	0.8448	0.05392	18.545	15.666	38.790

DBM	Penn	<sup>208</sup> Pb/ <sup>206</sup> Pb	<sup>207</sup> Pb/ <sup>206</sup> Pb	<sup>204</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
4333_13	30-12-111i	2.0781	0.8388	0.05348	18.698	15.684	38.857
4336_13	31-16-541B	2.0738	0.8340	0.05317	18.809	15.687	39.005
4342_13	30-12-118A	2.0845	0.8428	0.05384	18.574	15.655	38.716
4344_13	30-12-112	2.0829	0.8420	0.05371	18.619	15.677	38.781
4345_13	B17189	2.0780	0.8367	0.05339	18.732	15.672	38.925
<b>Brown_black pigments</b>							
4297_13	B16998b	2.0781	0.8398	0.05357	18.668	15.678	38.796
4303_13	35-1-66b	2.0658	0.8336	0.05328	18.769	15.646	38.771
4306_13	B16993 b	2.0775	0.8397	0.05354	18.679	15.684	38.806
4312_13	B16999?(y)	2.0835	0.8427	0.05373	18.612	15.685	38.778
4316_13	B17040b	2.0714	0.8350	0.05324	18.782	15.684	38.907
4317_13	30-12-113	2.0857	0.8400	0.05360	18.657	15.672	38.912
4319_13	B16998	2.0716	0.8349	0.05323	18.785	15.684	38.915
4325_13	35-1-66B	2.0907	0.8441	0.05391	18.550	15.658	38.783
4326_13	B17164	2.0714	0.8348	0.05323	18.785	15.682	38.912
4331_13	30-12-111hh	2.0740	0.8359	0.05329	18.764	15.686	38.917
4332_13	30-12-111dd	2.0808	0.8416	0.05368	18.627	15.677	38.759
4334_13	B16946	2.1130	0.8648	0.05516	18.130	15.678	38.309
4339_13	31-16-542M	2.0784	0.8391	0.05360	18.657	15.655	38.778
4346_13	B16999	2.0865	0.8448	0.05386	18.566	15.684	38.738
4347_13	30-12-111h	2.0719	0.8374	0.05338	18.733	15.686	38.813
<b>White and gray pigments</b>							
4310_13	30-12-188(x)	2.0833	0.8416	0.05376	18.603	15.655	38.755
4311_13	B16999?(x)	2.0866	0.8449	0.05389	18.557	15.680	38.720
4318_13	30-12-115	2.0815	0.8385	0.05352	18.684	15.666	38.890
4330_13	30-12-111no.no.	2.0703	0.8344	0.05320	18.796	15.684	38.914
4335_13	35-1-42	2.0674	0.8289	0.05283	18.930	15.690	39.135
4338_13	98-9-150	2.0744	0.8348	0.05327	18.773	15.671	38.943
<b>Red pigments</b>							
4327_13	B14989	2.0806	0.8392	0.05357	18.669	15.668	38.842
4328_13	35-1-661	2.0830	0.8406	0.05367	18.634	15.664	38.815
4329_13	35-1-660	2.0807	0.8388	0.05354	18.678	15.667	38.863

dia of the samples were extracted stepwise with a series of solvents of increasing polarity, following an extraction scheme developed for aged and degraded materials (Dietemann, et al., 2012; Koller, Fiedler and Baumer, 1998): isooctane, methanol, chloroform/methanol (7:3 v/v = % volume/volume), anhydrous oxalic acid in methanol (10 % w/v = mass/volume x 100). The solvent extracts were analyzed by gas chromatography (GC, Agilent GC 6890) and gas chromatography–mass spectrometry (GC-MS, Agilent GC 6890 coupled MSD 5975), with and without

prior derivatization with TMSH (0.2 M trimethylsulfonium hydroxide in methanol). Polysaccharides (gums) and proteins that remained after the solvent extraction were analyzed by GC–MS after methanolysis (0.1 N hydrochloric acid in methanol, Bleton, et al., 1996) and mercaptalization (Bonaduce, et al., 2007; Lluveras-Tenorio, et al., 2012) or by amino acid analysis (AAA, Biochrom 50 ion exchange liquid chromatography with post-column derivatization and photometric detection) after acidic hydrolysis (Koller, Fiedler and Baumer, 1998).

Table 5. Overview of identified organic materials in cosmetic pigments from Ur, Mesopotamia. Because the samples were contaminated with modern materials, the materials are divided into contaminations and presumably original constituents.

Sample	possibly original			proteins	probably later contamination		
	fat or oil	polysaccharides	bitumen or soot		mono-terpenes	modern wax	other compounds
4305/B16998a, light green-gray	++	n.a.		-	-	+	plasticizers, glycols
4306/B16998b, brown-black	++	n.a.	+ soot*	-	-	++	plasticizers, glycols
4299/B17186, light blue	+	(+)		-	(+)	+	plasticizers, glycols
4302/30-12-539, light green	++	n.a.		-	+	+	plasticizers, glycols
4302/30-12-539, light green	++	(+)		n.a.	+	(+)	plasticizers
4297/35-1-66B, black-brown	++	-	++ bitumen	-	(+)	(+)	plasticizers

Key: ++ = major amount; + = minor amount; + = traces; - = not detected; n.a. = not analyzed. \*wood pyrolysis product such as charcoal black or wood soot.

## Results and discussion

### Components and chemistry of the cosmetic pigments

#### a) Mineral / inorganic composition of green and greenish / bluish pigments

Green color dominates the investigated pigments, but there are smooth transitions to samples with bluish tints. The intensity varies from intensive (e. g., #4300/30-12-539; #4304/98-9-118) to light green. Variations in intensity are also found for the greenish / bluish pigments. A pale blue color is e. g. sample #4313/B17192 (see Figure 2). Most of these pigments were solidified or compacted, but others (# 4304/98-9-118) consist of a loose crumbly material.

The previous color is different from the striking blue of sample #4324/35-1-67. The sample is unique since it is made up of cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ). This is the major phase of the artificially produced pigment Egyptian blue. This synthetic pigment was used in Egypt since the Fourth Dynasty (see discussion in Lucas and Harris, 1962, p.342). Here, it is dated to Early Dynastic III in Mesopotamia.

Almost as a rule, the green pigments are comprised of oxidized copper minerals, and atacamite and paratacamite (Table 1 and 1a) form the main constituents.

The two minerals are chemically identical ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), but have slightly different crystal structures. In some of the green pigment samples also malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) was detected. Malachite and (par-)atacamite differ slightly in color: Whereas malachite is luscious green, (par-) atacamite is rather pale and usually of a light turquoise hue. As accessories, quartz, feldspar, calcite and dolomite were also identified in the green pigment samples. It is not clear at which point the accessory minerals entered the cosmetic pigments whether it was during the production process or by post-deposition in the tombs. Malachite may occur together with azurite ( $\text{Cu}_3(\text{OH})\text{CO}_3$ ) in ore deposits. Azurite in its pure form is famous for its deep blue color. Its intense color even remains stable when the mineral is powdered, as it is the case for the pigments in shells.

The copper concentrations in the green pigments often range in the ten percentage level. In seven of the 25 green and greenish pigments (#4296/B16998a, b, 4298/B17025b, 4299/B17186, 4300/30-12-539, 4301/31-17-93, 4302/35-1-66a, 4309/30-12-188e) the gold contents were elevated (elevated concentrations from 10 - 230 ppm). Likewise in almost all samples silver is also present with high values (up to 250 ppm,  $\emptyset = 42.3$  ppm).

Nickel and arsenic are present with concentrations above 100 ppm. We observed these concentrations

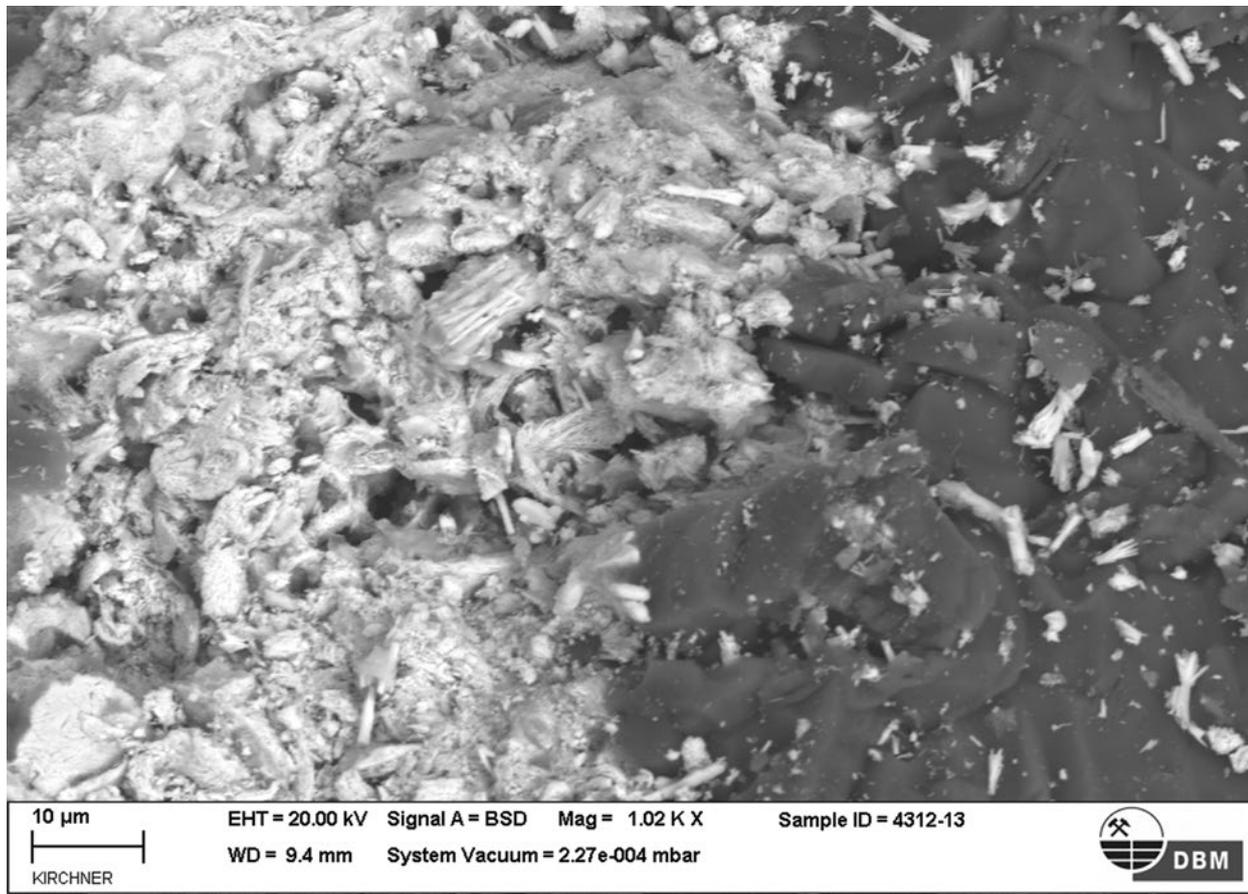


Figure 4. White pigment # 4311/B16999? (x) on the boundary to the black layer (#4312/B16999? (y)) in the same sample. Although lead and sulfur contents are high in this sample (bulk composition), remains of galena (PbS) were not identified as was assumed previously. This assumption was based on the presence of secondary lead minerals such as cerussite, laurionite and gypsum in the dark matrix. Scanning electron picture, backscatter mode. Photo: D. Kirchner, Deutsches Bergbau-Museum

in samples low in gold (#4304/98-9-118, 4309/30-12-188e, 4313/B17192, 4314/B17025, 4315/B17040a, 4316/B17040b, 4320/30-12-117O, 4321/30-12-117H, 4323/30-12-117D, 4336/31-16-541B, 4342/30-12-118A, 4344/30-12-112, 4346/B17189). Nickel and arsenic are well-known as chemical markers for specific types of ore deposits embedded in ophiolitic rocks. For instance, Begemann, et al. (2010) found nickel and arsenic to be characteristic accompanying elements in Omani copper ores.

