Received: 2021-04-12 | Accepted: 2022-05-16 | Published: 2022-12-30

Making Copper: Processing in Early Bronze Age Arslantepe (VI B2)

Andreas Hauptmann, Nikolas Heil, Gian Maria di Nocera and Thomas Stöllner

Keywords
Arslantepe VI B2, South-East Anatolia, Early Bronze Age, copper production, crucibles, slag petrology, partial smelting, "free silica slag", lead isotope analyses

Abstract

This paper presents results of archaeometallurgical finds from Arslantepe VI B2 and observations and geoscientific analyses of ores and ore deposits in East Anatolia which are connected with this site. Function and technology of Early Bronze Age crucible smelting in a small scale domestic mode of production are discussed. Ore and rock inclusions in slag and lead isotope analyses are consistent with the origins of various copper sources on the Black Sea coast in the north (Artvin/Murgul, Trabzon) and in the south (Ergani Maden, Upper Mesopotamia) and broadens the Early Bronze Age trade of the Kura Araxes cultural network. The petrology of slags also from Çayönü Tepesi and Nevali Çori shows their formation by partial (eutectic) smelting processes and the non-liquation of refractory materials. The model of deliberate fluxing in smelting copper is proven to be disputable. Smelting of copper was performed in portable crucibles of surprisingly large size with air supply from below.

Introduction

This paper deals with the scientific investigation of a series of archaeometallurgical finds from Arslantepe in Eastern Anatolia, dating to the period VI B2 (Early Bronze Age I, c. 3100-2800 BC), which represents an extremely important phase of the development of metallurgy in this settlement. After the societal collapse in the Late Chalcolithic (e.g. Di Nocera, 2013; Frangipane, 2018) Arslantepe experienced an innovative metallurgical development in the course of which new techniques of metal processing were practiced. Exclusively copper was smelted, as evidenced by ores, slags, and crucibles excavated from inside the site. This raises the essential question of the provenance of copper in different contexts. Were all the copper artefacts found in Arslantepe produced from the metal smelted within the settlement itself or were they acquired from the outside, by extensive trade networks?

The present study is assigned to a chronologically younger period of Arslantepe discussed by Heil, et al. (2022, this volume of Metalla) for the period VII (Late Chalcolithic 3-4, 3900-3400 BC). Their paper highlights a small selection of archaeometallurgical remains from this period, including lead and copper slags, crucibles, and metal objects. These are (by-) products of pyrometallurgical operations using lead, copper, or polymetallic ores primarily from nearby sources.

Numerous investigations of early metallurgical activities of copper, lead, silver, tin and gold in the highlands of Eastern Anatolia and beyond were undertaken by Halet Çambel, Ufuk Esin, Önder Özdogan, Aslıhan Yener as well as many other scholars. Perhaps the most comprehensive summary of early metalwork in this region and the Eastern Mediterranean was presented in the form of eight conference volumes edited by Ünsal Yalçın, entitled "Anatolian Metal" (Yalçın, 2000; 2002; 2005; 2008; 2011; 2013; 2016; 2018). There, much emphasis is placed on the important role of raw material deposits in shaping the regional development of metallurgy. Eastern Anatolia possesses enormously rich metal raw material resources located along an orogenic belt stretching from East to West. In Eastern Anatolia, systematic field surveys for raw materials and early mining and metallurgy have been performed by the team of the Arslantepe excavation (Palmieri, Sertok and Chernykh, 1993) and the Heidelberg group (summarised in Wagner

DOI:10.46586/metalla.v26.2022.i2.113-140

and Öztunalı, 2000). Later, Lehner and Yener (2014) continued such extensive investigations by compiling maps of metal sources in Anatolia and the locations of associated ancient settlements. Another enlarged part of these maps is displayed in Figure 1.

Apart from these long-lasting and fruitful researches, the site of Arslantepe plays an outstanding role in archaeological investigation. It is one of the best explored sites in Eastern Anatolia where the settlement mound has been intensively excavated since 1983 by La Sapienza University in Rome, first led by Alba Palmieri (Frangipane, et al., 1993) and then, after her death, by Marcella Frangipane (2010a; 1994). There is hardly any site in this region which has preserved such a continuous and detailed stratification from the Late Chalcolithic 3-4 (level VII; 3900-3400 BC) to the Middle Bronze Age (2000-1750 BC, levels V AI-V A2) (Di Nocera, 2013; Frangipane, 2017; Vignola, et al., 2019).

Of particular importance for the development of metallurgy were, among other things, the findings of nine swords, twelve spearheads, and a quadruple spiral blade in the so-called “hall of weapons” in the area of the palace (Frangipane and Palmieri, 1983; Di Nocera, 2013). Metals used for these artefacts consisted of arsenical copper with inlays of silver (Caneva and Palmieri, 1983), dated to the period VI A (3400-3200 BC). The remains of ores, slags, and crucibles are scarce in quantity, and therefore it is uncertain whether smelting operations, perhaps taking place in the crucible, were performed. A wealth of metal artefacts found in the “Royal” Tomb (Frangipane, et al., 2001; Frangipane and Erdal, 2020), made of arsenical copper and copper-silver alloy, signify a geographically wider phenomenon of metal use than previously thought (Palumbi, 2021). This metallurgical development marks the actual beginning of the Early Bronze Age in Eastern Anatolia.

The metallurgical finds of Arslantepe, recovered from a securely dated archaeological stratigraphy, offer a unique opportunity to explore the varieties of the *chaîne opératoire* in individual periods. It is unattainable elsewhere. This as more slags as well as ores found in archaeological context generally receive less attention than typical ceramics or metal artefacts.

This paper will therefore demonstrate how ores can be properly characterised, which criteria can be useful for examining crucibles, and what technical information can be extracted from the waste slags. These are achieved based on precise descriptions of the fabric and texture of ores (Taylor, 2009), their mineral compositions, trace elements, as well as the isotopy e.g. of lead. These strands of evidence can potentially hint at the origins of metal sources. Nonetheless, the provenance of metal requires a deep understanding of ore deposits, especially of their upper part in the gossan zone (Taylor, 2011) which might have been exploited for raw materials. Furthermore, this study can shed new light on the technology, on the earliest slags, their genesis and formation, the composition of charged materials (e.g. the use of fluxes or self-fluxing ores), which remain controversial topics in the archaeometallurgical literature (Hauptmann, et al., 1993; Craddock, 2013; Hauptmann, 2020; Pearce, et al., 2022).

In Old World archaeometallurgy, large smelting sites with thousands of tons of copper slag are well known from Cyprus (Stos-Gale, Maliotis and Gale, 1998), Rio Tinto (Rothenberg and Blanco-Freijeiro, 1981), Eastern Anatolia (Wagner and Öztunalı, 2000), Timna (Rothenberg, 1990), Faynan (Hauptmann 2007; Hauptmann and Löffler, 2013) and many other localities. A great deal of work has been carried out by many scholars who have been investigating the origin, formation, and composition of slags from these sites in order to better comprehend technology, social matters and the extent of early metal production. In most cases these are associated with the Late Bronze and Iron Ages, as well as with the Roman period, recycled in the Islamic periods, and they represent more advanced stages of metallurgy, which Craddock (1995) characterised them as results of “slag-producing smelting processes”.

All over Europe, in the Eastern Mediterranean and beyond, the archaeological record of metallurgical remains, such as slags and technical ceramics, is rather scarce from periods earlier than the Chalcolithic. Therefore, little is known about the incipient stages of extractive metallurgy. It is generally assumed that oxidic ores were first extracted, followed by the smelting of sulfidic ores in the Late Bronze and Iron Ages in more advanced technologies. Despite being a reasonable model, this assumption is vastly oversimplified because from the beginning of the Early Bronze Age at the latest, copper smelting has included sulfides. These may occur in the upper part even of oxidic sedimentary ore deposits such as Faynan or Timna. Native copper occurs frequently even in the gossan of sulfidic ore deposits, depending on the genesis and climatic conditions of geological periods (Smirnov, 1954; Taylor, 2011).

Studies of slags and/or crucibles from the very beginning of ancient metallurgy have sporadically been undertaken. Sometimes the authors show their rather desperate attempts to reconstruct the *metallurgical chain* based on little inclusive evidence. Glumac and Todd (1991) and Ryndina, Indenbaum and Kolosova (1999) analysed materials that were suggested to originate from Eneolithic cultures of the Balkans (6^{th} to 4^{th} millennium

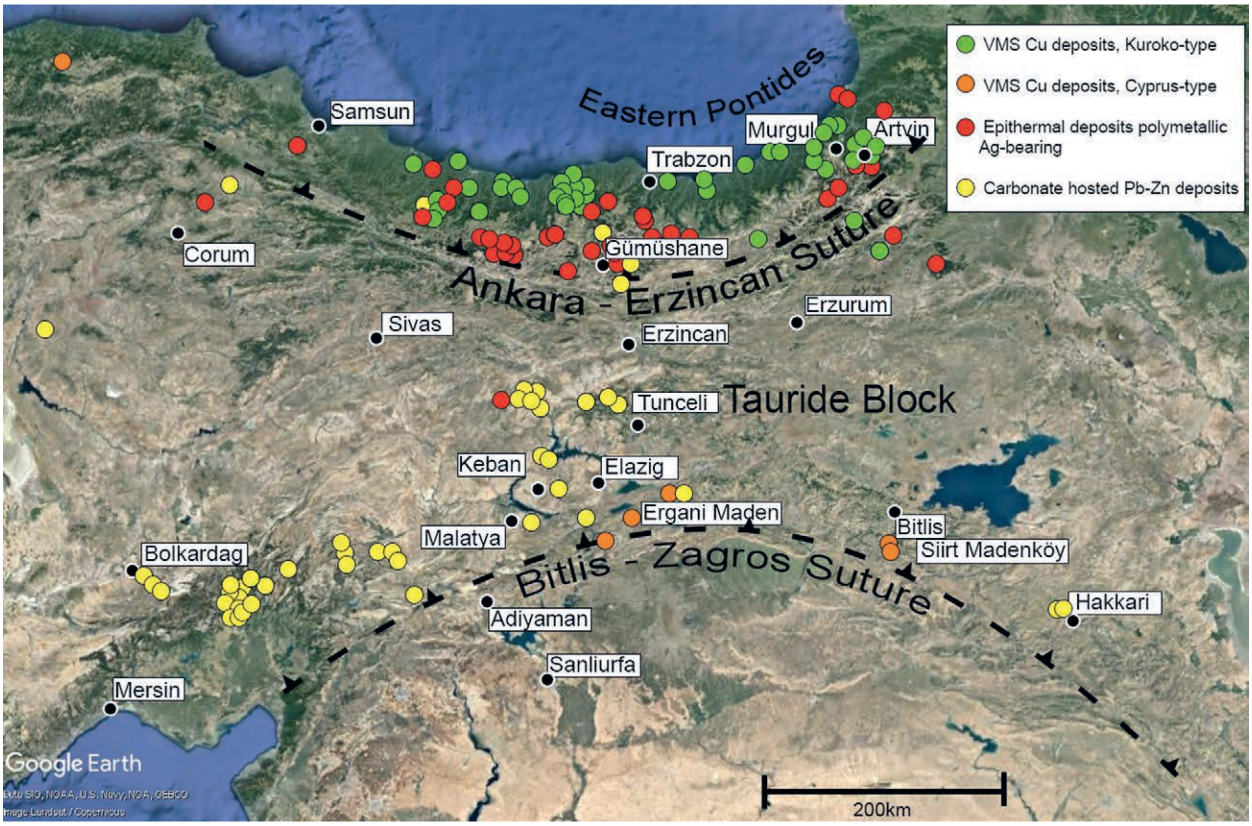


Figure 1. Geological map showing the enormous metal rich region of Eastern Anatolia with the distribution of volcanic massive copper sulfide deposits (Kuroko-type, Cyprus-type), feasibility studies, prospects and epithermal polymetallic ore deposits and carbonate rock hosted lead-zinc deposits. This is the possible archaeological influence area of Arslantepe (Malatya). Also shown are important geological tectonic features. Note the localities of the "giant" copper ore deposits of Ergani Maden and Artvin/Murgul. Modified after Yiğit (2009). This map is also based on data from Lehner and Yener (2014) and Salzmann (2019).

BC). Neuninger, Pittioni and Siegl (1964) investigated some "slag" specimens from Çatal Höyük (6th millennium) and concluded that these were by-products of copper smelting, due to the presence of the phase content (tenorite, cuprite, delafossite, glass and copper). These samples were re-analysed by Radivojević, et al. (2017) who tended to attribute them to a rather accidental heating of green copper ores. Furthermore, slags from Site F2 in the Timna Valley were used by Rothenberg (1973; 1990) and Merkel and Rothenberg (1997) to suggest the beginning of copper smelting in the 6th/5th millennium BC. Nevertheless, the dating of this site was not conclusive (Adams, 1999) and the more recent thermoluminescence dating (Hauptmann and Wagner, 2007) confirmed previously radiocarbon dating by Burleigh and Matthew (1982) of Late Bronze Age. Frame (2012) performed a very thorough analysis of Chalcolithic crucible fragments from Tal-Iblis (mid-6th millennium), Iran. She used different methods and was able to find out interesting details about (s)melting processes.