#### b) Mineral / inorganic composition of black / brown pigments

The black pigments comprise of black manganese-rich minerals such as pyrolusite, manganite and cryptomelane (Table 1 and 1a). They are often mixed with varying amounts of quartz, gypsum and calcite. In one brownish-black pigment sample (#4297/B1699b), also a fair amount of azurite and (par-) atacamite was detected. Obviously, the black manganese material could have been naturally mixed with copper minerals. Geologically, sedimentary depositions of manganese minerals are associated with volcanic massive sulfide (VMS) copper deposits as they occur in Cyprus and / or Oman. For the northern

part of the Samail ophiolite complex of Oman metalliferous manganese sediments with high concentrations of copper, lead, zinc and nickel are described (Wilson, 1997). VMS deposits in general are known for polymetallic compositions, which also includes gold and silver.

Most of the black colored cosmetics are stored in shells. Sample #4326/B17164 consists of fine-grained black powder that was stored in a small ceramic vessel.

Manganese is the major element. Five of the 13 black pigment samples contain gold and silver in elevated concentrations (Au = 8 - 950 ppm, Ag = 50 - 1670 ppm). In the sample with the highest concentrations (# 4331/30-12-111hh), also significantly high tin, antimony and lead contents were detected.

In contrast to the manganese-rich pigment samples, lead (59.7 %) is the major element in the single dark black pigment (#4312/B16999?(y)), and here also sulfur is present in percentage range (6 wt. % S; recalculated from SO<sub>3</sub>). The presence of the two elements is potentially an indication for the mineral galena (PbS), which is black in powdered form. However, galena was not detected (Figure 4), but gypsum, cerussite, caracolite and

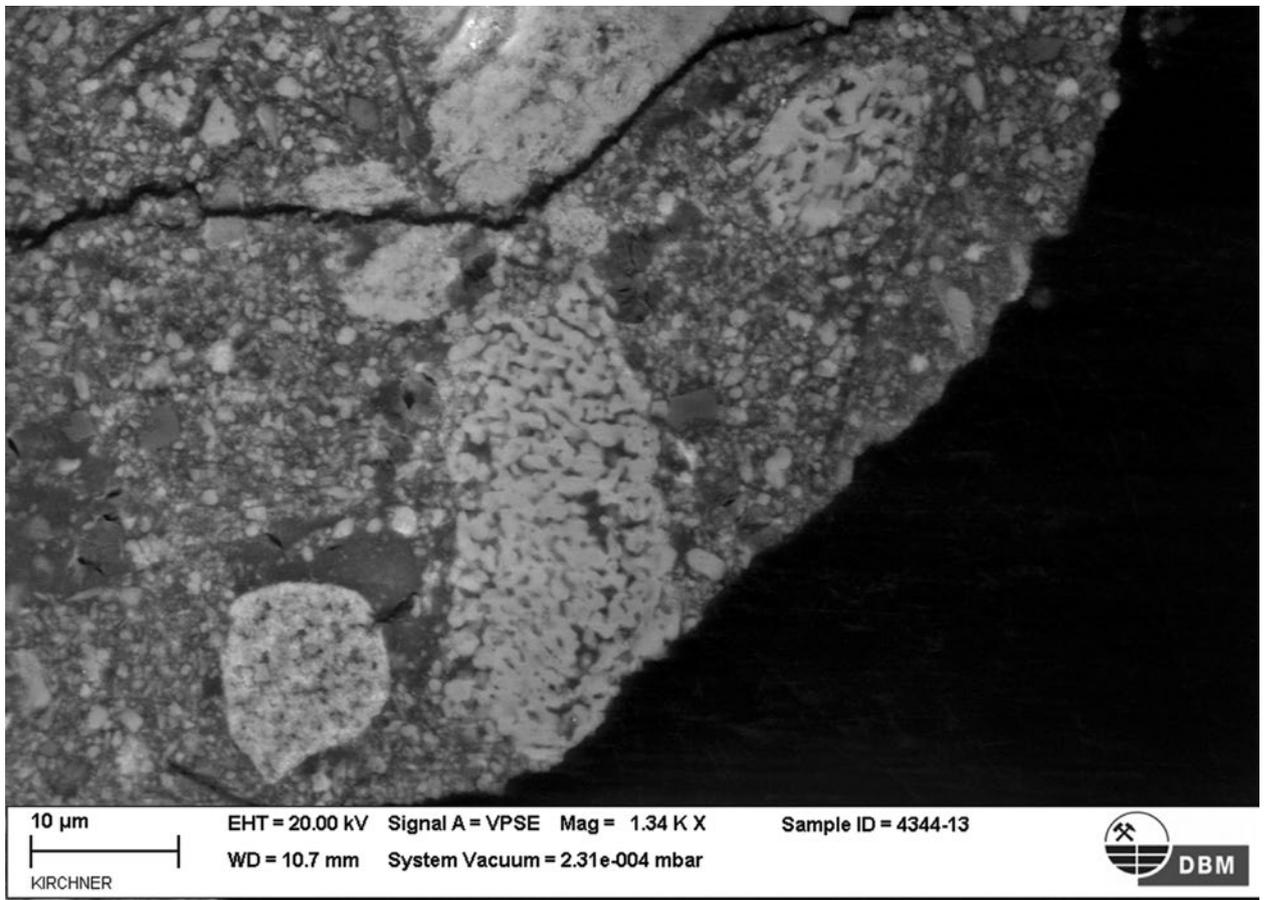


Figure 5. Green cosmetic pigment #4344/30-12-112. Individual grains of hydroxyapatite showing the original porous texture of (crushed) bone added to a mixture of secondary copper minerals. Scanning electron picture, secondary electron mode. Photo: M. Usadel, Deutsches Bergbau-Museum

laurionite were, and some of these are oxidation products of galena. The oxidation of the primary mineral is not only known from geological processes, but could have also occurred in the burial environment of the cosmetic shells and its subsequent weathering effects. The black color of this pigment may have been caused by the manganese mineral components, and / or, alternatively, by organic black pigments.

#### c) Mineral / inorganic composition of white and gray pigments

In comparison to the green or black pigments from Ur, the white and gray ones are much lower in number. Five white pigment samples from the collection in Philadelphia were accessible to us. It was possible to additionally sample a grayish sample that was stored in a stone vessel made of calcite with two receptacles (#4335/35-1-42, Figure 2). The cup is very similar to a pigment vessel of calcite (#35-1-186) with black cosmetic, which though was not included in this investigation. Shape and design of such vessels are comparable to those from Susa (Collin, 2003, p.303).

Three of the white and gray pigment samples (#4310/30-12-188, #4318/30-12-115, #4938/98-9-150)

are high in CaO (> 40 wt. %) and in P<sub>2</sub>O<sub>5</sub> (c. 30 - 40 wt. %). With one exception the lead content in these samples is less than one weight percentage. The mineral / phase composition of these samples comprises of a mixture of hydroxyapatite, calcite, ankerite (FeCO<sub>3</sub>) and quartz.

In two samples (#4311/B16999(x), #4318/30-12-115), the main elements are lead (39 - 47 wt. %) and sulfur (11.7 wt. % and 7.69 wt. %); silver was detected as a trace element (10 - 95 ppm). The lead-rich minerals cerussite (PbCO<sub>3</sub>), laurionite (PbOHCl) and gypsum (Ca[SO<sub>4</sub>].H<sub>2</sub>O) were identified. There is no evidence for any remains of galena (as suspected previously) within the oxidized lead minerals. The grayish pigment of sample #4335/35-1-42 contains about 4 wt. % lead and is high in calcium and silica. Predominant mineral / phase components are caracolite (Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>), gypsum, quartz and calcite.

#### d) Mineral / inorganic composition of red pigments

The dominate mineral in the red pigment samples is hematite (Fe<sub>2</sub>O<sub>3</sub>). Hematite is a widespread red-colored oxidized iron mineral, which is formed in many various rocks and sediments.

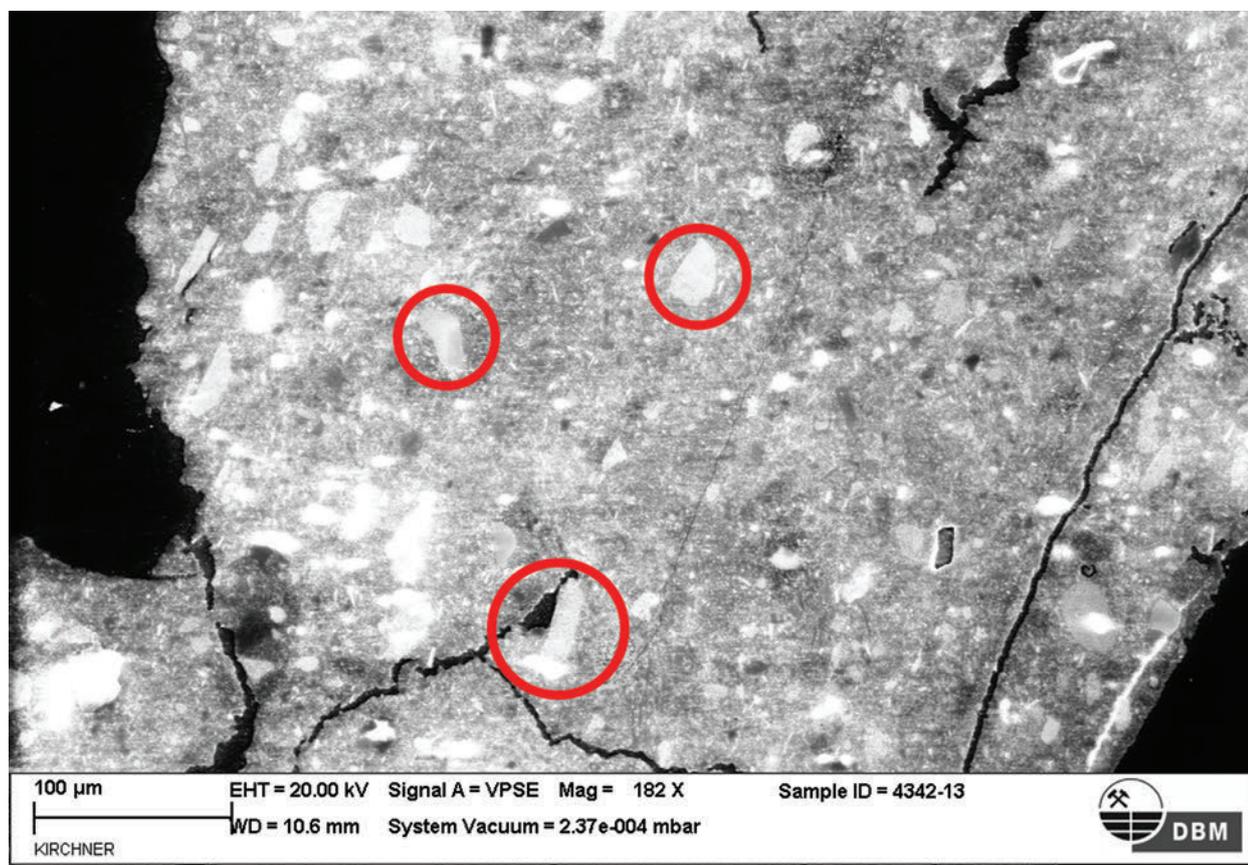


Figure 6. Green cosmetic pigment #4342/30-12-118A. Individual grains of highly burned hydroxyapatite (*ossa combusta*; exemplified by three red circles) are embedded in a matrix of various green secondary copper minerals. Due to their solubility of secondary copper minerals, they are recrystallized in situ to various extents. Some other inclusions of quartz are not specified. Scanning electron picture, secondary electron mode. Photo: M. Usadel, Deutsches Bergbau-Museum

Two of the three samples comprise of hematite, quartz, gypsum, and anhydrite. The third sample (#4329/35-1-660) consists of hematite, quartz and feldspar (~ microcline and albite). Feldspar and quartz may be accessory minerals of hematite ore, perhaps from a hydrothermal mineralization, whereas the assemblage with gypsum, anhydrite and quartz may originate from a sedimentary environment.