In Eastern Anatolia and Southern Levant, the more frequent and securely dated slags and crucibles come from the beginning of the Early Bronze Age I and the period a bit later (mid-4th to the beginning of the 3rd millennium BC) (Esin, 1986; Çukur and Kunç, 1989; Hauptmann, et al., 1993; Lutz, Wagner and Pernicka, 1994; Yalçın, 2017; Yalçın, et al., 1992; 2017). It is worth mentioning that in most cases small slag cakes were not located in the close vicinity of mines but were rather found within the settlements. This indicates a particular pattern of early craftsmanship, featuring a domestic mode of metal production (Hauptmann and Weisgerber, 1996).

Overall, we will discuss further compositions of formations of copper ores and slags from the Early Bronze Age II at level VI B2 in Arslantepe. To achieve this, we will present a description of the geological environment and the ore deposits from which raw materials were probably extracted. Special references will be made to two major copper deposits, namely Ergani Maden and Murgul. For a comparison, copper slags of the same period from Çayönü Tepesi and from Nevali Çori will also be examined. Previously, these have only been briefly discussed in Hauptmann, et al. (1993). In addition, the construction and function of crucibles will be discussed.

The geological environment: Ore deposits in Eastern Anatolia

Arslantepe, as well as Çayönü Tepesi, Nevali Çori, Norşuntepe and a number of other prehistoric sites in the Altınova in Eastern Anatolia, are located in a complex geological environment containing the major metallogenic copper-, lead-, zinc-, and silver-deposits in Turkey (Figure 1). These form the east-west orogenic belt of the Tethyans Eurasian Metallogenic Belt (TEMB) between the continental collision of the Eurasian plate in the north and the Arabian plate in the south (Yiğit, 2009; Kuşçu, et al., 2019). In between is the Taurid-Anatolian Platform with Upper Cretacous magmatic rocks and a series of ophiolithic rocks. Subduction, accretion, and collision events associated with the closure of the Tethyan Ocean, between the two plates happened during the Mesozoic period (summarised in Moritz and Baker, 2019 and Uçurum, et al., 2021). In the north, the Eastern Pontides, close to the eastern Black Sea coast, have their continuation in the metalliferous zone of the Transcaucasus. To the south, the metal rich belt is limited by the Bitlis-Zagros-Suture Zone, which marks a geographic borderline to the alluvial lowlands of Upper Mesopotamia – free of metallic raw sources.

The provenance research of ores excavated in archaeological contexts requires knowledge of the geological-geochemical environment and the mineralogical (infra-) structure of the ore deposits in question.

Volcanogenic massive sulfide deposits

Numerous volcanogenic massive sulfide deposits (VMS) were formed at the north-eastern (Ankara-Erzincan Suture) as well as at the southern tectonic belt (Bitlis-Zagros Suture; Yazar, et al., 2015). In the north, e.g. the actively mined ore district of Artvin-Murgul is located. In the south, among others, the Ergani Maden and Siirt-Madenköy deposits are located (Akıncı, 2009). These ore deposits count among the larger metallogenic provinces in Turkey. According to their genesis, the polymetallic VMS deposits are divided into two categories (Yiğit, 2009). Firstly, in the Kuroko-type deposits in the north copper ores are embedded in siliceous pumiceous dacitic tuffs (Kraeff, 1963; Çağatay, 1993). They are spread over Southern Georgia (Transcaucasia, e.g. the Madneuli in the Bolnisi district, Migineishvili, 2005) and Northern Armenia as far as to Anatolia, Bulgaria and Romania. They are associated with Late Cretaceous volcanic rocks (Çiftçi, 2019). The Cyprus-type VMS at the Bitlis-Zagros Suture is associated with mafic ophiolitic rocks (basalts, andesites, diabases, pillow lavas) and with (calcareous) sandstones and shales of the Early to Middle Eocene. In modern terms, these ore deposits are often called copper-gold deposits with pyrite and chalcopyrite as main ore minerals. However, it remains a difficult question whether gold, being a very rare metal, was exploited in prehistory (Stöllner, 2021).

The Heidelberg-Mainz team of Seeliger, et al. (1985), Wagner, et al. (1986; 1989), Wagner and Öztunalı (2000) and the Italian-Turkish team of Palmieri, Sertok and Chernykh (1993) investigated numerous sites showing evidence of ancient metal production in the East and in Northern Anatolia and beyond. Almost all these sites visited by these scholars, perhaps except the ore districts of Artvin-Murgul in the north and Ergani Maden in the south, due to its enormous dimension, have been of mean dimension until recently. In geological terms they were "giants". These ore districts were originally largely exposed to the surface. Mainly at Ergani Maden, due to their mineral contents, extensive, striking gossans of reddish red brown to orange or green colour developed. These parts of the ore deposits have been suggested to have been exploited in prehistoric times.

The north-eastern part of copper deposits with the ore district in the Artvin-Murgul region (Kraeff, 1963) is c. 600 km away from Arslantepe. The most extensive finds and findings as evidence of prehistoric mining and metallurgy come from Murgul itself (Wagner, et al., 1989; Lutz, 1990). Murgul itself consists essentially of two large ore bodies, Anayatak and Çakmakkaya (widths of each 700 by 500-600 m, depths 80 and 150 m). In addition, some smaller ore bodies are known. The mineralisation at Murgul occurs in stockwork veins within Upper Cretaceous intensively silicified and chloritised rocks. It contains predominantly pyrite and chalcopyrite (the ideal chemical composition of all minerals and phases mentioned in this study are compiled in Table 1). Today, minor quantities of galena, sphalerite and fahlore (tetraedrite-tennantite series) occur only locally (Schneider, Özgür and Palacios, 1988).

Table 1. The chemical compositions of minerals and phases mentioned in the text. Given are the ideal chemical compositions as published in Klockmanns Lehrbuch der Mineralogie (ed. Ramdohr and Strunz, 1978). Slag phases are also described by Hauptmann (2020).

Anglesite	$PbSO_4$
Argentite	Ag_2S
Atacamite	$Cu_2Cl(OH)_3$
Azurite	$Cu_3([OH\|CO_3]_2$
Barite	$BaSO_4$

Bassanite	$CaSO_4 \cdot ½H_2O$
Beudantite	$PbFe_3^{3+}[(OH)_6\|SO_4\|AsO_4)]$
Bieberite	$CoSO_4 \cdot 7H_2O$
Bornite	Cu_5FeS_4
Bravoite	$(Ni,Fe,Co)S_2$
Brochantite	$Cu_4[(OH)_6\|SO_4]$
Cattierite	CoS_2
Cerussite	$PbCO_3$
Chalcanthite	$CuSO_4 \cdot 5H_2O$
Chalcocite	Cu_2S
Chalcopyrite	Cu_2FeS_4
Chlorite (simplified)	$(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$
Chromite	$(Fe,Mg)Cr_2O_4$
Chrysocolla	$CuSiO_3$ + aq
Cobaltite	CoAsS
Covellite	CuS
Cuprite	Cu_2O
Cuprospinel	$CuFe_2O_4$
Delafossite	$Cu^+Fe^{3+}O_2$
Electrum	AuAg
Ettringite	$Ca_6Al_2[OH)_4\| SO_4]_3{\cdot}24H_2O$
Fayalite	Fe_2SiO_4
Ferrifayalite	$(Fe^{2+}\|Fe^{3+})_2SiO_4$
Freibergite	$Ag_6(Cu_4Fe_2)Sb_4S_{13-x}$
Galenite	PbS
Goethite	α-FeOOH
Gypsum	$CaSO_4 \cdot 2H_2O$
Hedenbergite	$CaFe[Si_2O_6]$
Hematite	Fe_2O_3
Hydrozincite	$Zn_5[(OH)_3\|CO_3]_2$
Iscorite	$Fe^{2+}{}_5Fe^{3+}{}_2SiO_{10}$
Jarosite	$K,Fe_3[(OH)_6{\cdot}\|SO_4]_2$
Jasper	SiO_2
Kaolinite	$Al_4[(OH)_8\|Si_4O_{10}]$
Laihunite	$Fe^{2+}Fe_2{}^{3+}(SiO_4)_2$
Limonite	FeO(OH) + aq
Mackinawite	$(Fe,Ni)_9S_8$
Maghemite	γ-Fe_2O_3
Magnetite	Fe_3O_4
Malachite	$Cu_2[(OH)_2\|CO_3]$
Marcasite	FeS_2
Palygorskite	$(Mg,Al)_2[OH\| Si_4O_{10}]{\cdot}4H_2O$
Pentlandite	$(Ni,Fe)_9S_8$
Pyrite	FeS_2
Pyrrhotite	FeS
Quartz	SiO_2
Smithsonite	$Zn(CO_3)$
Sphalerite	ZnS
Tennantite	$Cu_3AsS_{3.25}$
Tetraedrite	$Cu_3SbS_{3.25}$
Valleriite	≈ $Cu_3Fe_4S_7$ with Mg, Al-contents
Wuestite	FeO

Ergani Maden is only c. 130 km south-east from Arslantepe, and there is a great possibility that copper ores mined there were transported to this and to other sites in the Upper Euphrates region in the 4th/3rd millennium BC. But this has not been proven with certainty. Nevali Çori is about 140 km away, and Norşuntepe just 70 km. Çayönü Tepesi is the closest site to this ore deposit, being only approximately 7 km away from the outcrops. Considered in a supra-regional geographic context, Ergani Maden, located very close to the river Tigris, is a convenient location on an ancient trading route between the central part of Anatolia and Northern Mesopotamia. Hence, it is located within a region where very old craftsmanship of copper production and metal processing developed.

Here we will not consider trade activities from copper ore deposits further away, e.g. from south-west Arabia (Oman), which served as an enormous raw material supplier to Mesopotamia in the 3rd millennium BC (Begemann, et al., 2010). The transport of raw materials in the form of ores or rather metal from the Gulf or from Iran has already been discussed by Özbal, Adriaens and Earl (1999).

One of the biggest single ore bodies in the Ergani Maden district is called Anayatak. It is located near the village of Maden. Furthermore, there are mineralisations at Mihrap Daği and Kişabekir (the Weiss pit). Nowadays, Anayatak has been exploited in an open pit mine with a dimension of 1 x 0.5 km. The ore body itself has an extent of 550 x 300 x 50 m. According to Griffitts, Albers and Öner (1972); Akıncı (2009) and Bamba (1976), considerable masses of pyrite and related Fe(Ni)-sulfides constitute major parts of the ore body. Large veins and finely distributed chalcopyrite are intergrown with these sulfides. Of minor quantities are sphalerite, magnetite, native copper, bornite, and valleriite. The reality of ore petrology shows that sulfides such as pyrite, marcasite and chalcopyrite may contain arsenic, cobalt and nickel which have only been rarely mentioned in the geological literature. Pyrite may form exsolution lamellae of pentlandite or bravoite (which may cause minor concentrations of nickel in the resulting copper) or cobalt as cobaltite. The sulfide assemblage of pyrite/pyrrhotite-pentlandite-mackinawite-chalcopyrite with trace quantities of gersdorffite or valeriite is a typical feature of ore deposits in (ultra-)mafic rocks (Stanton, 1972). The ore body is embedded in slightly chloritised volcanic rocks and belongs to the immediate geological context of serpentinite.

Modern mining activities have largely destroyed the remains of ancient ore exploitation. Nevertheless, in a summary Wagner, et al. (1989) suggested that Ergani

Maden was one of the most important prehistoric copper sources in Anatolia. The reason for this suggestion was certainly the unique dimension of the gossan, originally cropping out for 750 m in east - southeast direction (Romieux, 1941). In ancient times it was probably much larger than the relics left today. Modern drill holes have shown that the gossan reached a thickness of at least 25 m (Griffitts, Albers and Öner, 1972). These data show that it counts among the most extensive gossans not only in Eastern Turkey. The authors described that it consists largely of black to yellow-brown and rather porous limonite, jarosite and limonite-cemented breccia with altered (chloritised) host rock. This material covers much of the mountainside between the Anayatak pit and the Tigris river. Other, similarly extended, gossans in the Old World have been described only from Rio Tinto (Salkield, 1987), Cyprus (Parvaz, 2014), Lasail and Aarja in the Sultanate of Oman (Hauptmann, 1985). Due to geological and climatic factors, surface near mineralisations at Artvin and Murgul are less pronounced.