#### e) Hydroxyapatite – animal / human bones

Besides the chromophoric constituents, 21 out of 25 samples of the green pigments, two of the white pigments (#4310/30-12-188(x), 4318/30-12-115) and a single black pigment (#4334/B16946) contain additionally the minerals hydroxyapatite ( $\text{Ca}_5[\text{OH}](\text{PO}_4)_3$ ), fluor- and / or chloroapatite ( $\text{Ca}_5[\text{F}](\text{PO}_4)_3$ ,  $\text{Ca}_5[\text{Cl}](\text{PO}_4)_3$ ) as major components. Because it is rather difficult to distinguish crystallographically between these various modifications of apatite, we henceforth will name these minerals / phases with the term hydroxyapatite. Scanning electron micrographs show two varieties of hydroxyapatite. The first one provides the original porous texture of bone particles (Figure 5) which are – if at all – only slightly heated.

The second type of inclusions are crystallized particles. The micrograph in Figure 6 shows individual (sub-) angular grains of this mineral / phase. These crushed and powdered particles are embedded in the green colored matrix. They were obviously mixed with copper minerals and kept their shape while the latter due to their high solubility were recrystallized multiple times.

Hydroxyapatite is biogenic, it is the main ossific constituent of bones and teeth of humans and animals. Such phosphorous-bearing minerals are known only as rare inorganic components in fossil shell material of geological ages (Dorozhkin and Epple, 2002), but a shell composition is usually dominated by aragonite ( $\text{CaCO}_3$ ). Most mineral deposits of secondary copper minerals are only rarely associated with phosphorus minerals. One exceptional example is the sedimentary deposit of Faynan, Jordan, where copper ores contain easily more than 10 weight percentage of  $\text{P}_2\text{O}_5$  (Hauptmann, 2007, p.74). However, the phosphorous ores at this locality are apatite, and not hydroxyapatite as detected in the pigments from Ur. In case of the pigments from Ur, we therefore propose a deliberate addition of biogenic hydroxyapatite to the pigment minerals.

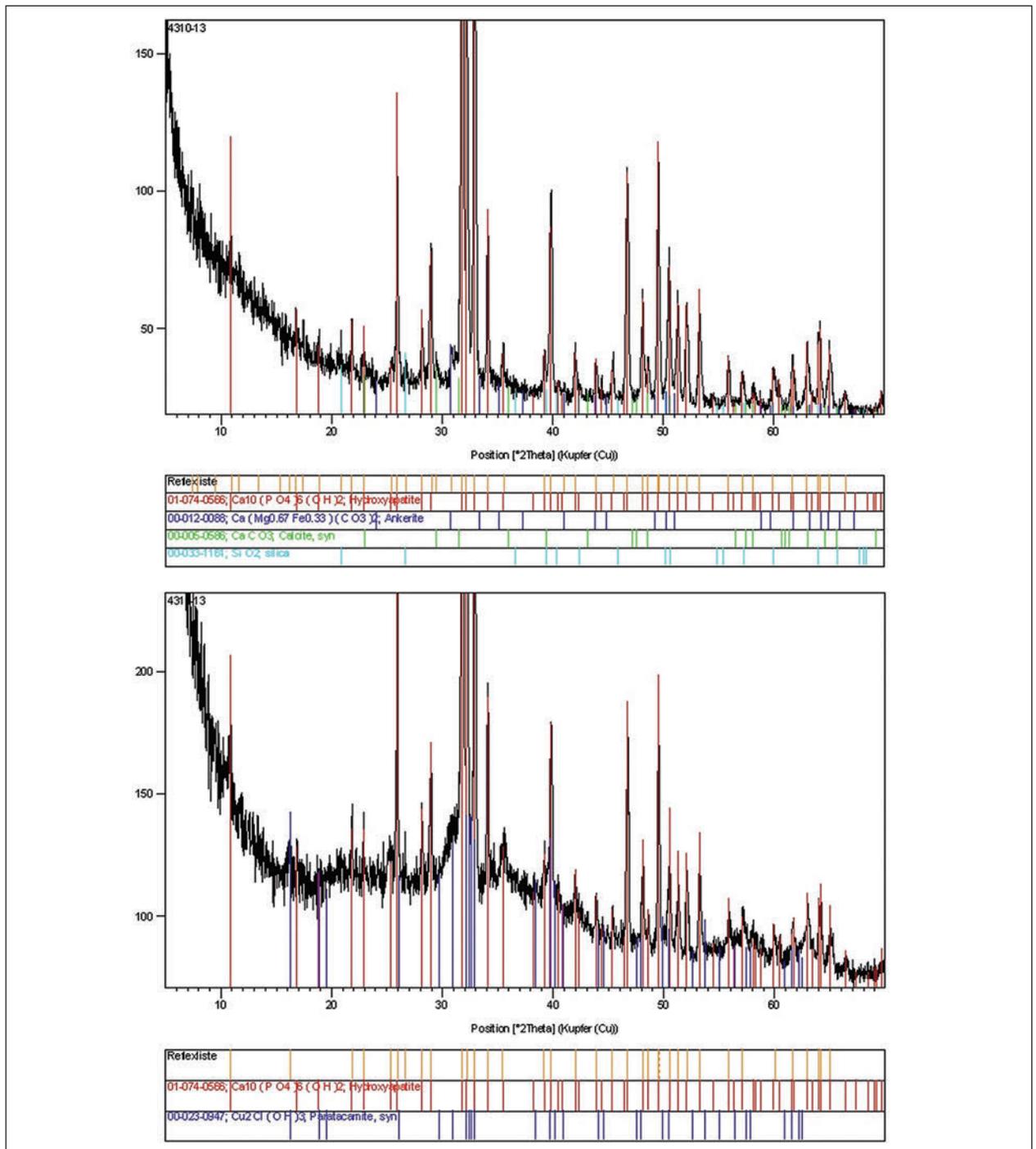


Figure 7. Two analyses of mineral / phase contents by X-ray diffraction (XRD) of two samples of cosmetic pigments from Ur. The diagram above shows a white pigment (#4310/30-12-188(x)), the diagram below a green one (# 4315/B17040a). Note the pronounced peaks of hydroxyapatite in both diagrams. These are comparable with fired bones up to c. 800 °C, according to Stage V after Wahl (1981) (see also Person, et al., 1996; Swillens, et al. 2003, p.207).

XRD measurements of inclusions of hydroxyapatite show sharp peaks and a pronounced splitting of the peaks of hydroxyapatite between 24 and 35° 2 $\theta$ . This is exemplified by the diagrams of a white sample (#4310/30-12-188(x)) and a green sample (# 4315/B17040a, both in Figure 7). In comparison with data from experimental bone firing (Person, et al., 1996; Swillens, Pollandt and Wahl, 2003) the diagrams of the samples from Ur are comparable with bones heated up to c. 800 °C, i.e., Stage

V after Wahl (1981). At these temperatures bones start to recrystallize and are transformed to a white chalky color. This material is termed “bone white” or “*ossa combustata*”. Hydroxyapatite in the black pigments do not show these sharp peaks. Obviously, the bone material added to the pigment in these cases were not heated as high as it was practiced with the white and green pigments. When cream colored bones are heated to c. 300 °C, the material will change to black (Person, et al., 1996, p.141).

## f) Organic materials - oil, fat, bitumen

In some black / brown pigments, manganese minerals were present in only poor quantity, the coloration was obviously obtained by organic black pigments, such as plant black, bister or soot. In one brownish-black sample (#4297/B1699b), a variety of compounds that are characteristic for pyrolysis products of wood were identified by GC-MS (vanillin, acetovanillin, oxodehydroabiatic acid; see Tables 1 and 5).

Besides this, the detection of asphalt or bitumen in a single black cosmetic pigment (#4303/35-1-66B) is worth mentioning. Hopanes and steranes were detected by GC-MS, which are typical of natural bitumen (Lan-guri, 2004; Peters, Walters and Moldowan, 2007).

As it happens quite easily through handling of archaeological material, many of the cosmetic samples were contaminated with modern organic materials such as paraffin wax, plasticizers, glycols and monoterpenes (Table 5). These materials were introduced during excavation or afterwards in subsequent conservation measures. There is no mention of specific conservation of the pigments by Plenderleith (1934), but it is clear that paraffin wax was widely used as means to conserve or stabilize objects during the excavation (Woolley, 1934, paraffin specifically mentioned on p.70 and 75). To limit the invasiveness of the sampling only small amounts of material could be taken from the uppermost surface of the pigments and, thus, the most vulnerable to contamination. It was not possible to take samples from below the surface, which would have been useful to evaluate the impact of contamination.

Nevertheless, five pigment samples were analyzed for organic components and (four green and one black cosmetic pigments, see above) revealed that an original binding medium could be present and is predominantly formed by fatty acids from an oil or fat. Main fatty acid components identified were palmitic ( $F_{C16}$ ) and stearic acid ( $F_{C18}$ ), as well as other saturated fatty acids with chain length from C8 to C17. The fatty acid profile is non-characteristic and an attribution to a plant oil or animal fat is impossible according to the aging and degradation of the samples. In general, in archaeological samples a distinction is always difficult to reach (Ribechini, et al., 2011). First of all, a huge variety of potential plant oils or animal fats usable as binding media exist (Serpico and White, 2000). Furthermore, oil or fat can undergo degradation and transformation during the production processes (e.g., by means of heating or roasting processes). Above all, specific burial conditions can change or degrade marker compounds (Dudd, Regert and Evershed, 1998; Jáky, Perédi and Pálos, 1964). Therefore, the origin of the oils and fats present in the samples must remain ambiguous.

Presumably, the various green, bluish and black pigments were originally mixed with a liquid vegetable oil or animal fat. Oil and fat were identified earlier as a component of archaeological cosmetics, but usually they occur in combination with waxes and resins (Charrié-Duhaut, et al., 2007; Cotte, et al., 2005; Ribechini, et al., 2011). Only modern paraffin wax and no beeswax, plant wax or ozokerite was identified by GC-MS.

Additionally, small amounts of polysaccharides were identified in the cosmetic pigments. So far, their interpretation in the archaeological finds of Ur is still difficult and a clear attribution is not yet possible. Similarly to the fat compounds, the preservation of saccharides is greatly influenced by the burial conditions (Bonaduce, et al., 2007; Lluveras-Tenorio, et al., 2012). In a Roman cosmetic container, which dates to the 2<sup>nd</sup> century AD, starch was found as an original component of a fat-based cream (Evershed, et al., 2004). As for the polysaccharides in the pigments from Ur, it should be taken into consideration that alternatively they might also result from post-depositional contamination.

## g) Metal-organic compounds

We detected basic copper (II) acetates and associated formic acids in the cosmetic pigments (Table 3). Both compounds are concentrated mainly in the greenish pigments in concentrations of the tenth percentage level, but they may reach up to one percent. In brown / black pigments the metal-organic compounds reach the level of a few hundred parts per million only.

The group of basic copper (II) acetates form the typical bluish-green pigments of *verdigris*. The modification  $Cu(CH_3COO)_2 \cdot H_2O$  is by far the most common of these compounds. In general, copper acetates are far more common than the formic acid (HCOOH). The bluish-green color may change after a while to green (Scott, Yoko and Emi, 2001, pp.74, 76). *Verdigris* is soluble in many oils and resins and can be dissolved in gelatin to make a copper proteinate. This versatility is what made *verdigris* such a useful pigment.

## The mixing and making of cosmetic pigments

In focusing on the making of the cosmetic pigments there are the following major issues: 1. original constituents and colors of pigments, 2. the role of hydroxyapatite as an additive, 3. binding media.

1. Do the archaeological finds, which were excavated in the 20<sup>th</sup> century as cosmetic pigments in shells, represent the originally produced pigments in their full extent? Are

the pigments in their original condition as far as color and composition are concerned? Or were the pigments conversely affected and transformed to secondary products, e.g., through weathering and corrosion processes after burial in the soil for 4500 years?

An interesting find in this context is a chlorite flagon found at the early urban site of Shahdad in Iran (Vidale, et al., 2012). It was filled with a (most likely) deliberately made cosmetic pigment, which now mostly consists of lead carbonates. The pigment minerals show different layers with galena at the bottom of the vessel changing to cerussite and hydrocerussite at the top. It is suggested that this variation is due to corrosion, but chemical processing of lead is discussed and it is assumed that white lead-rich cosmetics were used in the prehistoric Old World.

Atacamite and paratacamite were identified in the green pigment samples as the major coloring minerals / phases. These two copper chloride minerals are present in many outcrops of copper deposits in arid regions as mentioned above. The dominant presence of the two green minerals in the pigment samples might be an argument that they were collected as natural pigments from such copper mineral outcrops, and that non-coloring minerals (quartz, feldspar, calcite, dolomite) could result from relics of host rocks. On the other hand, the Cu-chlorides could have been formed easily in the post-burial environment by the geochemical interaction with the soil, because Ur is located at the entry of the two rivers Euphrates and Tigris at the Shatt al-Arab. It is an expanded marshland, swamp and lake zone, the so-called Ghors. In the Ghors, soils are rich in chloride salts, gypsum and lime. In between salty mud plains occur without any vegetation.

As for the green pigments, especially such with a slight bluish hue, it has to be taken into consideration that they may have had a more bluish rather than greenish tint when they were originally made in the Early Dynastic period. A more intensive blue of the pigments during their use as cosmetics would match much better with the colors of the jewelry that were worn at Ur, which was dominated by the countless beads and other items of intense blue lapis lazuli (see Zanon, 2012). Green jewelry has yet to be found. Over much of history and even today, clothing, jewelry and cosmetics are the three decorative elements, which are complemented by matching colors, so the use of green cosmetics in Ur seems therefore surprising.

Azurite, which was identified in some of the pigments, is an intensive blue secondary copper mineral. It alters under weathering conditions as a pseudomorphosis to malachite. Crystallographic analysis on such a material will still result in the identification of azurite,

but the original blue pigment has turned to green. Both minerals are chemically and crystallographically closely related, and azurite is easily replaced by malachite (Koritnig, 1981). The correct identification of azurite vs. malachite is not straight forward when azurite alters only partially so that green color shades admix with blue ones. This effect is even stronger, when the pigments are used as powdered material. Also (par-) atacamite is mentioned as an (indirect) green product from the decomposition of blue azurite. The cosmetic thus is of green rather than the original blue color as it probably was in ancient times. This phenomenon was previously observed in historic pigments in other context, e.g., in ancient (wall) paintings (Schweppe, 1993, p.548).

Another theory for the presence of (par-) atacamite in the pigment samples is a deliberately initiated wet-chemical corrosion of copper metal or bronze alloys to produce green secondary copper minerals for pigment production. Two different treatments are reasonable: a) the formation of (par-) atacamite resulting from a direct corrosion of copper metal or bronze alloys, or b) indirectly processed as a two-stage treatment: First-step formation of basic Cu(II)-acetates, i.e., of *verdigris*, and subsequent transformation over the millennia to copper chloride in the soil (Scott, 2002, pp.270-271). The color of *verdigris* ranges from pale blue through turquoise to green, as seen, e.g., in Figure 2, sample C (#4313/B17192).

*Verdigris* is a widely produced corrosion product of copper and bronzes, and there is a variety of simple recipes to deliberately produce synthetic *verdigris*. *Verdigris* was well known at least from Roman and Greek times. It is described, e.g., by Theophrast (4<sup>th</sup> century BC), Pliny the Elder (1<sup>st</sup> century AD), by Dioscorides (c. 40-90 AD) and later by other scholars (detailed discussion in Scott, 2002, pp.270-271). To produce copper acetate, various organic agents were applied, but one of the most effective known is adding vinegar, honey and salt to the metal. The following discussion of the green pigments' lead isotope results and their comparison with copper and bronze artefacts from Ur will present a strong argument towards a striking similarity of green-bluish pigments and artefacts, which underlines the above "*verdigris*-theory".

Formic acid, in general, is a common pollutant which may emanate from organic acid vapors such as from wood. The formation of formic acids is discussed intensively in the context of recent corrosion of works of art in museum environments where objects are often shown in wooden show cases (e.g., Gibson, 2010). For the origin of formic acids in the cosmetic pigments of Ur, we suggest a post-burial formation in the tombs. For the construction of the Royal Tombs in the necropolis of Ur stone, clay bricks and also wood were used, and this material was

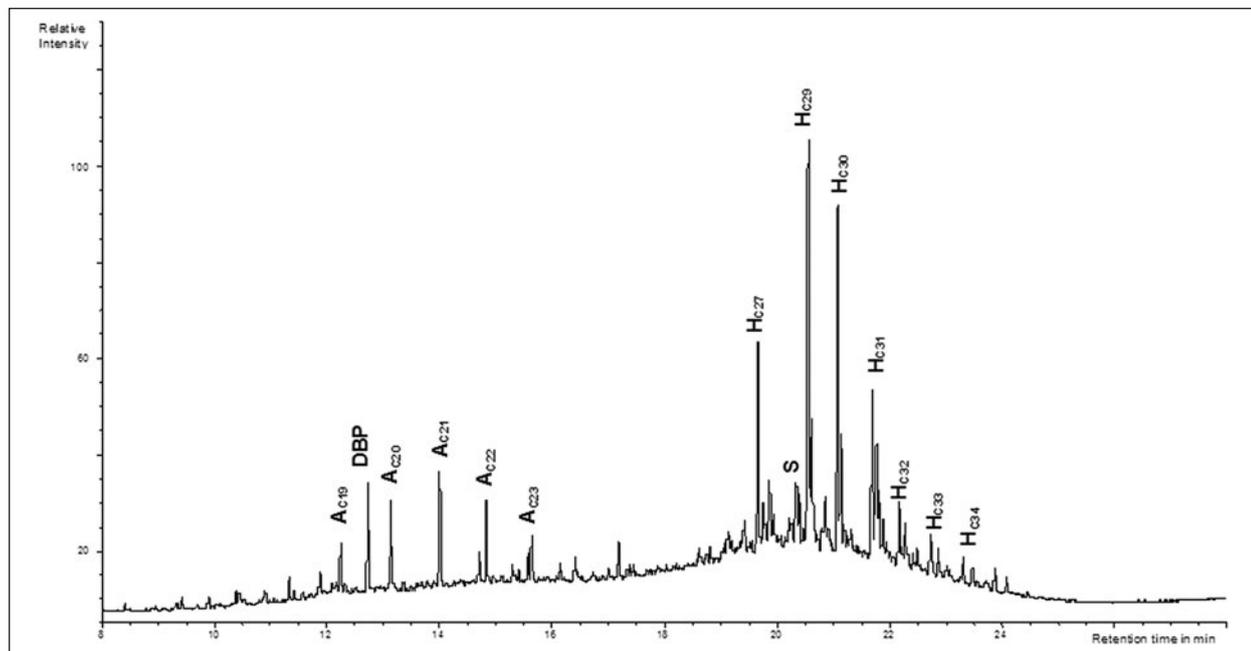


Figure 8. Pigment sample #4303/35-1-66B. The gas chromatogram of the iso-octane extract shows small amounts of paraffine wax (alkanes with carbon chain length between C19 and C23). Dominating in the profile are hopanes typical for natural bitumen (C27 to C34). Abbreviation: A = alkanes, DBP = dibutylphthalate, H = hopanes, S = steranes, Cxy = carbon chain length.

used for manufacturing grave goods and furniture such as chests or chariots within the graves.

## 2. The role of hydroxyapatite as an additive

As seen in Figures 4 and 5, hydroxyapatite was added in finely crushed powders to the green pigments. Bone was a well-known raw material source in Early Dynastic Mesopotamia (Potts, 1997, p.97) and was frequently used, e.g., for decorative inlays or figurines. It would be surprising if the artisans of Ur had not known that animal bones or teeth were fired, crushed and finely ground to produce “bone white”, “bone ash” or “ossa combusta” and that this material would subdue intensively colored pigments. Much later, these materials were common in admixtures, e.g. in medieval painting (Heraclius, 12<sup>th</sup>-13<sup>th</sup> c. AD, p.40; Hering, 2000, pp.65-66). Modern “bone white” comprises of anhydrous  $\text{Ca}_3(\text{PO}_4)_2$ , but Harbeck, et al. (2011) observed that hydroxyapatite stay stable even at 1000 °C when bones were burnt. Bimson (1980) detected hydroxyapatite in white pigments from the Ur collection of the British Museum and found them to be identical with the X-ray diffraction pattern of (fired) calcined bones. She suggested that the apatite component of the pigments originated from bone material also, but had not excluded the alternative explanation of the use of natural hydroxyapatite mineral component.

## 3. Binding media

During burial, soil deposition, later excavation and initial conservation practices, contamination of the cosmet-

ic pigments with different organic constituents occurred and all make a proper analysis of original constituents difficult. Besides these, oil and fat and in small amounts also plant gum were identified in the five of the pigment samples analyzed. Binding media in antique cosmetics were only rarely analyzed. However, similar findings of fat or oil in such samples are mentioned in the literature, but mostly in admixture with waxes or resins (Charrié-Duhaut, et al., 2007; Cotte, et al., 2005; Ribechini, et al., 2011). In a roman cosmetic jar (200 BC) starch was identified as polysaccharide and original compound of an oil containing cream (Evershed, et al., 2004). Whether oil and fat were deliberately added binding media or rather effects of soil deposition or conservation practices is difficult to decide. In any case the binding material used to prepare the cosmetic pigments from Ur consolidated rather quick. This is indicated by their flow structures and the coin-like shapes preserved (Figure 2).

We point to the individual black cosmetic sample, in which bitumen was detected, thus most probably originating from local sources (Figure 8): Huge oil resources and bitumen are known in the estuary area of Euphrates and Tigris. The reason why the ancient site of Ur was called by the Arabs “Tell al-Muqayyar” or „mound of pitch“ was the great quantity of surficial bitumen lumps and cakes (Woolley, 1929). In antique Iran, bitumen was found repeatedly as an adhesive or as a component in the process of mummification (Connan, 1999). However, we regard the use of asphalt or bitumen as a component in black cosmetics to be a unique appearance.

If any raw material for making the cosmetic pigments may have arrived already in shell containers at Ur is an open question, but the final preparation and mixing with oils or fats, if this was done, was most probably done in the workshops at Ur. Based upon the complex compositions of all the cosmetic pigments from Ur, we hesitate to accept the idea that the cosmetics were imported “ready for use” despite the finding of a prepared cosmetic pigment in Oman not far from a manganese deposit from which it may have originated (Cleuziu and Tosi, 2007, p.176).