Malachite, chalcanthite, azurite, and other Co-bearing secondary copper minerals (cattierite, bieberite; Griffitts, Albers and Öner, 1972) are further minerals in the gossan of Ergani Maden, which today are distributed in trace amounts only. They probably occurred in much larger quantities in ancient times, often forming massive chunks. Veins of opaline silica in the ore body or siliceous jasperoidal alteration in the gossan are the result of the weathering of silicates in the host rock. Relics of sulfidic ores such as pyrite, pyrrhotite, chalcopyrite, bornite and chalcocite are further minerals in the gossan. Of particular importance is the occurrence of native copper in the near-surface parts of the Anayatak and the Mihrap Dağ (Weiss-deposit) deposits. At Anayatak, green secondary copper ores and native copper have been used in the Pre-Pottery Neolithic, as early as the 8th millennium BC (Özdoğan and Özdoğan, 1999), to make beads. At Murgul, according to current knowledge, copper was smelted as early as the Chalcolithic period (Lutz, Wagner and Pernicka, 1994; Wagner, et al., 1989). As the potential of using trace elements for provenancing copper is rather limited, we will focus next to conduct isotope analyses on mineralogical and ore deposit issues.

Obviously, the supergene enriched part of ore bodies below the gossan was entered by ancient miners as well. Minerals found there were copper-rich sulfides (chalcocite, bornite, covellite). Next to the major components, iron, sulfur, copper, minor and trace elements, relevant for archaeometallurgy are chromium, cobalt, and nickel. Arsenic, lead, and silver contents are very low. Apart from siliceous gangues, the sulfur-containing barite should be mentioned. Çağatay (1993) and Bamba (1974) reported chromite in the ore body of Anayatak but particularly rich occurrences in the sheeted dike complex of the Weiss copper deposit.

Carbonate rock hosted lead-zinc deposits

South and Southeast Turkey possesses many (partly argentiferous) lead-zinc deposits hosted by Devon/Upper Perm/Late Triassic to Jurassic carbonates (Hanilçi, Öztürk and Kasapçı, 2019). Geographically they are located in between the northern and southern belt of copper deposits shown in Figure 1. They are partly in closest neighbourhood to the settlements of Arslantepe and around (Yiğit, 2009). They include Mississippi valley type (MVT), sedimentary-exhalative type (SEDEX), and carbonate-replacement type (CRD) deposits. Many of these lead-zinc-deposits are epigenetic mineralisations. As discussed by Heil, et al. (2022), they were exploited since the Chalcolithic period of Arslantepe VII and were smelted inside the settlement.

MVT deposits are associated with karstic phenomena. Lead isotope ratios show large variations (see below). The Bolkardağ and the Malatya districts (Cafana) have carbonate replacement type deposits which are partly high in gold. Keban contains skarn deposits and replacement mineralisations.

Though many of these lead-zinc deposits contain only small reserves of resources (Yahyalı and Tufanbeyli, Aladağ), the main important feature of several of the deposits is that they possess non-sulfide (oxidic) lead and zinc ores (smithsonite, hydrozincite, cerussite, anglesite, minor amounts of sphalerite, galena, plumbojarosite and beudantite). They are low in copper. But the latter two minerals may contain silver. Argentiferous plumbojarosite is a common mineral at Bolkardag, and argentite, electrum, native silver and freibergite were also found in this deposit (Temur, 1991). It remains an open problem which significance these silver minerals had for the prehistoric production of silver in the 4th millennium BC in Southern Anatolia.

Epithermal polymetallic deposits

In Figure 1 a number of this type of epithermal polymetallic modern prospects or feasibility studies, and, in a few cases, ore deposits are shown (Yiğit, 2009). They are mentioned in this paper because there are usually not only gold- but also silver-bearing mineralisations

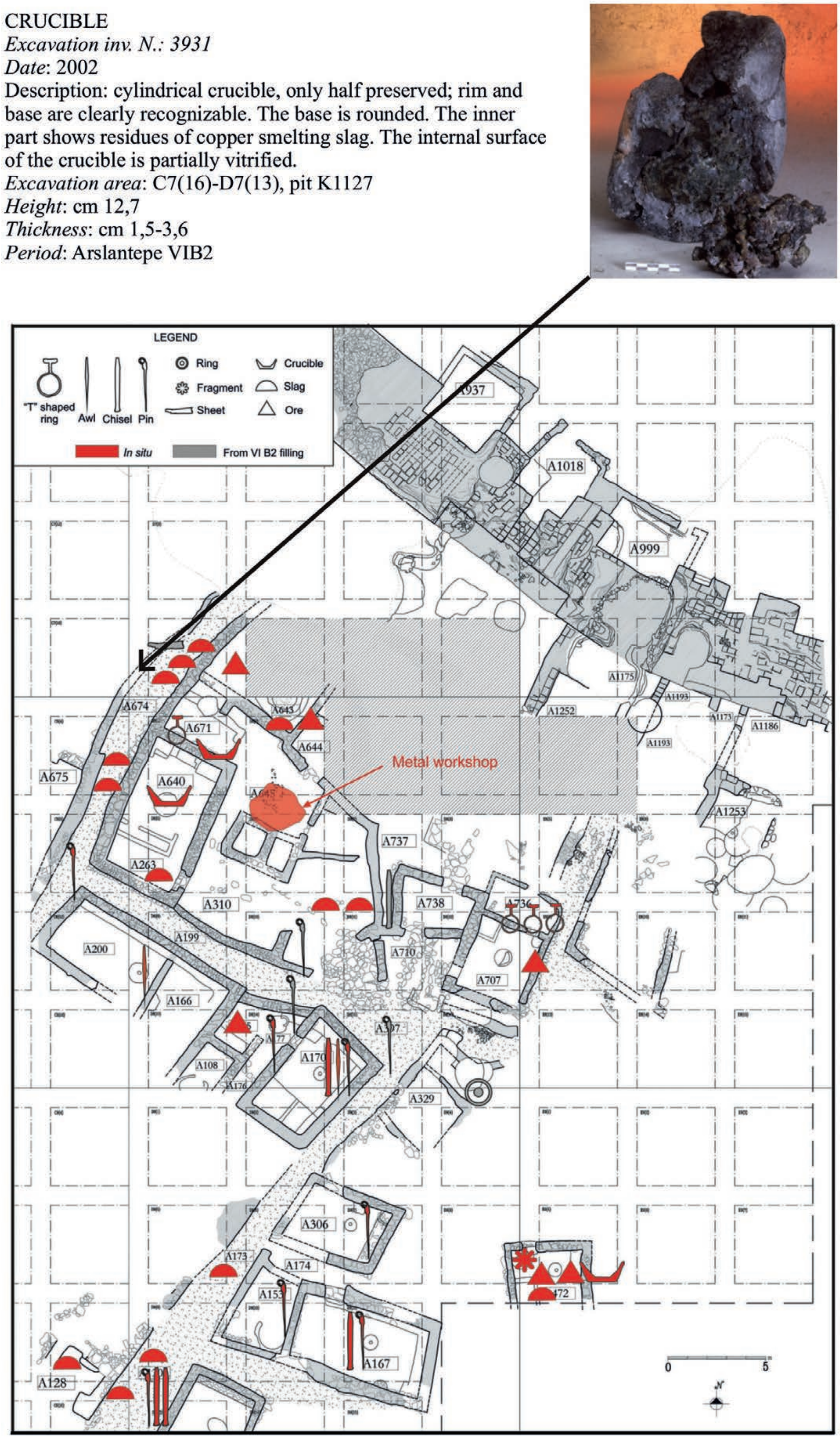


Figure 2. Low resolution map of the VI B2 village of Arslantepe, showing the distribution of metallurgical objects, crucibles, slag, and ores. The large red spot indicates a workshop where crucible and slag fragments were found scattered on the floor. The red coloured fire pit was probably the place where the smelting was carried out. Close to it there was a bench where small ore fragments and several big stone pestles were found (see Figure 3), which were probably used to crush ores and slags. Especially indicated is the crucible from excavation at C7(16)-D7(13), pit K1127xxx (Inv. N.: 3931). From Di Nocera (2013).

Figure 3. Arslantepe VI B2, A671.
Field evidence from metallurgical chain: hammer stones (pestles) and anvil stones, crucible fragments, slags and crumbly small fragments of ores found in a workshop. The suite of these finds is evidence that imported ore was processed in the village by beneficiation and finally smelted into metal (Palmieri, Sertok and Chernykh, 1993; Frangipane and Palmieri, 1994-1995). In addition, the crushing of copper- and/or matte-containing slag is also evidenced. This was found in the archaeological context too. Photo: R. Ceccacci, by proxy Missione Archeologica Italiana nell'Anatolia Orientale (MAIAO), Sapienza University of Rome.

(Au-Ag-Hg-As-Sb). They may contain chalcopyrite, pyrite, sphalerite, and galenite in quartz veins and/or stockwork zones hosted by upper Cretaceous rhyolites and dacites.

The archaeometallurgical finds from Arslantepe VI B2

Some special features

Here the period around the Early Bronze Age I (level VI B2; c. 3100-2800 BC) will be in focus. A complete set of archaeometallurgical finds, including ores, slags, crucibles, moulds and metal artefacts dating to this period was found. These finds show that a drastic change in metallurgy took place compared to previous periods. This may also be underlined by 75 metal artefacts found in the "Royal Tomb", probably dated to the beginning of VI B2 (Frangipane and Erdal, 2020). Chemical analyses (Hauptmann, et al., 2002) revealed that several kinds of copper based alloys were used: copper low in arsenic (1- <4 wt.% As), objects made of nickel-bearing arsenical copper (< 1–3 wt.% As, < 1–2 wt.% Ni), and silver and silver-copper alloys (c. 20–60 wt.% Ag). Silver, as an especially "noble" alloy, was already used at Arslantepe in earlier times (levels VII and VIA). The formation of copper-silver alloys and the problem of patination was not solved satisfyingly in this context.

Palmieri, Sertok and Chernykh (1993) have already observed that metallurgical remains and residues are widely spread at Arslantepe VI B2. They are evidence that imported ore was processed and subsequently smelted and shaped at workshops within the settlement (Figure 2), apparently indicating the existence of groups of specialised metallurgists. The domestic mode production was a widespread pattern at the beginning of extractive metallurgy in the Old World. In Eastern Anatolia it has been documented at Arslantepe, Norșuntepe, Nevali Çori (Hauptmann, et al., 1993; Hauptmann, 2007) and at Faynan, Tell Magass, Tell Hujayrat, al-Ghuzlan, and Tell Abu Matar in the Southern Levant (Bourgarit, 2007). On the lberian Peninsula, remains of early metallurgy were found in settlements such as Zambujal, Los Millares, Almizaraque, and others (Gauß, 2016).

A metallurgical workshop (A645/A343) was excavated at Arslantepe VI B2 (Frangipane, 1992; 1993). It is an open kind of courtyard, whose northern part was used for metallurgical activities, and the southern part was used to slaughter domestic animals (like a butchering activity area). Two pits located there show traces of fire. One of the two was also filled with ash and a crucible fragment, it can be seen as a relic of (s)melting. Otherwise, pieces of ores, crucible fragments, slags and hammer stones (Figure 3) indicate the processing not only of ores but also of slag as well. In contrast, slags found in the immediate vicinity and as a packing layer in the roads around indicate smelting operations within the settlement. Metallurgy, and not just processing, was an important part of the village economy at the beginning of the 3rd millennium (Frangipane, 1992). At Arslantepe in the Early Bronze Age IB a spatial distinction was made between domestic and craft activities. Only a little later, in the Early Bronze Age III (period VI D), numerous small crucibles for casting metal and casting moulds indicate more widespread metal processing (Palmieri, 1973). Slag finds appear only sporadically.

The crucibles

At Arslantepe VI B2, mostly in close context with the slags and ore remains, numerous cm^2-sized fragments of slightly curved crucibles were recovered. The crucibles were made of cm-thick ceramic material and covered on the inside by about 0.5-1 cm thick slag incrustations that could not have been caused just by heating up the ceramic material. Such fragments could only be assembled into a larger model of a crucible in one case, so that its shape and design could be clearly recognised and made it possible to reconstruct the sub-cylindrical, beaker-shape of the crucible (Figure 4a). It was roughly described by Palmieri and Morbidelli (2003) and Di Nocera, Hauptmann and Palmieri (2004). The crucible had a height of about 22 cm, an outer diameter of 13-16 cm and an inner diameter of c. 10-13 cm, i.e. they reached a surprising dimension for a crucible known from this period. The slag incrustation was particularly pronounced in the inside. The upper part of the crucible wall was very slightly reddish in colour, while the lower part was more clearly greyish. These colour differences are based on different redox conditions during the smelting process, i.e. on the effect of changing CO/CO_2 ratios on the Fe-oxides contained in the ceramic: red colour is caused by a rather strong oxidation e.g. to hematite, a grey colour is due to a relatively strong reduction e.g. to magnetite.

Figure 4a. Arslantepe, level VI B2, C7(16)-D7(13), pit K1127, Excavation inv. no.: 3931. Reconstruction of a sub-cylindrical smelting crucible. Note the incrustation of slag in the upper part inside the crucible. Slag fragments and cakes arranged around the crucible have been found in the immediate archaeological context. Their sizes and dimensions are suitable for the formation of a smelting process in the crucible. Photo: R. Ceccacci, by proxy Missione Archeologica Italiana nell'Anatolia Orientale (MAIAO), Sapienza University of Rome.