### Lead isotopes and chemical composition: Towards possible origins of the pigment minerals

Until the recent past, provenance studies of minerals or metals, which were found in various localities of Mesopotamia, rely in large part on the interpretation of written texts as well as on the knowledge of raw material sources from (modern) geological investigations. On the latter much has been written, and from the archaeological point of view there are extensive but sometimes conflicting thoughts on this topic. Concrete facts, however, were found only in a few cases. One eminent exception is the exact provenance of lapis lazuli. All artifacts from this semi-precious stone found in the ancient Near and Middle East originated from the deposit of Sar es-Sang in Badakhshan (northeast Afghanistan). Due to its regional / geological uniqueness this locality functions in the archaeology of the Middle East as an anchor for the reconstruction of trade relations and routes (Casanova, 2013).

Often the origin of ores and metals cannot be identified with any certainty by using chemical and isotopic compositions. But recently the picture has changed significantly with an increasing number of lead isotope data of ores and metals from this part of the Old World. Begemann and Schmitt-Strecker (2009), Begemann, et al. (2010), Hauptmann (2007), Jansen (2011), Pernicka, et al. (2011), and Yener, et al. (1991) provided sufficient data and also their consideration within the archaeological context. Today, more than 400 references of lead isotope analyses from ores, slags, and also metal objects of the above regions are available. However, this amount of data is still very selective rather than representing the full statistical variety and spread of all ore deposits in the regions of interest.

The lead isotope ratios of the pigment samples from Ur are normalized to  $^{206}\text{Pb}$  and are presented as bivariate diagrams ( $^{207}\text{Pb} / ^{206}\text{Pb}$  vs.  $^{208}\text{Pb} / ^{206}\text{Pb}$  and  $^{207}\text{Pb} / ^{206}\text{Pb}$  vs.

$^{204}\text{Pb} / ^{206}\text{Pb}$ ). They are compared with lead isotope signatures of copper metal objects from Ur and with reference data from potential raw metal sources from southwest Asia.

#### a) Copper sources for the green and greenish / bluish pigments: Potential copper-rich deposits and lead isotope signature

The striking elevated concentrations of arsenic, nickel, gold and silver confirms our presumption that the provenance of these ores is from ophiolite-bound deposits. In those ore deposits nickel, iron, copper, chromium, cobalt, PGE mineralizations and arsenic are dominant trace elements. As reported by Hannington, et al. (1998), Herzig, et al. (1991), and Wilson, (1997), increased precious metal concentrations may also occur in gossans of recent and fossil volcanic massive sulfide deposits, which are located within ophiolite complexes.

The lead isotope signatures of the green and greenish / bluish pigments are plotted in Figures 9a-b and 10a-b. Their isotope ratios  $^{208}\text{Pb} / ^{206}\text{Pb}$  range from 2.068 to 2.092. They mostly form a homogeneous group with the exception of two individual samples. All green and greenish / bluish pigment samples are identical in all isotope signatures with previously analyzed copper and bronze artifacts from Ur (Begemann, et al., 2010). The lead isotope ratios of copper and bronze artifacts from Ur plot in two major groups, which differ in lower or higher  $^{207}\text{Pb} / ^{206}\text{Pb}$  ratios. The lower group consists of pure copper metal and only a few tin bronze artifacts, while the artifacts of the higher group consist almost completely of tin bronzes. Between these, a gap exists for both the pigments and the artifacts, which ranges between 0.85-0.86  $^{207}\text{Pb} / ^{206}\text{Pb}$ . According to Begemann, et al. (2010), the lower copper and bronze artifacts match the copper ore deposits of the Samail Ophiolite Complex of Oman, i.e., they are identical with the lower field. The origin of copper metal excavated from Early Dynastic (and later) tombs at Ur, of Oman is also confirmed by textual evidence (Potts, 1997).

The comparison of the copper ores from Oman in Figures 10a-b with the copper metal from Ur (which probably comes from Oman, also, see Figures 9a-b) now demonstrate that they have a much larger spread than the metals. If the original pigments have actually been collected from the various ore deposits, we would expect a comparably high spread. That is not the case. There is a strong isotopic match between metals and pigments meaning that the pigments could have been obtained from precisely the same ores used to make the copper metal, or, more likely, this is an indication of a synthetic production of verdigris made from copper metal (the

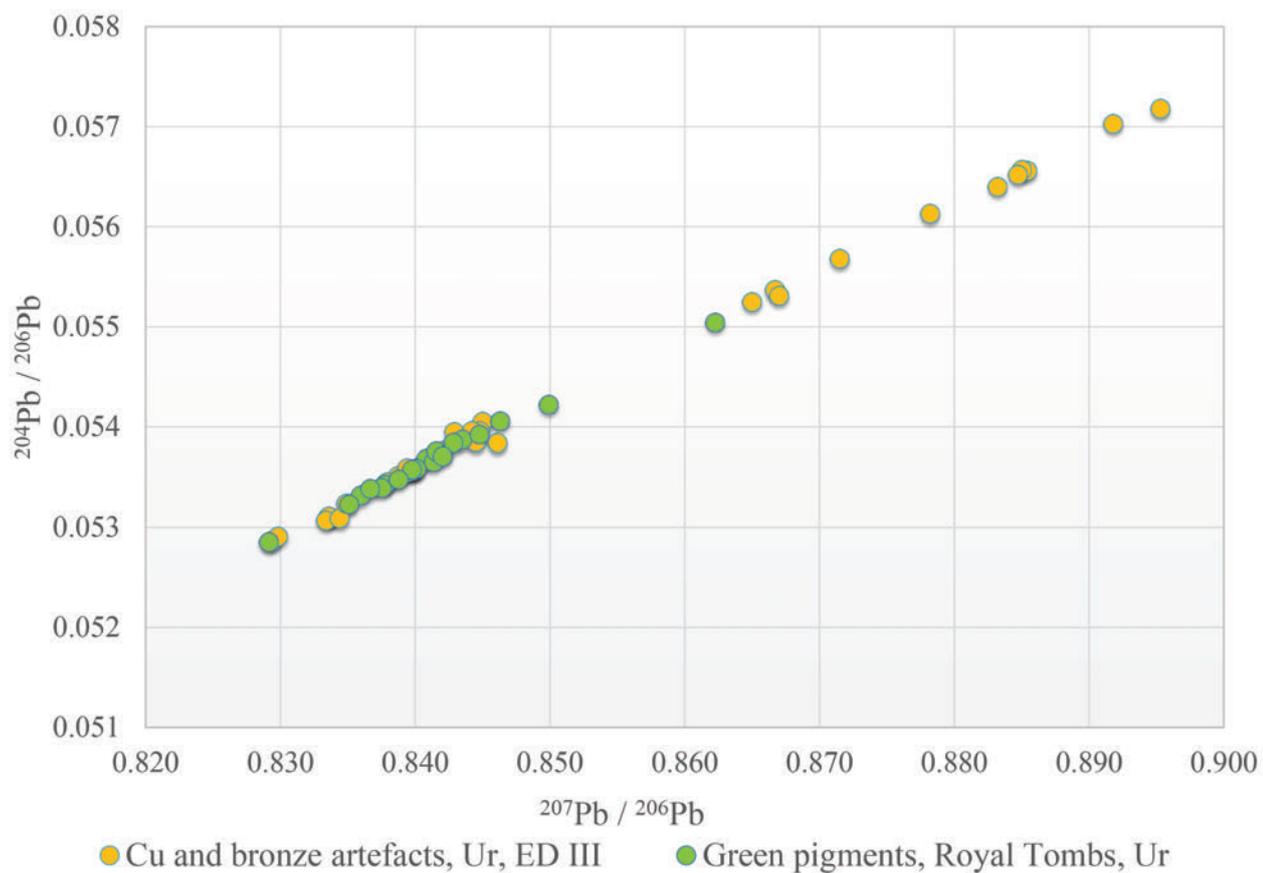
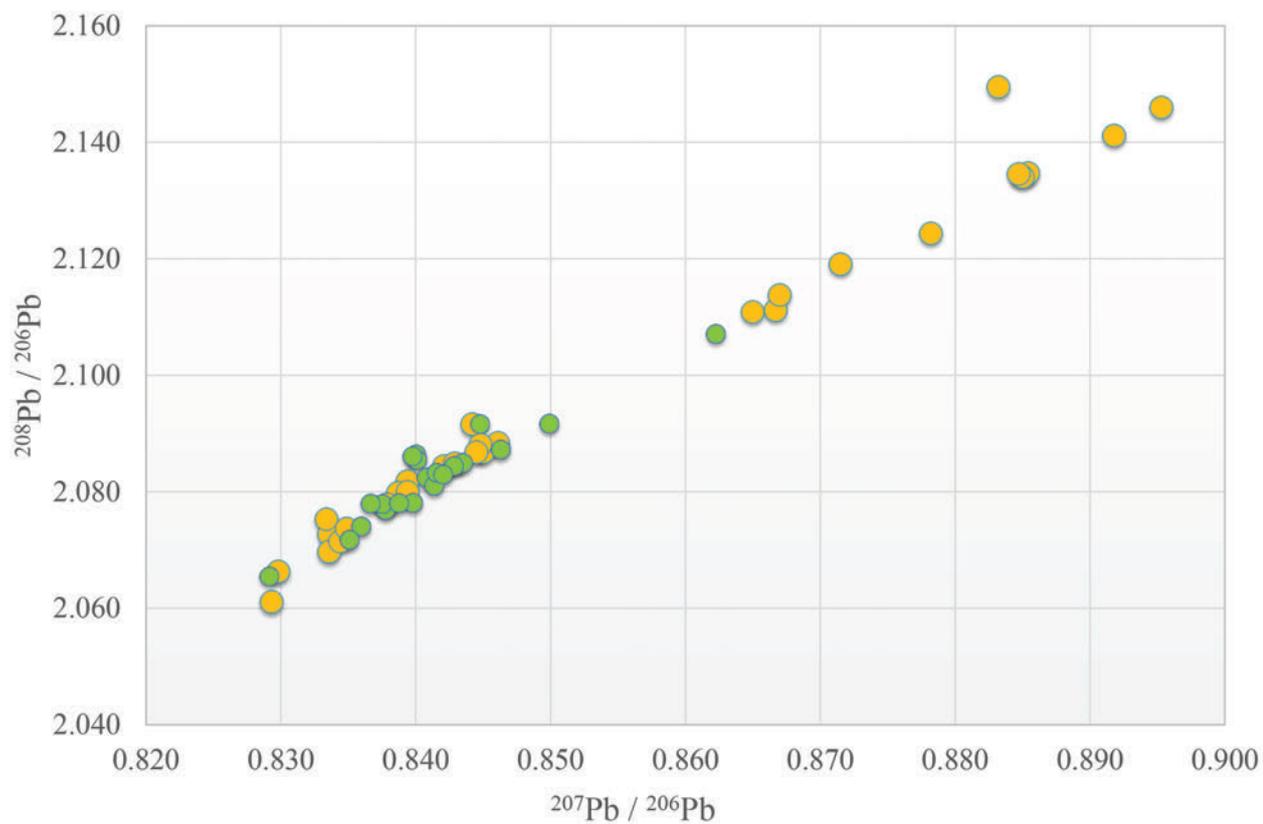


Figure 9. Bivariate diagrams of  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{208}\text{Pb} / ^{206}\text{Pb}$  (Figure 9a) and  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{204}\text{Pb} / ^{206}\text{Pb}$  (Figure 9b) of green, copper-rich pigments from Ur in comparison with copper and bronze artifacts from the Royal Tombs of Ur, Early Dynastic III (Begramann and Schmitt-Strecker, 2009). A perfect match of some pigments with the artifacts can be seen which suggests a direct origin of the cosmetics out of the metals. Standard deviation of own measurements (pigments): The error bars are smaller than the symbols.

latter then transmitting the lead isotope signature to the synthetic *verdigris*), as described above.