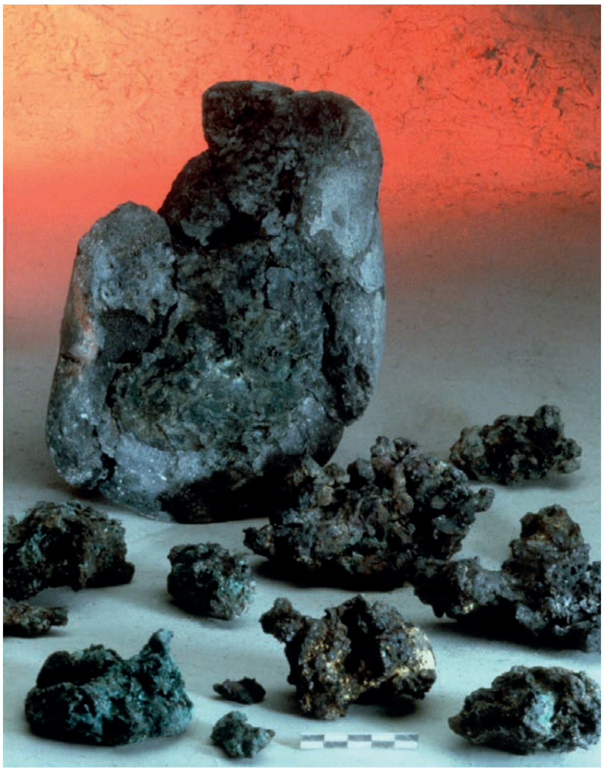


Figure 4b. The same crucible, here at an exhibition of the Archaeological Museum in Malatya. Note the round hole in the lower part of the vessel (red circle), most probably used for air supply during the smelting process. Photo: A. Hauptmann, Deutsches Bergbau-Museum Bochum.

One side of the crucible is broken, it is widely opened. On the backside, in the lower part, there is a roundish hole with a diameter of 2-3 cm (Figure 4b). It seems possible that in this part of the crucible, where the produced material was taken off after firing, one or two air inlet holes were perforated. A construction of metallurgical reaction vessels with an air inlet system of two holes in the lower part was known at Arslantepe as early as the Chalcolithic period (Arslantepe VII; Frangipane, et al., 2019). Examples are ceramic roundish pots with a diameter of 20 cm found in A1415 1aR,i,20/15. The air holes (ø c. 2.5-3 cm) are just slightly vitrified (Hauptmann, et al., in prep). Constructions like that are rare. Of a similar construction is only one beaker crucible from Ikiztepe. A picture in Bilgi, et al. (2004) shows at least one air hole in the lower part of this vessel. However, the crucible is dated to a younger period than Arslantepe VI B2, to the 23rd century BC. Unfortunately, there is no further detail known of this particular construction.

We suggest, based on practical terms that the crucible from Arslantepe VI B2 was supplied with air by using either blowpipes or, alternatively, tuyères from below in a way similar to all the basic constructions of smelting furnaces from later periods. The charging of ore and small pieces of charcoal was done from above, air was supplied from below. As shown by the experimental work of Laschimke and Burger (2020), in order to produce liquid copper and slag, i.e. to reach ca. 1100 °C, the contact just with the glowing charcoal was not sufficient. The material must have come into close contact with the distinctly hot flames produced by the combustion of gases (CO/CO_2). This was more efficiently organised by an ascending stream of gases than by heating up a jar-like crucible from above.

Palmieri, Sertok and Chernykh (1993) retraced this type of heating experimentally in a simple fireplace. They produced slags similar to those from the archaeological context which indicates that the separation of metal from slag was by no means complete. About a third of the crucible was broken. It is very likely that it was broken up immediately after finishing the smelting process in order to remove the products. This is probably the main reason why crucibles of this shape are rarely preserved in their archaeological context, similar to the remnants of smelting furnaces.

Arslantepe VI B2 crucibles (and slags) show similarities to finds from several other Early Bronze Age I locations, such as Çayönü Tepesi or Nevali Çori (Hauptmann, et al., 1993; Müller-Karpe, 1994, p.127). This supports the similarities of many metal objects from these localities described by Di Nocera (2013). The two sites are located on the middle Euphrates, c. 90 km south-east of Arslantepe. Both have an early Neolithic past.

The ores

A limited number of small ore pieces were found together with big stone pestles on a bench close to the fire pit in the courtyard of the VI B2 village, where metallurgical activities took place (Frangipane and Palmieri, 1994-95; A 671; see Fig.2), and in the fillings of the occupation layer (A472c.300). In parts they were chemically and mineralogically analysed by Palmieri, et al. (1999) and Hess (1998). Predominantly they consist of a variety of secondary minerals intergrown with relics of Cu-Fe-sulfides. Even if these "hand-sized" samples have to be seen just as small sections which will hardly provide information on the macro-texture of an ore deposit, they are characteristic for oxidation zones of sulfidic iron-copper deposits. As a special stable accessory the authors identified chromite as a typical component of (ultra-) basic rocks in ophiolites.

In this study we analysed and re-analysed copper ores and slags we collected from the archive of the Dipartimento Scienze Storica Archeologica Antropologica Antichità at the Sapienza Universià, Rome, from the archive of Karsten Hess at Deutsches Bergbau-Museum, and from the archive of the University of Pennsylvania Museum for Archaeology and Anthropology, Philadelphia (received from the late Dr. Tamara Stech). These are: 8 copper ores from Arslantepe VI B2. For a comparison, we analysed four ores from Ergani Maden and one copper ore from Çayönü Tepesi. In addition, two copper slags from VI B2 and Çayönü Tepesi were analysed. We conducted bulk chemical analyses with ICP-AES, the lead isotope analyses with MC-ICP-MS. Details of all these samples are compiled in Tables 2 and 3.

Three samples are described in more detail for their mineralogical composition and texture.

- Fine grained soft earthy iron ore (earthy gossan) of ochreous colour (Table 2, 5304-20; Figure 5a). It shows a cellular sponge boxwork which is formed by the decomposition of pyrite due to weathering. It is a characteristic feature of material from a gossan. According to the "limonitic colour chart" published by Taylor (2011), the striking yellow-orange colour is also typical for this. Mineralogically it consists primarily of quartz, limonite (goethite), jarosite, gypsum, bassanite, and ettringite. The latter two minerals are created by heating gypsum, which leads to dehydration and reaction with the environment. They are

Table 2. Chemical bulk analyses of some copper ores from Arslantepe, layer VI B2, from Çayönü Tepesi, and from Ergani Maden. In addition, one slag cake from Arslantepe low in copper, and an extremely copper rich small fragment of a slag from Çayönü Tepesi are listed. Values given from SiO_2 to Cu in wt.%, and from As to Cr mostly in parts per million (ppm). Abbreviations: n.a. = not analysed.

Lab-no. DBM	Hess-no. 1998	Locality	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	BaO	ZnO	K_2O	Na_2O	P_2O_5	S	Cu	As	Sb	Bi	Co	Ni	Pb	Ag	Sn	Cr
Cu-, Fe-ores																									
5304_20	no nr.	Arslantepe VIB2, A472/300/87	31.7	0.021	0.90	40.2	0.008	0.12	4.46	0.001	0.003	1.92	0.21	0.05	5.52	1.57	40	<15	1.9	15	20	15	6.5	6.3	190
5305_20	no nr.	Arslantepe VIB2, A472/300/87	26.4	0.203	4.81	3.05	0.03	2.45	0.78	0.01	0.03	1.27	0.23	0.25	2.08	38.1	45	<15	<1	155	220	13	2.4	1.7	270
5308_20	no nr.	Cayönü Tepesi, CT86-19 green	10.5	0.154	1.71	1.33	0.002	0.23	0.13	0.008	0.07	0.44	0.03	0.04	0.52	57.1	20	<15	<1	<0.5	80	25	570	1.5	110
No ID	TR-8/82	Arslantepe VIB2, D8(14) A177aR2c.9	n.a.	n.a.	n.a.	22.40	n.a.	n.a.	n.a.	n.a.	0.03	n.a.	n.a.	n.a.	n.a.	7.9	<10	30	<10	50	<5	600	10	90.0	n.a.
5179-21	TR-18/1	Ergani Maden, Anayatak	5.1	0.04	1.85	25.1	0.04	0.31	0.02	0.020	0.199	0.01	0.18	2.40	0.30	29.6	340	1990	2860	500	210	1000	200	360	250
5180-21	TR-18/2	Ergani Maden, Anayatak	0.31	0.26	0.34	1.72	0.004	0.31	0.01	0.001	0.23	0.01	0.02	3.20	14.50	43.50	580	2240	3730	200	90	1200	130	330	120
5181-21	TR-18/4	Ergani Maden, Anayatak	25.8	0.53	0.71	33.9	0.02	0.02	0.01	0.006	0.007	0.09	0.001	0.70	0.30	8.0	820	1090	1190	200	200	500	120	260	200
5182-21	TR-8/36	Arslantepe VIB2, D8(10)13/02,c.205	3.38	0.02	0.15	63.1	0.03	0.11	0.43	0.03	0.03	5.15	0.09	0.84	11.8	0.1	850	10	11	100	<5	110	<2	<3	10
5183-21	TR-8/118	Arslantepe VIB2, A472/300 /87	9.7	0.02	1.21	29.83	0.03	0.03	5.40	0.001	0.006	2.98	0.19	0.05	7.49	1.4	50	60	70	80	460	2.01%	10	10	178
5184-21	TR-8/34	Arslantepe VIB2, E8(9) A707OM2FR,c.220	9.69	0.21	0.93	42.3	0.03	0.14	4.37	0.04	0.006	6.98	0.23	0.51	14.10	0.0	60	3	15	<2	20	<7	<2	<3	210
5185-21	TR-8/33	Arslantepe VIB2, D8(9)13b2c.203	2.87	0.03	0.15	53.6	0.04	0.06	0.44	0.04	0.05	0.12	0.05	0.62	44	1.8	760	26	20	150	<5	250	4	<3	40
5186-21	TR-8/30	Arslantepe VIB2, E8(13) A666RP1c.213	45.8	0.87	17	4.45	0.37	4.58	6.25	0.03	0.46	1.99	1.71	0.39	0.15	5.97	<5	2	<5	30	40	6	2	<3	90
5187-21	TR-18/4a	Ergani Maden, Anayatak	64.1	0.86	0.44	8.3	0.04	0.08	0.19	0.02	0.03	0.02	0.08	0.09	0.35	13.5	14	23	5	30	180	<7	<2	<3	140
Cu-slags																									
5307_20	no nr.	Arslantepe VIB2, 24/25-9-98 b	45.1	0.132	4.67	35.7	0.04	1.91	3.60	0.004	0.02	0.23	0.11	0.12	1.56	2.58	11	<15	<1	90	40	7.2	6.3	2.9	290
No ID	TR-8/89	Arslantepe VIB2, E8(9)K1004.3c18	40.2	0.11	5.00	43.8	0.04	1.31	4.96	0.007	0.03	0.56	0.34	0.32	2.16	4.27	530	840	720	290	300	700	135	<50	270
5309_20	no nr.	Cayönü Tepesi, CT78-green	10.7	0.018	0.39	2.503	0.031	0.021	0.109	0.002	0.389	0.072	0.0331	0.084	0.05	58.4	30	<15	<1	290	460	60	45	1.21	60

rare in nature, but they may occur in the context of a gossanous environment. They also occur as synthetic phases (firing gypsum, cement industry). This sample has almost 32 wt.% SiO_2, the iron-oxide content is 42 wt.%, sulfur is 5.5 wt.%. Parvaz (2014) found identical earthy gossan samples at Kokkinopezuola on Cyprus. This sample is not a pure copper ore. It contains < 2 wt.%.

- Very fine grained blue-green coloured pieces of copper ore (Table 2, 5305; Cu = 38 wt.%), brittle, up to c. 1 kg. Copper minerals are brochantite, atacamite and malachite. It has a porous and spongy texture of fine mineral components (quartz, palygorskite, kaolinite) and suggests a texture of a silicified pumiceous dacitic tuff ("siliceous sinter"; SiO_2 = 26.4 wt.%). This sample is a rich copper ore. Identifiable by naked eye are nodules of chrysocolla indicative of a formation in a nearly neutral to alkaline environment (low pyrite available). The pieces are very low in iron (c. 3 wt.%) and also low in nickel and arsenic. (cf. Figure 5b).
- Of special interest is a few cm-spheroidal piece of ore showing a pronounced green-brown zoning (Table 2, 5183; Figures 5c and d). It was found in room A472 (Frangipane and Palmieri, 1994-1995) and was analysed by Hess (1998) and Palmieri, et al. (1999). The core consists of brown quartz-bearing limonite. Its iron-content is 66 wt.%, sulfur is low (< 1 wt.%). The green incrustation is made of quartz-bearing secondary copper ores (brochantite, atacamite, malachite). This zoning is caused by the formation of secondary oxides and hydroxides from mixed sulfidic CuFe-ores due to the following chemical reactions:

Pyrite, pyrrhotite:
$$2FeS_2(s) + 15O_2 + 14H_2O(aq) \rightarrow 2Fe(OH)_3(s) + 8H_2SO_4(aq)$$

Chalcopyrite:
$$4CuFeS_2(s) + 17O_2 + 10H_2O(aq) \rightarrow 4Fe(OH)_3(s) + 4CuSO_4(s) + 4H_2SO_4(aq)$$

These equations mean that sulfidic ores (pyrite, chalcopyrite; solid = s) from an ore deposit break down to sulfuric acid (H_2SO_4; aqueous = aq) and limonite (solid = s). Limonite is insoluble in water and remains in the core. Copper is dissolved by the sulfuric acid. The core is "leached" and the copper ions are transported to the outside where again they precipitate as oxidics. It depends on the chemical composition of the archaeo-sediments or hard-rock environment if these oxides are copper carbonates, sulfates or chlorides.

It is an open problem where and when the latter chemical reactions took place. Geologically, ores of all the compositions and textures mentioned are typical of a weathering process in gossan environments of VMS deposits such as Ergani Maden, where iron- and copper-iron-sulfides decomposed in the course of centuries and millennia. Weathering processes of sulfidic ores may also occur even within decades in a sedimentary soil-environment, so in the archaeo-sediments of Arslantepe during 5000 years. This means that we have to consider that at least parts of the original copper ores excavated were transported in sulfidic composition from the sources to the Early Bronze Age sites in Anatolia.

Numerous small ore fragments were found together with big stone pestles on the bench close to the fire pit in the courtyard of the VI B2 village, where metallurgical activities took place (Figure 3). This shows that apart from slags also ores were crushed at Arslantepe to extract copper.

Çayönü Tepesi

Çayönü Tepesi is a most prominent settlement of early Pre-Pottery Neolithic B (PPNB), i.e. 9^{th}-8^{th} millennium BC (Grill Building sub-phase). It is, however, also a habitation site of younger periods. Late Chalcolithic and Early Bronze Age I/II levels (Çambel and Braidwood, 1980) are present too, even if these are heavily eroded.

At the PPNB levels Özdoğan and Özdoğan (1999) found 545 beads and another 3670 unworked pieces of green secondary copper minerals, mostly described as malachite. Because of the immediate geographical proximity of Çayönü Tepesi to the vast copper ore deposits of Ergani Maden, the origin of these ores from the outcrop of this ore deposit seemed to be given. It is also given by lead isotope measurements of one copper ore and a sample of a slag from Çayönü Tepesi (see below).

The earliest pyrotechnological knowledge of making metal artefacts at Çayönü Tepesi dates to the second half of the 8^{th} millennium BC. It was focussed on manufacturing tiny artefacts such as beads and awls from native copper by cold working and annealing at temperatures of not more than c. 500 °C (Maddin, Muhly, and Stech, 1999).

Exciting and exotic discoveries among the copper ores and the metal finds from Çayönü Tepesi were a few specimens of copper slags from the beginning of Early Bronze Age I. Altogether, not more than four slag cakes with diameters between 5-8 cm and a weight of 70-140 g were picked up along with some nut-sized fragments of slags (Özdoğan, 1990, oral communication).

Radiocarbon-dating of a charcoal inclusion in the slag produced an age range of 3095-2710 BC (Hauptmann, 2003).

Due to the rather puzzling archaeological circumstances under which the slags were found, it is not clear whether they indicate an extraordinary smelting activity at the site or if they are remnants of a small-scale "domestic mode production" or "cottage-industry", as it was practised in the entire area of the upper Euphrates-Tigris region during the Late Chalcolithic/Early Bronze Age I (Yalçın, et al., 1992; Palmieri, Sertok and Chernykh, 1993) or in the Levant (Hauptmann, et al., 1993; Adams and Genz, 1995; Shalev, 1994). Unfortunately, no crucible fragments or any furnace constructions could be excavated so far in the context of the slags from Çayönü Tepesi. These are, therefore, the only indications related to local smelting operations.

The slags

Altogether, an amount of approximately 15 kg of slags were excavated at Arslantepe VI B2, much more than were collected from level VII. Because the site provided evidence of Late Chalcolithic to Early Bronze Age metallurgy (Palmieri, et al., 1999; Di Nocera, et al., 2004), it

Figure 5. Arslantepe, level VI B2, A472 camp. 300/87. The following four ores described were found at a metal workshop where more ores were obviously stored (Palmieri, et al., 1999) along with slags and crucible fragments. These finds and findings may lead to the statement that during this period ores were smelted inside settlements.
a) Yellow-orange, ochreous lump of soft iron-rich minerals (limonite (goethite), jarosite, gypsum and other Ca, SO_4-rich minerals) (5304-20). It was formed under acid conditions in an earthy gossan, the original sulfic ore was very rich in pyrite. Note partially porous boxwork. Photo: A. Hauptmann, Deutsches Bergbau-Museum Bochum.
b) Lumps of blue-green secondary copper ores intergrown with very fine grained quartz, kaolinite, anorthite (5305-20). Finely dispersed secondary copper ores (rims) with dots of chrysocolla, malachite, atacamite and brochantite in a pumiceous tuff. Original image detail size 2 cm. Photo: A. Hauptmann, Deutsches Bergbau-Museum Bochum.
c, d) Globular lump of iron-hydroxides (limonite), jarosite mixed with quartz, gypsum, bassanite (core) and surrounded by a layer of secondary copper ores (brochantite, atacamite, chalcopyrite)(5183-21). Photos: R. Ceccacci, by proxy Archive MAIAO (Missione Archeologica Italiana nell'Anatolia Orientale), Sapienza University of Rome. Diameter: 25 cm, weight: c. 1kg.

can be considered a small centre of copper-production, perhaps also of silver- and lead-production (Heil, et al., 2022) in this region in these periods.

Slag finds from Arslantepe VI B2 can generally be classified into several groups. Slag cakes dominate, furthermore there are slags crushed into cm-sized pieces. They were examined to find out whether they were produced together with the making of the slag cakes or by a separate metallurgical operation. In addition, a small amount of fine grained "slag sand" was excavated (Frangipane, oral communication). This, however, has not been investigated so far.

The slag cakes have the shape of palms of hands with a diameter of c. 10-12 cm (Figure 6a). These are the largest slag finds from this period. They weighed around 150-400 g each, i.e. the ore charge that had to be smelted must have been slightly above. The slags had very rough and irregular surfaces all around, which were indistinguishable from each other. Hence, they were not tapped from a furnace or crucible and did not cool down on flat ground. A typical feature of these slags is their dense loading with inclusions of cm-sized unmelted or partly molten pieces of various host rocks or gangues.

Crushed slags (Figure 6b) were speckled conspicuously by green corrosion minerals of copper caused by inclusions of metal and/or metal sulfides. In contrast to the slag cakes, they are sharped-edged everywhere, but a clear differentiation between the two types of slags is not possible in every case. Because the crushed slags and the slag cakes as well come exactly from the same archaeological context (a pit with discarded slag, probably belonging to the first phase of period VI B2 (D7/(9-13) A929 1b, camp. 139/98 and D7(9-13) A929 1b, camp. 144/98), it could initially be assumed that they belong together. The crushing of slags, smelted in comparably small reaction vessels, seemed to have been a necessary step of metal production at Arslantepe, but not only there. Because the way of producing metal at many sites was far from satisfying, an efficient separation of metal from slag was a difficult affair (see also Palmieri, Sertok and Chernykh, 1993). If oxidic copper ores were reduced to metal at all, it was often present in droplets or lumps in the slag and had to be removed mechanically after cooling. Copper sulfides had to be treated by subsequent sulfur removal processing.

Petrology of slags

Slags like those found at Arslantepe VI B2 and some other Early Bronze Age I - sites mentioned are useful materials to investigate the composition of the charged ores, gangue materials and host rocks and to gain information on early metallurgical operations. The following thermodynamic parameters are decisive for the formation of slags:

- Maximum temperatures reached in a vessel.
- Duration of firing in a vessel.
- Redox conditions resulting from the combustion of charcoal.

Figure 6a. Arslantepe VI B2, slag sample from square D7 (9-13) A929 1b 144/98, 25th 9, 1998.
The slag (weight 335 g, dimension 14.5 x 7 x 2.5 cm) has a rough, craggy surface. No upside and downside of the slag are visible. It is only partially liquefied. It shows reddish batches rich in copper compounds. Only some dots of corroded green secondary copper minerals probably derive from copper droplets included in slag.

Figure 6b. Arslantepe VI B2, slags from D7 (9-13) A929 1bc 139/98, 24th/25th 9, 1998.
Deliberately crushed slags (cm-sized) to extract copper droplets. These fragments show dots of green coloured minerals as results of corroded metal. They are mostly low in copper.
Photos: A. Hauptmann, Deutsches Bergbau-Museum Bochum.

Temperatures reached during melting and/or smelting, and redox conditions as well can be estimated by phases or phase intergrowths (Hess, 1998; Kronz and Keesmann, 2005; Hauptmann, 2007). It is the second aspect that presents the most difficulties, because no reasonable data are available on the reaction kinetics of ancient smelting processes. For a comparison, the firing of ceramics is a short-term event, and the time during which the object is subjected to the maximum firing temperature is rarely sufficient to attain any equilibrium situation (Heimann and Maggetti, 2014). Noll and Heimann (2016) argue that this could also be true for the production of slags. Based on simple crucible smelting experiments, Palmieri, Sertok and Chernykh (1993) found that a reduction of copper ores to metal from sites in Eastern Anatolia could happen as soon as after some 10 minutes of firing.

Basic methods of the analytical examination of archaeometallurgical slags are well known and have been described previously. Still underestimated are investigations in the macro-scale, i.e. the possibility to study small slags in their unspoiled entity in the cm-scale. In geoscience, presentations of carefully sliced rocks and ore mineralisations in the macro scale was applied, e.g. by Maresch, Schertl and Medenbach (2014), and by Taylor (2009).

Texture and phase content

The hand-sized, flat slag cakes from Arslantepe VI B2, and from Çayönü Tepesi as well are of a very similar and characteristic, brecciated to porphyric textures. They are heterogeneously composed and full of bubbles. The unmelted inclusions make up to c. 30 vol.% (Figures 7a and b). Siliceous or iron-rich materials are mixed with copper ores and are embedded in a matrix of dark, very fine grained or glassy slag which obviously was liquefied. Similar slag cakes have been described previously from Nevali Çori (Hauptmann, et al., 1993).

Slag cakes like these seem to be a supra-regional phenomenon of prehistoric copper production. They represent an early stage of copper smelting, and they are observed from the Middle East to Europe (overview in Hauptmann, 2007; 2020, and further discussion in Pearce, et al., 2022).

Inclusions

Inclusions consist of a variety of different mineralogical and chemical materials which indicate erratic mixtures of the charged materials.

The light-coloured inclusions consist mostly of mm- to cm-sized, angular, broken quartz grains, of host rocks interspersed and impregnated by inclusions of iron- and copper-iron sulfides. Due to solid state reactions, inclusions of quartz may show coronas of high-temperature modifications cristobalite or tridymite (Hauptmann, et al., 1993). There are also small edged fragments of black iron-oxides.

Hess (1998) described partly molten inclusions of feldspar-rich inclusions of andesitic or dacitic rocks, the texture of which was affected by a short terminated high temperature impact. Almost frequent accessory in the slag cakes is mm-sized chromite (Hauptmann, et al., 1993; Hess, 1998) which was also observed in ores from Arslantepe VI B2. This mineral is extremely refractory and will survive the temperatures of ancient smelting processes. It can be used for provenance studies. Like andesite and dacite, chromite-bearing rocks are not rare in South-Eastern Anatolia (see above). They are parts of the ophiolite suites in this region, especially at Ergani Maden. Apart from Arslantepe, chromite was also observed in slags from Nevali Çori, Çayönü Tepesi and Norșuntepe (Hauptmann, et al., 1993). The lead isotope analyses of the latter slags were concordant with the composition of the Ergani Maden fields (Seeliger, et al., 1985).

One must distinguish between two sorts of magnetite in the slag:

- Magnetite I: remains of (reduced) iron-rich ore.
- Magnetite II: crystals precipitated from a $Fe^{2+,3+}$-rich liquid.

Irregularly shaped agglomerates of magnetite (I) are mainly semi-liquified remains of iron-rich components of the charged material. Such agglomerates are also well known from iron-smithing slags of much younger age. However, in those slags they originate from pieces of hammer scale physically included in the slag (Goldenberg, 1990). Magnetite I is a metastable phase, which is formed by the dehydration of iron^{3+}-hydroxide (limonite) under high temperatures. In our case, agglomerations of magnetite I are associated and impregnated by copper-iron sulfides and copper.