Next to the major copper source of Oman / *Magan* there are some prominent copper deposits along the corridor from northeast Afghanistan to Makran in the south which should be included in our discussion. Unfortunately, from this area only upon few samples were available. Examples are copper ores from the “giant” porphyry copper deposit of Reko Diq in Western Pakistan, ores, slags and copper from the Early Bronze Age settlement of Shahr-i Sokhta (Hauptmann, Rehren and Schmitt-Strecker, 2003) and some ore without precisely known origin from the Chagai Hills. According to the isotopic data, the pigments do not indicate a relationship to copper metal or copper ore from these regions. Also other copper deposits from Iran plot almost completely outside of the trend line of the pigments, so this is an argument against the Iranian Plateau as a source.

The most evident outlier, the green cosmetic pigment sample #4301/31-17-93, has elevated ratios of  $^{208}\text{Pb} / ^{206}\text{Pb} = 2.10716$ ;  $^{207}\text{Pb} / ^{206}\text{Pb} = 0.86224$ . Low amounts of trace elements were found in this sample with exception of lead (480 ppm). It also contains 0.4 wt. % uranium, which is therefore in line with ore from the phosphorous bearing copper-manganese deposits in the Wadi Arabah in the southern Levant.

#### **b) Manganese sources for the black / brown pigments: Potential manganese-rich deposits and lead isotope signature**

In the diagram  $^{208}\text{Pb} / ^{206}\text{Pb}$  vs.  $^{207}\text{Pb} / ^{206}\text{Pb}$ , except one sample, the black / brown pigments are very homogeneous with 2.06575 to 2.09070  $^{208}\text{Pb} / ^{206}\text{Pb}$ , 0.83364 to 0.84411  $^{207}\text{Pb} / ^{206}\text{Pb}$  (Figure 11a), and also in  $^{204}\text{Pb} / ^{206}\text{Pb}$  and  $^{207}\text{Pb} / ^{206}\text{Pb}$  ratios (Figure 11b). Manganese occurrences are geologically associated with copper ore. This geological association is underlined by elevated copper concentrations that were analyzed in the black / brown pigments from Ur. It is therefore crucial in this case to discuss both copper and manganese-rich ore deposits as potential ore sources. Compared with ore from Oman, Faynan and Timna as a first approach, it becomes evident that the homogeneous isotope group of black pigment samples is isotopically identical with manganese-bearing ore from Oman. Manganese-bearing copper ore deposits occur in northern Oman at, e.g., Semdah, Assayab, Aarja and Lasail in the Suhar district (Begemann, et al., 2010).

The single black pigment # 4334/B16946 that plots apart from the group has elevated isotope ratios ( $^{208}\text{Pb} / ^{206}\text{Pb} = 2.1129$ ). Although gold contents as appearing in the sample (20 ppm Au) are not characteristic for Wadi Arabah ore, the sample is isotopically consistent with

copper-manganese ore from the Wadi Arabah (Faynan and Timna).

Besides these ore sources, the lead isotope ratios of the black pigment samples do partially overlap with ore and metal objects from Cyprus (Ling and Stos-Gale, 2015). But with a closer look, the pigments are only tangent to the Cyprus field and therefore do not fit well together. This observation is strengthened by the fact, that until present, not such early evidence for mining activities in Cyprus was found. As a further possible candidate, Iranian manganese mineralizations lack discussion, but insufficient information is available in literature (Ghorbani, 2013).

For geochemical and archaeological considerations we therefore favor the southeastern Arabian Peninsula as the most prominent supplier for the black / brown pigments from Ur.

#### **c) Lead sources for the white and grayish pigments: Potential lead-rich deposits and lead isotope signature**

The lead isotope ratios of these pigment samples range from  $^{208}\text{Pb} / ^{206}\text{Pb}$  2.06736 to 2.0866. The number of pigment samples was too low to argue for a homogeneous group, but they plot reasonably close to each other. Sample #4310/30-12-188(x) is not displayed in the diagrams, because its lead concentration is below 0.1 wt. % (see above).

In Figures 12a-b, the lead isotope ratios of five lead-bearing white and grayish pigments from Ur are compared with potential lead ore districts. Both, the Turkish southeastern Anatolia and Taurus Mountains on one hand and the Iranian Plateau on the other appear as potential sources. In both, large lead-silver-zinc deposits occur frequently. Isotopically, the regions are difficult to distinguish, but if linear trend lines are drawn (Figure 12b), the line's slope for Anatolian and Taurus ores appears more congruent with the pigment samples than the one for Iranian ore.

The lead-rich sample #4330/30-12-111 from Ur is identical with the isotope composition of lead ores analyzed by Yener, et al., (1991) from the Taurus Mountains. Furthermore, we plotted lead isotope ratios of litharge cakes from Habuba Kabira (Pernicka, Rehren and Schmitt-Strecker, 1998). Pigment sample #4318/30-12-115 show close similarities: It matches the isotope signatures of Taurus lead ores as well as that of the litharge cakes from Habuba Kabira.

The lead isotopy of the grayish pigment (#4335/35-1-42) cannot be clearly assigned to specific ore deposits. It plots close to lead ores analyzed by Begemann and Schmitt-Strecker (2009) from Tabris in northwestern Iran, but it is also close to ores of the Taurus Mountains.

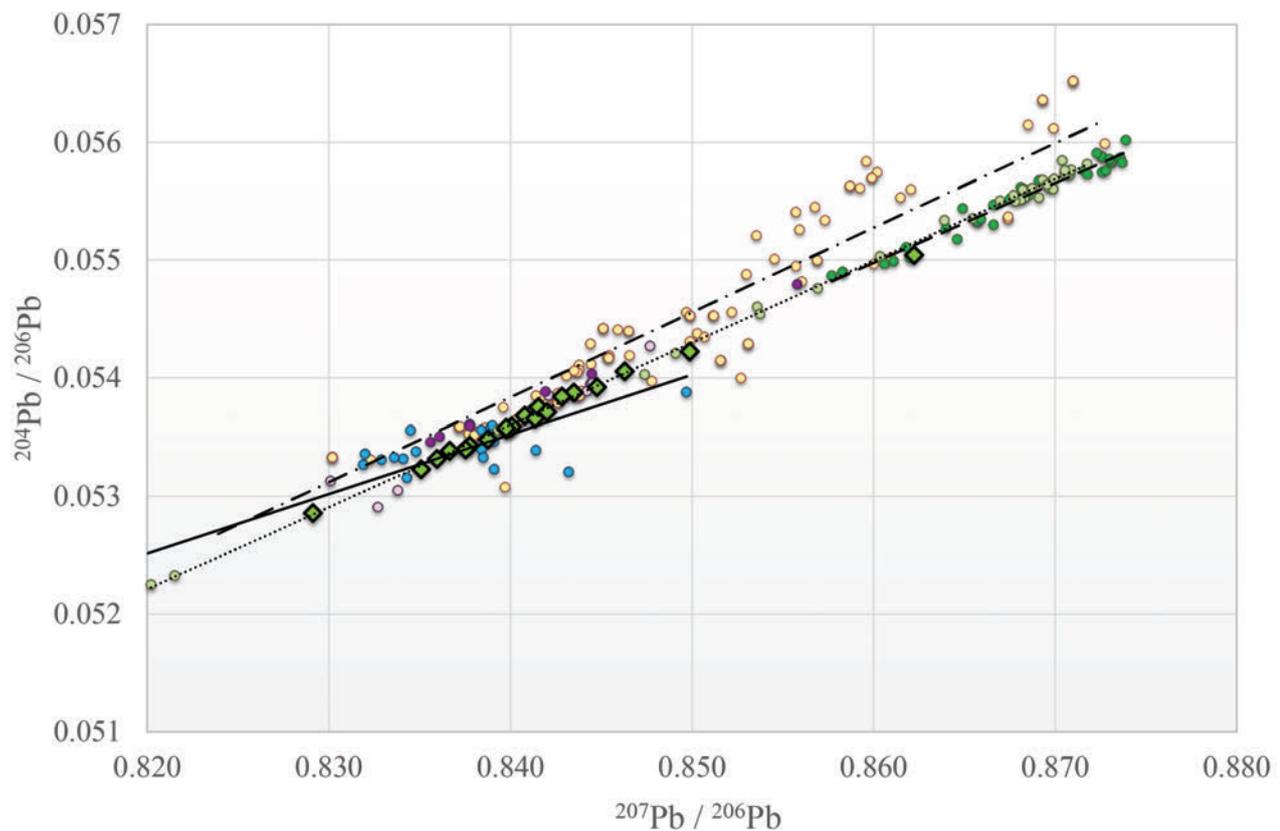
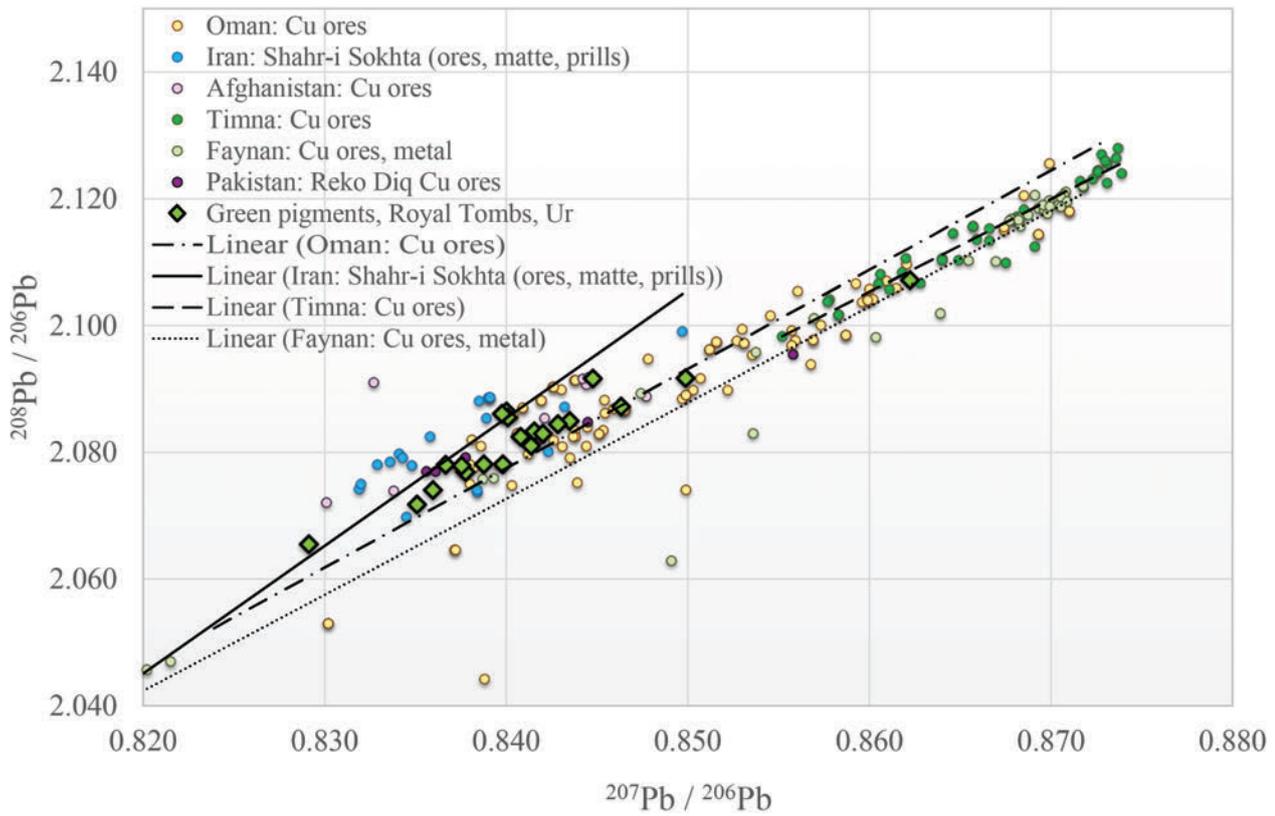


Figure 10. Bivariate diagrams  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{208}\text{Pb} / ^{206}\text{Pb}$  (Figure 10a) and  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{204}\text{Pb} / ^{206}\text{Pb}$  (Figure 10b) of greenish copper-rich pigments from Ur in comparison with copper ores from Oman, Iran (Shar-I Sokhta; reference data from ore and artifacts) and Pakistan (Reko Diq copper ore). One green pigment (#4301/31 17 93) has elevated lead isotope ratios and so far only copper mineral signatures from the Wadi Arabah (Faynan, Timna) would match. Standard deviation of own measurements (pigments): The error bars are smaller than the symbols.