Inclusions of copper and copper compounds

Moderate copper concentrations were observed in cm-sized crushed slags from Arslantepe VI B2, Nevali Çori, Çayönü Tepesi, and Murgul (Hauptmann, et al., 1993). They occur as finely dispersed droplets of metallic copper, often framed by copper-sulfides (chalcocite). Droplets of high-grade CuFe-sulfides, such as chalcopyrite or bornite, are often replaced by covellite. Whether this phenomenon is caused by metallurgical processing or by 5000 years of corrosion in soil storage is still open. The sulfides are embedded in a fayalitic matrix, in silicate

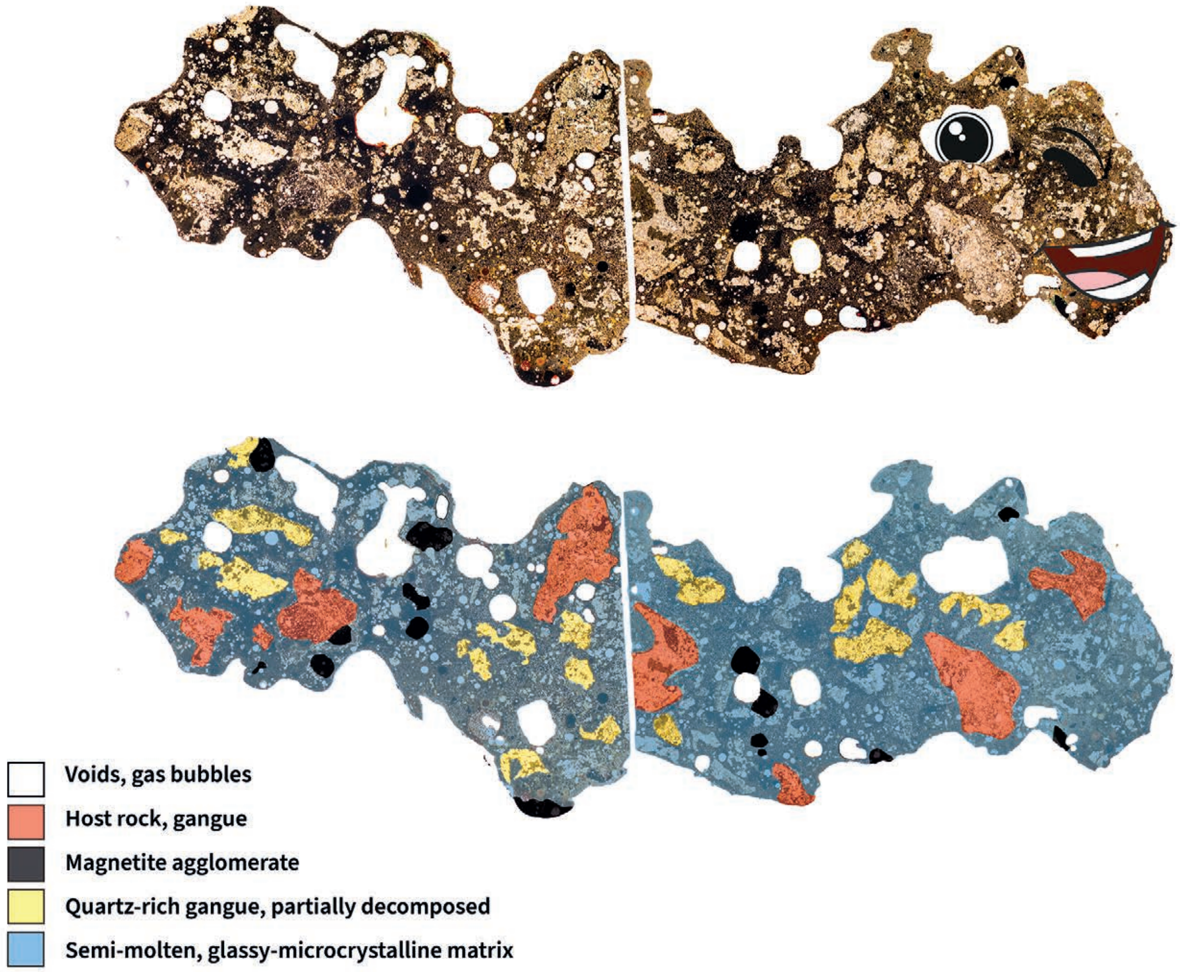


Figure 7a. Arslantepe, level VI B2, Area D7, 9 – 13, Loc. 139, 149 (Early Bronze Age IB, c. 3000 BC)
Bochum sample no. TR-8/112.
A section of a slag cake, composed of two thin sections. The typical texture of a partially molten copper slag showing breccia or porphyric-like appearance ("Drago che non constituisce scorie"). Relict inclusions of (quartz-rich) gangue, magnetite agglomerations, and host rocks, embedded in a fine-grained, glassy matrix of slag. Note the high porosity caused by thermodynamic decompositions of rocks and ores. Width of the original complete sample: 8.2 cm. From Hauptmann (2020). A simplified version of these constructional units is shown below.

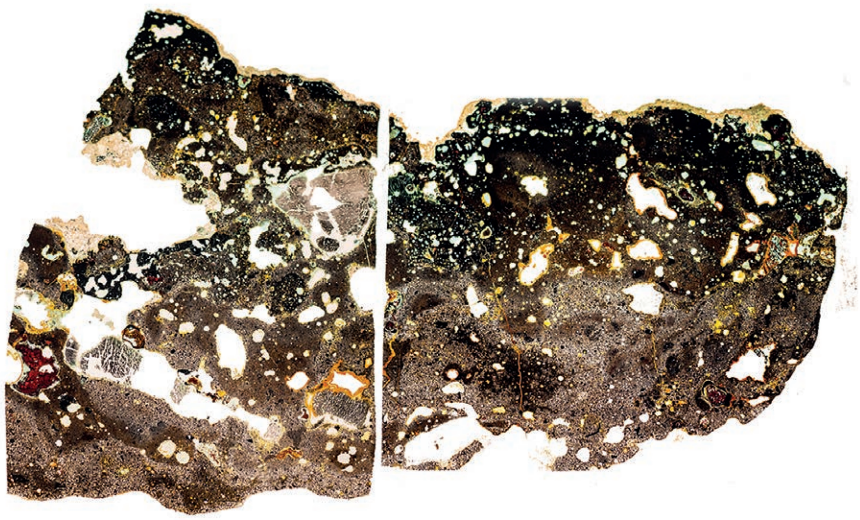


Figure 7b. Çayönü Tepesi, CT-84/27-04-15, Early Bronze Age I.
A section of a part of a slag cake, composed of two thin sections (original dimension 7 x 5 x 2 cm). Its weight is 143 g. It shows a highly similar texture and phase content to the slag cakes from Arslantepe VI B2. Width of the sample: 4.6 cm.

glass, in magnetite agglomerations or in siliceous and/or iron-rich gangue or host rock.

The smelting of such ores are the basics of matte-smelting, i.e. a separation of lower-melting sulfide components from highly viscous silicate slag liquids full of restites. Temperatures as low as approximately 800-900 °C were sufficient for quickly and (in the best case) almost completely separating sulfides even from unmelted rock or gangue inclusions or from a just partially liquefied siliceous melt (Hauptmann, 2003; Hauptmann, 2020; Metten, 2003).

Agglomerates of chalcocite show characteristic eutectic intergrowths with cuprite (Cu_2S - Cu_2O). According to Oelsen (1952), this can be seen as a desulfurisation of matte by a surplus of oxygen, which will lead to the precipitation of copper. Cakes consisting of high-grade copper sulfide and metal segregated by exsolution from siliceous slag have as yet not been excavated at Arslantepe. But they are known from Chalcolithic Murgul (Lutz, Wagner and Pernicka, 1994), Early Bronze Age Shahr-i Sokhta (Hauptmann, Rehren and Schmitt-Strecker, 2003), Shahdad (Meier, 2015), Al-Maysar (Oman) (Hauptmann and Weisgerber, 1980) and, according to Keesmann, Kronz and Maier (1994), from Los Millares (Spain).

Another interesting phase is massive cuprite, because it may apparently not only be created by the reduction of malachite by a metallurgical operation. It occurs in mm-sized crystals which rather indicate shape and texture of an original ore instead of crystals precipitated from the liquid state. One would easily accept the use of massive native copper + cuprite, as it may still be collected today in the region (Wagner, et al., 1989; Palmieri, Sertok and Chernykh, 1993).

Liquefied matrix

According to their mineralogical phase content, the molten parts of the slags are siliceous glass with magnetite (II), fayalite, clinopyroxene as the predominant phases. Wuestite precipitated less frequently. Usually it forms rounded to idiomorphic and skeletal-like crystals. The paragenesis of iron-oxides with fayalite (and with iscorite especially in slags from Çayönü Tepesi) or with glass is a function of the degree of oxidation to which the slags were exposed (see below). Maghemite was also identified. It is a metastable phase created by the dehydration of iron-hydroxide and/or by the oxidation of magnetite under high temperatures.

In all slags from Arslantepe VI B2, fayalite is low in MgO, CaO, and MnO (total < 3 wt.%) (Hess, 1998). They are below the concentrations of many other fayalites in prehistoric copper smelting slags (Hauptmann, 1985). In specific parts of the slags this phase exhibits a dark brown colour or is even opaque in transmitting light. This phenomenon is hardly due to corrosion. Hauptmann (2003) stated that this phenomenon is due to a high-temperature oxidation of fayalite, which led to the formation of the two-phased-structured "ferrifayalite" (Kondoh, Kitamura and Morimoto, 1985; Schäfer, 1983).

Instead of fayalite, clinopyroxene (e.g., hedenbergite), along with delafossite, cuprite, and cuprospinel are common constituents in copper slags of the Chalcolithic and Early Bronze Age (Hauptmann, 2020). Iscorite occurs as a product of rather moderate temperatures (570 < T < 1.100 °C) (Rose, Endlicher and Mucke, 1990; Keesmann, 1989; Smuts, Steyn and Boeyens, 1969). Such conditions exist, e.g. when (liquid) slag is "tapped" from a metallurgical vessel or furnace and is exposed to the air. The crystallisation of iscorite is limited to mm-sized rims if the interval is very short, but it may be formed in large quantities if the (semi-) liquid slags are held at higher temperatures, e.g., in a heated pit of a slag pit-furnace (Ganzelewski, 2000).

Hence, the early slag cakes from the investigated localities show evidence of smelting processes under rather low-reducing conditions prevailing in small reaction vessels such as the crucibles discovered at Arslantepe VI B2.

Between the crystals there occurs interstitial "glassy" material. Mostly it is not completely amorphous but exhibits transitions from microlithic formation to cryptocrystalline areas or crystallised as clinopyroxene.

Chemical compositions and eutectic melts

Thermodynamically, the slags did not reach equilibrium but represent domains of a number of small micro-equilibria containing restites. Basically, we have to observe the behaviour of a batch of copper ore at rising temperatures, from the beginning of the smelting process onwards, and not that of a slag during the final cooling from a (homogeneous) melt. In a phase diagram, this is rather the "view from below", i.e. the view during heating up the charged material, and not the "view from above", i.e. the view during cooling down from liquid to solid.

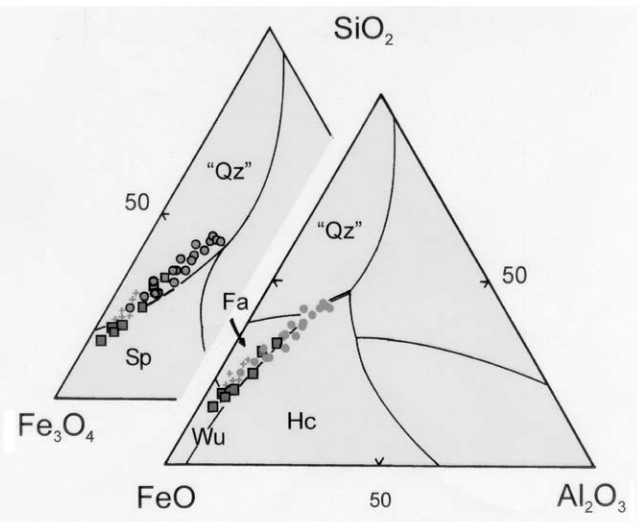
To better understand the beginning of slag formation under rising temperatures, tiny, mm-sized sections of microscopically identified molten parts in the slag cakes were analysed. These showed the following variations of the main components (Hauptmann, 2003):

FeO/Fe_3O_4	= 30 – 62 wt.%
SiO_2	= 22 – 36 wt.%
Al_2O_3	= 3 – 13 wt.%
CaO	= 2 – 3 wt.%

To study slag formation and crystallisation, the main components were plotted in the equilibrium triangle phase diagram SiO_2 – FeO/Fe_2O_3 – Al_2O_3 (Figure 8). Note the correlation between SiO_2 and Al_2O_3, which ideally follows the cotectic, low melting line between the fields of hercynite/spinel and "Qz" (i.e. tridymite/cristobalite). The diagram shows that the Early Bronze Age I slag cakes show minimum-temperature melts only in selected sections, which is caused by an initial melting of charged components in the crucible.