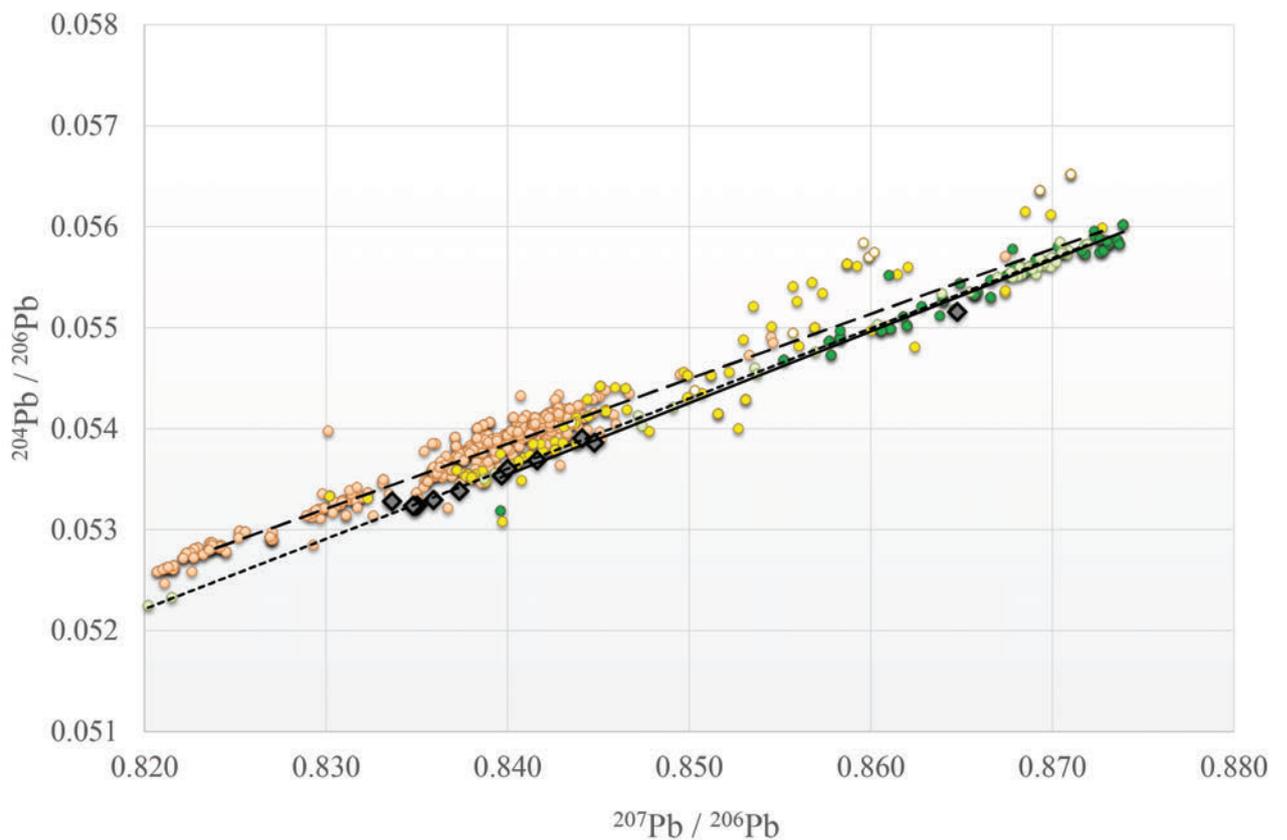
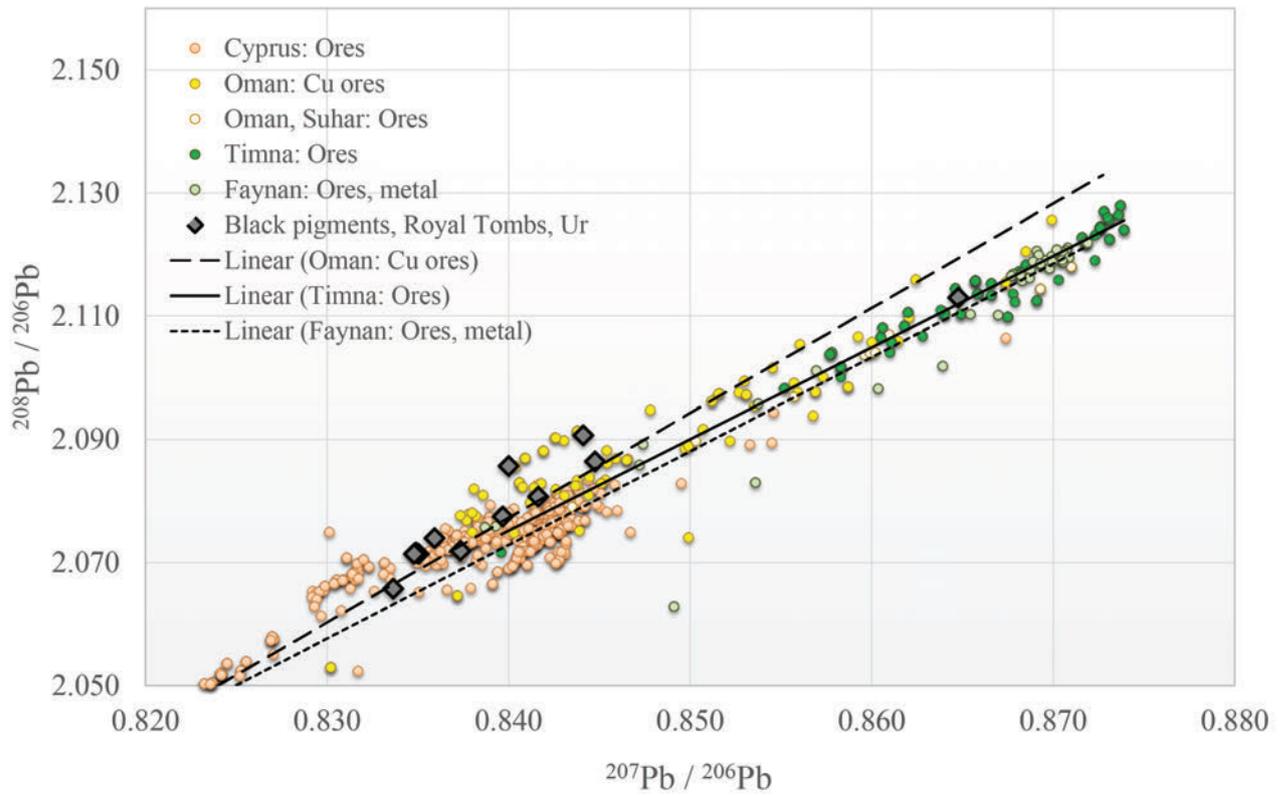


Figure 11. Bivariate diagrams  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{208}\text{Pb} / ^{206}\text{Pb}$  (Figure 11a) and  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{204}\text{Pb} / ^{206}\text{Pb}$  (Figure 11b) of black manganese-rich pigments from the Royal Tombs of Ur in comparison with copper ores from Oman and Wadi Arabah (Faynan, Timna). Separated are those copper ores which are associated with manganese sediments in the region of Suhar in the north of Oman (Begemann, et al., 2010). Also shown are ores from Cyprus. The trend lines show that the black pigments are just tangent to the Cyprus cluster at its upper periphery, while they are more consistent with ores from Oman and Wadi Arabah. Standard deviation of own measurements (pigments): The error bars are smaller than the symbols.

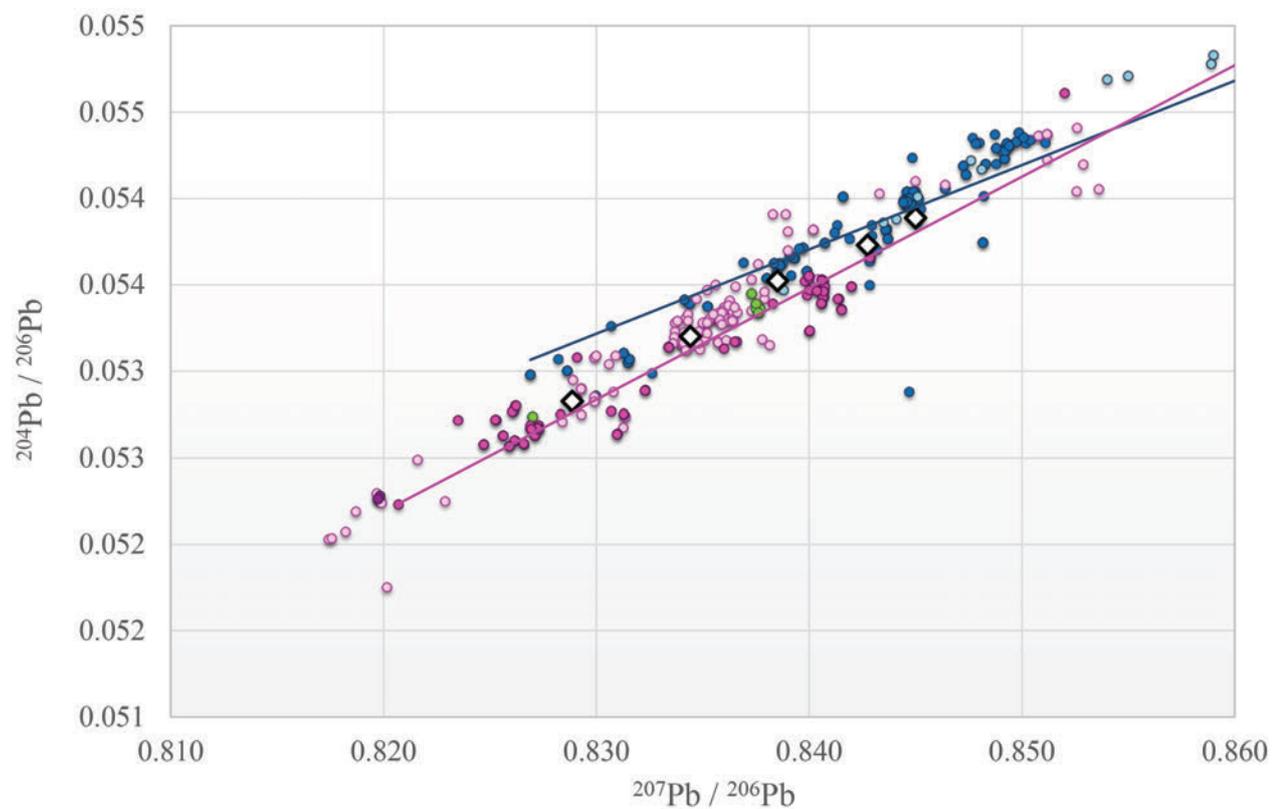
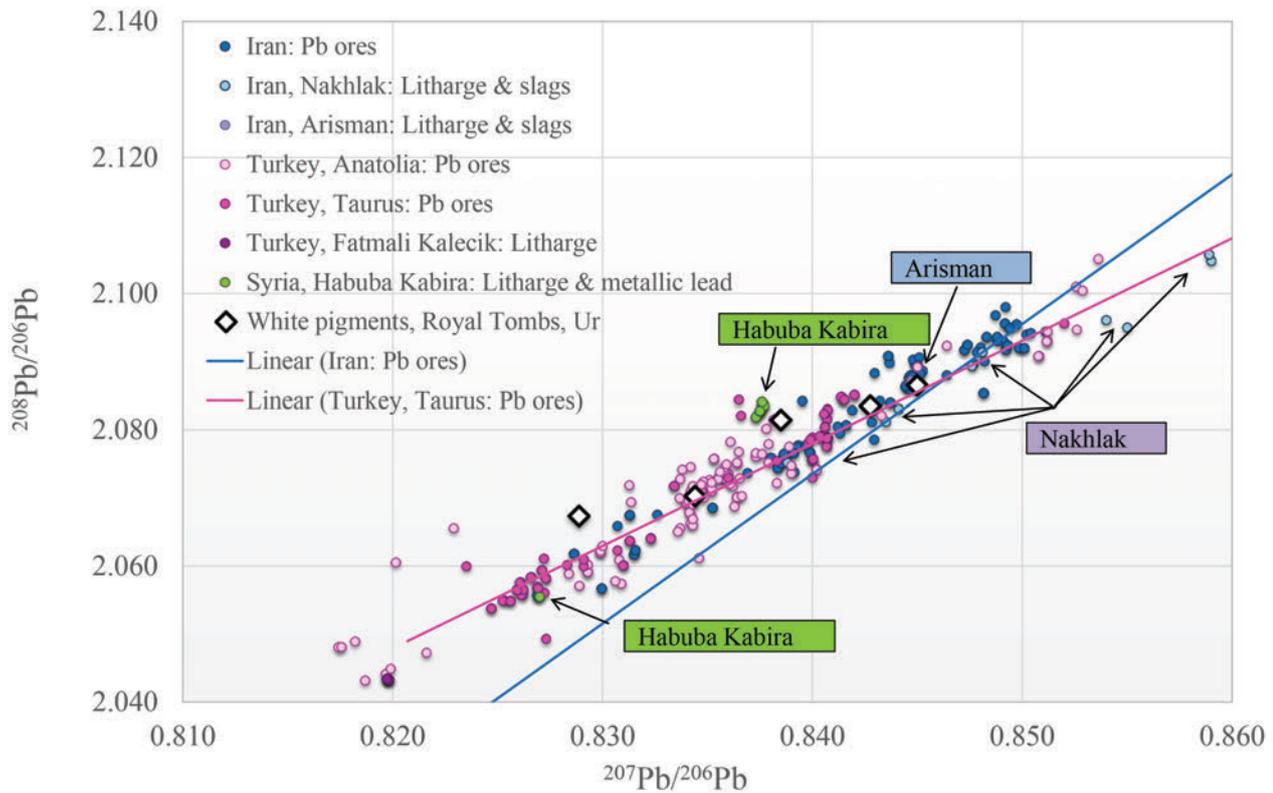