Considering the melting temperatures of the system, one could assume that these parts of the slags were exposed to temperatures between 1150 and 1200 °C. In reality, by the "view from below", the liquid might have been formed at much lower temperatures by the addition of minor components such as CaO, MnO, alkali-oxides, CuO, sulfides and hydrous phases. Such a composition could have originated e.g. from ores of a gossan of a sulfidic ore deposit (oxidation zone), where mixtures of Fe-(hydr-) oxides, earthy masses of jarosite, siliceous gangue and alkali-rich phyllosilicates occur, which were formed by altering the host rock by hydrothermal activities. Oxidic and sulfur-containing copper ores are intermingled. Such materials may decisively contribute to creating a freely running liquid at temperatures below this level (Lowell and Guilbert, 1970). Iron-hydroxide would be reduced to iron oxides

Figure 8. The ternary systems SiO_2-FeO/Fe_3O_4- Al_2O_3. Partial melting in Early Bronze Age I, slags from Arslantepe (D7, 9-13, Loc 179, 149; D7, 9-13, A929, 1b, camp. 144/98, 25.8.98) and Çayönü Tepesi (CT 84-27 0/15 1/d 828.04, CT 84 30/O 1-2 3/a 826.90, CT 84 30/O 1-2 2/a 826.95). Chemical composition of liquefied parts between un-decomposed inclusions. Note the succession of micro-equilibria following the eutectic/cotectic troughs (Muan, 1955; Eugster and Wones, 1962). Abbrevations: "Qz" = quartz/tridymite/cristobalite; Sp = spinel; Fa = fayalite; Hc = hercynite; Wu = wuestite. Data from Hauptmann (2003).



like Fe_3O_4, rather than to FeO which would form a liquid with reactive SiO_2 and alumina from the decomposition of clay minerals. Alumina would efficaciously contribute for lowering the melting point. Exposed ore deposits (gossans) provided the ancient smelters with such materials. Copper ores embedded and impregnated in volcanic rocks, in serpentinite are rather common in South-Eastern Anatolia, especially at Ergani Maden. As long as no archaeological evidence proves the opposite, there is no need to claim a deliberate use of fluxes to enhance the formation of a slag.

In every sample analysed, the main components are Fe-oxides and SiO_2. The total amount of Fe-oxide was calculated as $Fe^{2+}O$, although Fe^{3+}-containing phases have been identified. The Fe^{2+} : Fe^{3+}-ratio is affected by relics of ore, re-oxidation, and by corrosion. Therefore, it would not represent the original oxygen pressure of a continuous smelting operation. Other elements are mostly below 3 wt.%, except for copper with up to 15 wt.% and sulfur with up to 9 wt.%. Zinc was only analysed in a few phases; in most cases it was below the detection limit. In addition, arsenic, nickel, and barium were detected in very low concentrations.

Lead isotope analyses of ores and slags

Lead isotope ratios of 12 Cu(Fe-) ores and 3 copper slags from Arslantepe VI B2, Ergani Maden, and Çayönü Tepes were analysed in the course of this study. They are compiled in Table 3. Comparable with Heil, et al. 2022, the ratios $^{208/206}$Pb vs. $^{207/206}$Pb and $^{208/204}$Pb vs. $^{206/204}$Pb are plotted along with other data for comparison, in Figure 9. The new measurements were performed by Dr. M. Jansen at the laboratories of DBM, using a multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS, type Neptune XT, Thermo Fisher Scientific, following the methodology described by Klein, et al., 2004) (see also Heil, et al., 2022). Two samples have previously been analysed by Prof. Dr. S. Klein in Frankfurt am Main.

The report by Seeliger, et al. (1985) contains lead isotope data from ores and slags collected during their field work in Eastern and Northern Anatolia. Based on lead isotope analyses, Yener (2021), and Sayre, Joel and Blackman (2001) suggested the following groups or regions:

- Taurus 1A: Bolkardağ valley. Ores and slags from this group are geologically the youngest.
- Taurus 1B: East of Niğde, and at Yahyalı. „Mixed group"; ores from geographically higher areas in the Bolkardağ valley and from Kestel.

Table 3. Lead isotope data of copper ores and slags found in the settlement of Arslantepe VI B2 and some other sites in Eastern Anatolia (squared symbols). Details of samples see Table 2.

Lab.-no. DBM	Hess-no. 1998	Locality					
			206Pb/204Pb	207Pb/204Pb	208Pb/204Pb	207Pb/206Pb	208Pb/206Pb
Cu-ores, Fe-ores							
5304-20	No ID	Arslantepe VI B2	18.364	15.580	38.411	0.84844	2.0915
5305-20	No ID	Arslantepe VI B2	18.569	15.666	38.641	0.84371	2.0808
5308-20	No ID	Cayönü Tepesi	18.757	15.653	38.732	0.83462	2.0648
No ID	TR-8/ 82	Arslantepe VI B2	18.570	15.614	38.644	0.8408	2.0810
5179-21	TR-18/1	Ergani Maden	18.990	15.659	39.084	0.82468	2.05804
5180-21	TR-18/2	Ergani Maden	18.982	15.662	39.082	0.82514	2.05875
5181-21	TR-18/4	Ergani Maden	19.000	15.669	39.104	0.82478	2.05798
5182-21	TR-8/36	Arslantepe VI B2	19.163	15.588	39.081	0.81349	2.03929
5183-21	TR-8/118	Arslantepe VI B2	18.780	15.698	38.899	0.83594	2.07115
5184-21	TR-8/32	Arslantepe VI B2	18.994	15.670	38.895	0.82506	2.04767
5185-21	TR-8/33	Arslantepe VI B2	19.169	15.586	39.081	0.81316	2.03863
5186-21	TR-8/30	Arslantepe VI B2	18.744	15.669	38.821	0.83598	2.07091
5187-21	TR-18/4a	Ergani Maden	19.046	15.711	39.189	0.82492	2.05793
Cu-slags							
5307-20	No ID	Arslantepe VI B2	18.339	15.625	38.421	0.85205	2.0949
5309-20	No ID	Cayönü Tepesi	18.936	15.655	38.861	0.82679	2.0520
No ID	TR-8/89	Arslantepe VI B2	18.559	15.601	38.583	0.8406	2.0789

- Taurus 2A: Northeast of Yahyalı, in the Aladağ-ranges, between the Ecemis fault and the Zamantı-river. Ores and slags from this group are geologically the oldest.
- Taurus 2B: Kestel, Çamardı (Aladağ-ranges). Ores from the eastern area close to the Ecemis fault and slags from Çamardı. Numerous occurrences of Pb-Zn- and Fe-skarn and replacement ore bodies with polymetallic mineralisations high in silver. At Kestel and in the mining district of Bolkardağ tin ores occur.

According to Seeliger, et al. (1985), the copper ore mine of Ergani Maden shows a surprisingly narrow cluster of compositions ($^{208/206}$Pb ≈ 2.060-2.064 vs. $^{207/206}$Pb ≈ 0.825-0.829). This, in comparison with other VMS deposits, e.g. from Cyprus (Stos-Gale, Maliotis and Gale, 1998), needs to be evaluated. Wagner, et al. (1986) published two new data of ores from Ergani Maden which deviate from this cluster (TG176A-2: $^{208/206}$Pb = 2.0697; TG176B-2: $^{208/206}$Pb = 2.0371), showing that the composition of the lead isotopes seems to be more variable.

They point out that these remarkable deviations may have been caused by the separation and enrichment procedure of the analysis, when only small amounts of samples are available, with very low lead concentrations, and finally reduced to small amounts needed for analytical purposes. Hence, the interpretation of analytical data must be done with care. Perhaps at best, larger averages of ore deposits should be available as processes of the modern metal production. Average values can be expected only in ancient slags which were more or less completely molten. However, it might be a question whether averages are useful or, in our case of very small-scale prehistoric copper production, all single exceptional data have to be considered – as it was also done in Cyprus. Mineralogical provenance indicators such as chromite might provide valuable information for that question.

The new measurements underline that the narrow cluster from Ergani Maden has to be enlarged. It is not surprising to realize that the Early Bronze Age copper slag no. 5309-20 from Çayönü Tepesi, which was smelted in the immediate vicinity of Ergani Maden, plots very close the cluster (Figure 9). From the archaeological point of view, its provenance from there is clear. Also lead isotope ratios of the Norșuntepe were concordant with the composition of this ore deposit (Seeliger, et al., 1985). Surprisingly, a piece of malachite from Çayönü (5308-20) plots apart from the Ergani-cluster. It is questionable whether it comes from ore deposits of the Taurus 2B-group or, alternatively, from the North Central

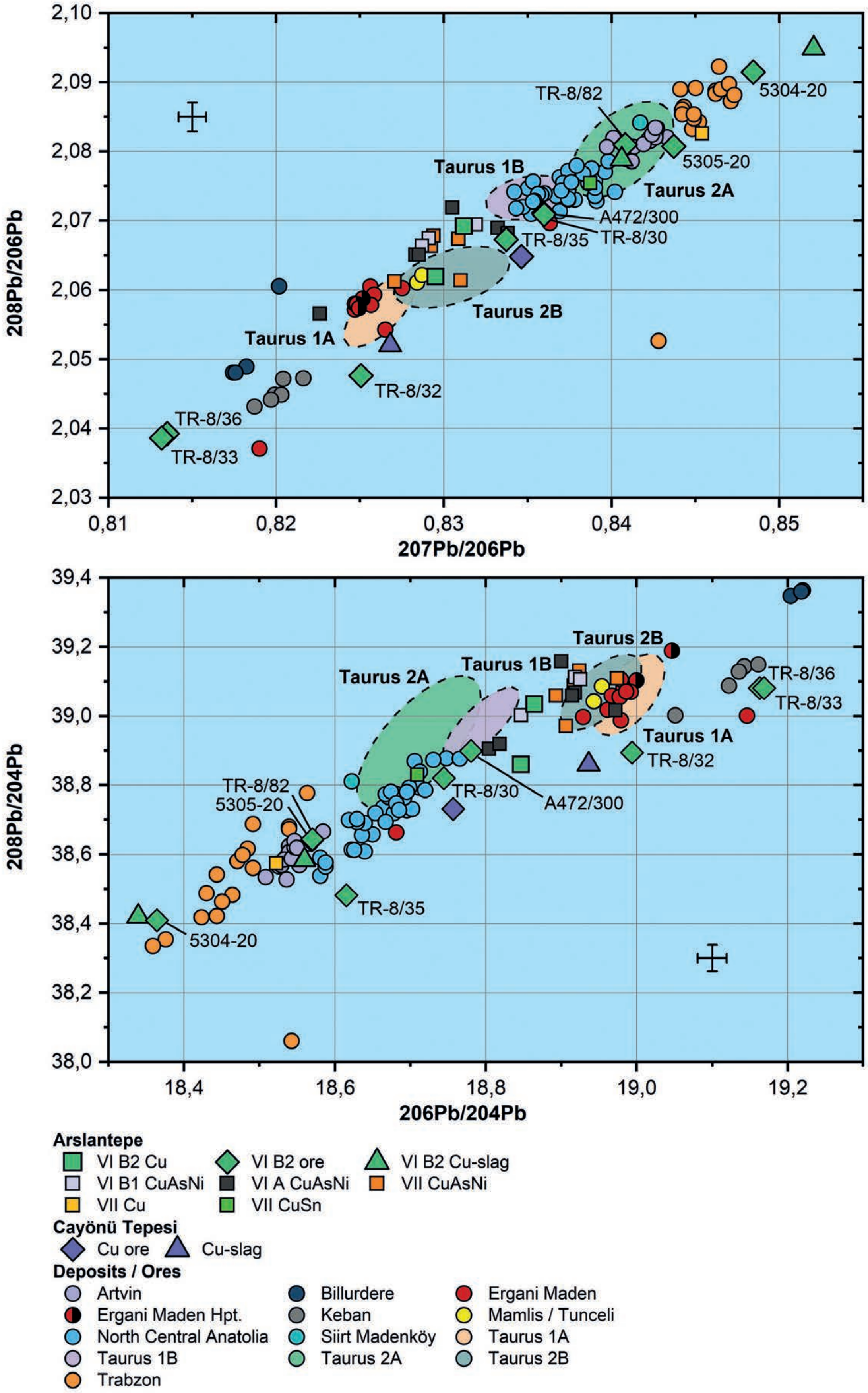


Figure 9. Lead isotope compositions of copper ores and slags found in the settlement of Arslantepe VI B2 and some other sites in Eastern Anatolia (squared symbols). Depicted are compositions of ores from various ore deposits, as compiled by Sayre, Joel and Blackman (1992) and Heil (2022). For Ergani Maden, some new measurements were performed as shown in Table 3: Note the cluster of compositions. Also note the cluster of dark green ores from Taurus 2A which are overlapping the ore group of Artvin (Murgul). The Taurus 2A ores derive from lead-zinc deposits near Bolkardağ in southern Anatolia, the ores from Artvin (Murgul) from copper deposits of VMS of the Kuroko type in north-eastern Anatolia.