Figure 12. Bivariate diagrams  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{208}\text{Pb} / ^{206}\text{Pb}$  (Figure 13a) and  $^{207}\text{Pb} / ^{206}\text{Pb}$  versus  $^{204}\text{Pb} / ^{206}\text{Pb}$  (Figure 13b) of white and grayish lead-rich pigments from Ur in comparison with lead ores from Anatolia (Seeliger, et al., 1985; Yener, et al., 1991) and Iran (Begemann and Schmitt-Strecker 2009; Pernicka, et al., 2011). In addition, some finds of litharge from Habuba Kabira (Syria, upper Euphrates; Pernicka, Rehren and Schmitt-Strecker, 1998) and from Fatmali Kalecik (DBM, unpublished data) are plotted. Standard deviation of own measurements (pigments): The error bars are smaller than the symbols. Note that one lead ore sample from the Taurus Mountain is covered by a number of green symbols from the litharge cakes from Habuba Kabira, and the cluster of green symbols is close to white pigment 4318/30-12-115. The red trend line supports a source for the pigments from the Taurus Mountains (and from Habuba Kabira), but also Nakhlak and Arisman cannot be excluded as potential sources.

For the two white pigment samples with the highest lead isotope ratios (#4319/30-12-188(x) and #4311/B16999?(x)) alternatively, Iranian litharge cakes from the settlement of Arisman and also with ores from the deposit of Nakhlak show similarities. Nakhlak is a reasonable candidate, in this case, because first it was (and still is) one of the major lead deposits of the Iranian Plateau and second it is suggested to have been the raw source for lead / silver at Arisman in ancient times (Pernicka, et al., 2011). We therefore argue with good probability that ore minerals originating from this deposit also may have reached the city of Ur.

## Conclusions

### Value of the cosmetic pigments

Cosmetic pigments were found in extraordinary quantities in the Royal Tombs of Ur. They are a type of find which so far have attracted little attention in the (pre-) historic archaeology of southwest Asia. We emphasize their role as high valuable burial objects. The cosmetic pigments represent a material that was of limited accessibility and required complex and labor intensive process to produce. Therefore, especially for the greenish-bluish pigments, they probably had a high social and ritual value: in some instances they were stored in shells made of gold and silver (Zettler and Horne, 1998, p.135). Through their use as grave goods in the burials of political leaders, as temple offerings for the gods (such as at Kish) and their potential use as elegant make-up for the living elite, the cosmetic pigments must have had high symbolic significance. We argue that the pigments from the Royal Tombs of Ur can be regarded as prestige goods.

Pigments for cosmetics were manufactures from natural minerals and also from synthetic phases that were processed from minerals or metals. The three favored colors at Ur, for which there are parallels between pigments and jewelry, were: Blue or bluish (lapis lazuli beads vs. copper-based pigments), red (carnelian beads vs. red hematite pigments) and white (silver jewelry, marble or agate beads, ivory and shells as inlay materials in head-dresses vs. white and grayish pigments). Black (manganese pigments, bitumen) only occur in the cosmetic context (eyeliners), but does not appear in the jewelry. It can thus be treated important as an additional decorative color, as known for Khol Kajal in Egypt and other cultures. Further, most important in the jewelry is gold, but its color has no counterpart in the pigments in Ur.

The pigments can undergo changes in color (e.g., bluish to green) caused by a modification of the original

inorganic / organic compositions to weathering products due to burial environment in the saline soil.

### Materials and technology

Many of the cosmetic pigments are complex mixtures of chromophoric materials, binders and extenders. Different sources far beyond Mesopotamia functioned as suppliers for the pigments. Not only natural minerals, but also synthetic agents were known in Ur's Early Dynastic period. Egyptian blue is supposed to have been in use in Egypt since the Fourth Dynasty (Lucas and Harris 1962, p.342). In the bluish cosmetic pigments from Ur, Egyptian blue occurs at the same period as a coloring constituent.

The technique of making *verdigris* produces pale bluish / greenish synthetic pigments. The synthetic production of such pigments by intentional corrosion of copper metal or its alloys is strongly supported by the matching of lead isotope signatures of green pigments and copper and bronze metal artifacts from Ur and through the existence of copper acetates in the pigments. The recipes are generally unknown in the textual evidence of the 3<sup>rd</sup> millennium BC, but they are quite simple, and (liquid) agents such as vinegar would have been available everywhere to the artisans in Ur to be used in metal vessels.

Most of the green pigments were mixed with hydroxyapatite, which results from thermal alteration of bones and is therefore also a synthetic product. It usually functions as brightener and extender. Besides this mixture, fats and / or oil were identified as possible binding media. A deliberate addition seems reasonable and corresponds to the macroscopically pasty texture of the green pigments. However, the samples were contaminated with modern conservation materials which hinders the identification of the original organic components.

The cosmetic pigments may have been blended from their individual pigment, extender, and binding components on-site at Ur, but no conclusive proof was found yet.

### Raw material sources, trading

The interpretation of analytical data to assign the chromophoric material to specific geological regions or ore deposits are reasonable in the context with the archaeological (textual) evidence. But it has some uncertainties. First of all, the materials used in making the cosmetic pigments were created over a relatively long period of time of c. 400 years, between the Early Dynastic III to the Akkadian period (c. 26<sup>th</sup> to the 22<sup>nd</sup> century BC; cf. Helwing, 2014, p.412; Zettler and Horne, 1998). During this time span, trade routes developed, changed, and were abandoned. Trade and production are not static. The markets of Ur received commodities from various regional sourc-

es, changing from time to time, depending on political developments and threats. But it is a period in which supra-regional contacts were intensified and raw materials can be seen to move over long distances, Amiet (1986) coined the term “Age of Exchange” (see also Helwing, 2014, p.413). Examples of diverse time-dependent copper and bronze artifacts in Mesopotamia from various raw sources were reported previously from Begemann and Schmitt-Strecker (2009).

A second aspect is the fragmentary knowledge about ore deposits in the cultural regions discussed, about their dimensions, their economic meaning and importance in antiquity. The quantity and quality of ores (rich metal ores, surface-near secondary ores) are often not sufficiently described.

On the one hand, the structure of ore deposits may show considerable variations in chemistry and isotopic compositions. On the other hand, many of them – ore deposits from Anatolia to the Iranian Plateau – originate from a similar geological context, in the Tethyan Metallurgical Eurasian metallurgical belt (Janković, 1997). A sufficient number of samples would be required to characterize the deposits and to determine if they can truly be distinguished – a situation which is not guaranteed at the present stage of knowledge.

Nevertheless, the present study contributes to the definition of a number of potential raw mineral sources within the archaeological context. The ore supply from Taurus Mountains in Anatolia and / or the Iranian Plateau (the large mining area of Nakhlak) became obvious through the white, lead-rich pigments, even if Schmidt (2005, pp.98-99) postulated that at least since the time period of the Akkad rulers a large cultural gap between the Iranian highlands and the Mesopotamian lowlands existed. However, it is conceivable that the export of (secondary) lead ores (and of lead and silver) to Ur has not played a major role, but due to the evidence we found through our isotope measurements of the pigments, it does not mean that trade contacts between Mesopotamia and the Iranian highlands can be completely negated.

Comparing the isotope data of the green pigments with copper (metal and ore) from Oman / *Magan* puts this region into the discussion, too. According to the overwhelming textual and analytical evidences for the trade of raw materials from *Magan* to Mesopotamia in the Umm an-Nar period (Crawford, 2013, pp.452), both by land routes via *Dilmun* and then by the Gulf route, the tremendous ore deposits in the Samail ophiolite complex of Oman had an outstanding position and their products dominated the economy in this part of the world. This is true for copper and manganese ores and for copper metal as well.

Only few lead isotope reference data exist for Afghanistan-Pakistan-Iran in the regions of Makran, Baluchistan, and Seistan and this is insufficient for a comparison of pigments and ores. It is therefore difficult to fully integrate these regions into the discussion, even if trade relations of northeast Afghanistan with Ur are firmly established by the unique occurrence of lapis lazuli, and possibly also by gold (Jansen, et al., 2016).

Neglected at least in textual discussions on the provenance of raw materials found in Mesopotamia, the connections to the west, e.g., the Wadi Arabah, the district of Faynan (and Timna), may have supplied copper and manganese ore. During the Early Dynastic IIIa period in Mesopotamia (Early Bronze Age III in the southern Levant), copper production at Faynan showed an enormous boom of possibly supra-regional importance (Hauptmann, et al., 2015 ; Levy, et al., 2002). Evidence for such a trade in this time period is not yet available in the wider archaeological record, but the question remains if only an increased demand of Arabah copper in Egypt was the reason for the boom of copper production.

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## Note

- 1 Overviews, see Aruz, 2003; Kenoyer and Miller, 1999; Kohl and Lyonnet, 2008; Moorey, 1994; Muscarella, 2003; Pigott, 1999; Potts, 1993; 1994; 1997; Schmidt, 2005; Stech and Pigott, 1986.

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