Anatolia-group. It may not originate from Taurus 2B, because in this area Pb-Zn- and Fe-skarn and replacement polymetallic ore bodies occur, and no pure copper ores like that were found there. An origin of this sample from an enlarged Ergani Maden-cluster would be a more reasonable solution.

Beside these data, two copper ores from Arslantepe (TR-8/30; TR-8/118 or A472/300) plot close to this high outlier. We should remind here that the complexly composed VMS deposit of Ergani Maden is exposed not only in one single deposit, the large open air mine, but in several ore bodies around the village. Probably most of the ore samples collected by several authors (Seeliger, et al., 1985; Wagner, et al., 1986; Hess, 1998) came from this open air mine and inevitably resulted in the tight cluster at $^{208/206}Pb \approx 2.06$ in Figure 9.

However, lead isotope data of the yellow-orange, ochreous lump of soft iron ore (5304-20; Figure 6a), of the green copper ore (5305-20), and of the sulfidic ore TR-8/82 are indicative of an origin from an ore deposit of geologically much older age than Ergani Maden. We therefore may rule out an origin from there. These data are compatible with copper deposits located in the Pontides in North-East Anatolia, close to the Black Sea coast (Artvin, Murgul, Küre, Trabzon). Hauptmann, et al. (2002) found that the ore TR-8/82 (and a piece of slag (TR-8/89) from level VI B2) do fit together. This means that these ores from the north were imported to Arslantepe and that they were smelted into copper there. Their silicified and kaolinised textures of a mineralised pumiceous dacitic tuff is described in detail by Çağatay (1993) and Yiğit (2009) from the ore deposit of Murgul. Here, this petrographic peculiarity is supported by lead isotopy.

Conclusions

The investigation of metallurgical finds from Arslantepe level VI B2 and from some other Early Bronze Age sites in South-Eastern Anatolia showed that exclusively copper was produced. Lead-silver metallurgy, which had been practised in earlier periods (Arslantepe VII, VI A; Heil, et al., 2022), was given up. The locations of raw material sources changed.

Not only copper artefacts were traded to Arslantepe. Also copper ores were imported from various raw material sources, both located in the vicinity, and also from far away. The processing of ores was performed within the settlements. Excavations have shown that ores were also smelted in small-scale metallurgical operations in special workshop areas (Di Nocera, 2013). It was a social pattern of a limited metal production all over regions in the Near and Middle East and beyond. The reconstruction of the organisation of mining activities and interactions between settlements and raw sources is, however, a difficult and versatile problem. To do this, one has to understand not only the social and economic practices of ancient societies but also needs knowledge of the mineralogical and geochemical complexity of ore deposits as well as of the technology of ancient metallurgical operations applied (Stöllner, 2018). Most probably, there must have been larger-scale exploitations at the "giants" to supply all the villages, all the larger centralised systems and early urban societies in Eastern Anatolia and beyond with ores.

Based upon chemical analyses, Palmieri, Sertok and Chernykh, et al. (1996, a) could show that the nature of the ores used and excavated at Arslantepe changed from the Chalcolithic period VII to period VI, from complex polymetallic ores to relatively simply composed copper-iron ores. However, they did not succeed with provenancing these ores, because of the large variety of ore deposits. Ores high in lead and arsenic were found at level VII. In the Early Bronze Age, almost exclusively relatively pure - oxidic and sulfidic - copper ores low in arsenic, nickel and lead were imported. Mineralogical investigations and lead isotope analyses indicate a provenance from gossan materials of ore deposits rich in pyrite and chalcopyrite. Accessories such as chromite, found in ores and slags, underlines that obviously Ergani Maden was the important, nearby copper source. This is also shown by new lead isotope ratios. However, these are also identical with copper deposits in the Pontides area in North-Eastern Anatolia (Trabzon, Artvin/Murgul) and also in the Transcaucasus region (Madneuli).

In any case, this shows that Arslantepe must have been a link in the metal (and ore) trade between the Black Sea coast in North and Upper Mesopotamia in the south (Di Nocera, 2013), even if the metal production itself happened only on a limited scale. The connection to the north is not a new cultural link. Already at Arslantepe VII metal objects could be found with a signature of ores from near the Black Sea coast (Heil, et al., 2022). This underlines the suggestion by Frangipane, et al. (2005) that Transcaucasian groups would have been present at Arslantepe before the beginning of the 3rd millennium. And also part of the metal artefacts excavated from the "Royal Tomb" clearly indicate Kura-Araxes traditions and even provenances from the northern Caucasus (Palumbi, 2021). And this means that a trade of ores would be compatible with the "expansion" of the Kura-Araxes culture from its traditional territory to the Iranian plateau and to the Anatolian highlands, and finally to the Levant in the south (Palumbi and Chataigner, 2014).

New information on some technological aspects of metallurgy at Arslantepe VI B2 were also provided in the course of this study.

One issue was to find out, by slag investigation, whether deliberately added fluxes were used for smelting processes or, alternatively, if ores and gangue had „self-fluxing“ properties. If ores were mixed with gangues and host rocks in suitable proportions, the charge would be completely melted, and additional fluxes would not have been necessary. However, in the case of high $SiO_2 : FeO/Fe_2O_3$-ratios, quartz or SiO_2-rich host rocks would not completely be dissolved in the developing liquid. Being refractories, they will remain as restites in the solid state and form inclusions in the only partly liquefied slag. Such a kind of slag got the nickname "free silica slag" (Rothenberg and Blanco-Freijeiro, 1981; Metten, 2003; Anguilano, 2012). Based upon such slags from Bronze Age Trentino (Italy), Pearce, et al. (2022) suggested that it was perhaps not even the intention of the ancient smelters to convert the entire raw material charged into a fully liquid slag. The main purpose was rather the reduction of ores to metal and/or a feasible segregation of (sulfidic) material, i.e. the matte in reasonable time segments (tapping) as well as a reasonable consumption of charcoal. This means that, generally, as long as the archaeological evidence is not conclusive, any claims for the deliberate adding of fluxes for smelting operations must be left open.

A particular focus was on the operating mode of the crucibles from Arslantepe VI B2, especially to the sub-cylindrical shaped crucibles. Due to their air openings in their lower parts, they are maybe a link in the technical development from crucibles to portable furnaces. Air was blown into the vessels by blowpipes or tuyères in a way similar to all the constructions of shaft smelting furnaces of later periods, especially for iron production. The dimensions of the Arslantepe VI B2-crucibles were sufficient only for the formation of highly viscous hand-sized slag cakes, as shown in Figure 6a and Figure 7, with inclusions of metal and matte which – after they were broken out of the crucible – were crushed to enrich these inclusions just mechanically. There is no indication of slag tapping. The shape and design of the slag cakes show that they cooled down inside the vessel. Metal and slag were extracted by breaking the vessel after finishing air supply and firing. Obviously, they were used only one time. Due to their low melting temperatures, the Cu-Fe-sulfides easily separated from the emerging liquid slag. Copper droplets were co-melted to larger units.

The type of the crucible from VI B2 was based on vessels from earlier periods. At Arslantepe VII, fragments of crucibles equipped with two air-inlets also in the lower part of the vessel were excavated (Hauptmann, et al., in prep.). They were used for low temperature smelting or just for melting operations.

Somewhat later, the construction of VI B2-crucibles was obviously widespread in Eastern Anatolia. The smelting of copper may have taken place within the settlements but was limited to a scale of domestic mode production. Their output must have been small. For Hacınebi (upper Euphrates, Late Chalcolithic period), Özbal, Adriaens and Earl (1999) assumed that the efficiency of copper ore smelting in crucibles depended besides of the quality of the ores charged also of the air supply. They stated that blow pipes would have been at least 50 times less efficient than bellows and did not allow for large-scale operations. Their experiments in crucible smelting using blowpipes have always shown to yield only small amounts of copper.

Two tools necessary for copper production in crucibles are surprisingly missing from the inventory of Arslantepe VI B2. First of all, there is no evidence of how the air supply was organised to heat up the charge in the crucibles. It is possible that blowpipes made of reed and topped with small clay tuyères (as opposed to bellows) were used. This type of tool, however, would hardly survive any metallurgical operation. Secondly, there is no evidence of crucibles in which small prills and lumps of metal, produced along with smelting slags, could be melted together to larger units. This might have been the case e.g. with those ingots or quantities used to form adzes, excavated from VI B2, which had weights between 150–500 g. Most of the produced slags are wastes. They contain only very small inclusions of copper-rich materials. Therefore, as mentioned above, slag was also crushed to cm- to mm-sized grains, probably to recover copper-rich inclusions. This processing may have served for re-(s)melting these to larger units. At Arslantepe, vessels of similar size and shape for such a purpose were found at level VII (Late Chalcolithic, 3900-3400 BC). Here, they were called (casting) moulds (Di Nocera, 2013; Heil, et al., 2022). They are evidently older than the crucible from level VI B2.

Other examples from outside are known but rare. Laschimke and Burger (2018) suggested, based on finds from late Neolithic levels (Pfyn culture) from Switzerland, that more angular trough-shaped, longish crucibles, which Leuzinger (1997) termed casting moulds ("Gusstiegel"), could have been also used for such a re-(s)melting.

Our observations and (geo-)analytical results of metals, ores, slags, crucibles and other waste products may contribute to better understanding the development of the Chalcolithic and Early Bronze Age metallurgy within a complex trade system in the region of Eastern Anatolia – (Trans-)Caucasus – North-Western Iran. It becomes more and more apparent that the metallurgical reconstructions delineated here reflect widespread manual craftsmanship. Obviously Arslantepe was of special importance there.

Acknowledgements

We gratefully acknowledge the overall help by Prof. Dr. Marcella Frangipane, the former excavator of Arslantepe, for her generous graciousness and attitude in many respects. She was the scientist who provided us with all the material discussed in this publication. We are most appreciative of the ideal support of late Dr. Alberto Palmieri, who was one of the first scientists to recognise the enormous meaning of analytical investigations of ores, slags and raw material sources to understand the prehistory of Arslantepe. Later Dr. Nima Nezafati, Deutsches Bergbau-Museum Bochum, continued our mineralogical discussion on ore deposits. Thin sections were prepared in excellent quality by Andreas Ludwig, and later an exhilarant visual presentation was prepared by Christoph Hauptmann. Chemical and lead isotope analyses were performed by Dr. Michael Bode and Dr. Moritz Jansen, also Deutsches Bergbau-Museum.

References

Adams, R., 1999. *The Development of Copper Metallurgy During the Early Bronze Age of the Southern Levant: Evidence from the Feinan Region, Southern Jordan*. Ph. D. University of Sheffield.

Adams, R. and Genz, H., 1995. Excavations at Wadi Fidan 4: A Chalcolithic Village Complex in the Copper Ore District of Feinan, Southern Jordan. *Palestine Exploration Quarterly*, 127, pp.8-20.

Akıncı, Ö.T., 2009. Ophiolite-hosted Copper and Gold Deposits of Southeastern Turkey: Formation and Relationship with Seafloor Hydrothermal Processes. *Turkish Journal of Earth Sciences*, 18, pp.475-509.

Anguilano, L., 2012. *Roman lead silver smelting at Rio Tinto: the case study of Corta Lago.* Ph. D. University College London.

Bamba, T., 1974. Copper deposits in the Ergani mining district, southeastern Turkey. *Mining Geology*, 24, pp.389-400.

Bamba, T., 1976. Ophiolite and Related Copper Deposits of the Ergani Mining District, Southeastern Turkey. *Bulletin of the Mineral Research and Exploration*, 86, pp.36-50.

Begemann, F., Hauptmann, A., Schmitt-Strecker, S. and Weisgerber, G., 2010. Lead Isotope and chemical signature of copper from Oman and its occurrence in Mesopotamia and sites on the Arabian Gulf Coast. *Arabian Archaeology and Epigraphy*, 21, pp.145-179.

Bilgi, Ö., Özbal, H. and Yalçın, Ü., 2004. The First Metal: Copper. In: Ö. Bilgi, ed. 2004. *Anatolia - Cradle of Castings*. Istanbul: Döktaş. pp.3-43.

Bourgarit, D., 2007. Chalcolithic copper smelting. In: S. La Niece, D. Hook and P. Craddock, eds. 2007. *Metals and Mines. Studies in Archaeometallurgy*. London: British Museum, Archetype Publications. pp.3-14.

Burleigh, R. and Matthew, K., 1982. British Museum Natural Radiocarbon Measurements XIII. *Radiocarbon,* 24(2), pp.151-170.

Çağatay, M.N., 1993. Hydrothermal Alteration Associated with Volcanogenic Massive Sulfide Deposits: Examples from Turkey. *Economic Geology*, 88, pp.606-621.

Çambel, H. and Braidwood, R.J., 1980. *Prehistoric Research in Southeastern Anatolia – Guneydoğu Anadolu Tarihöncesi Arastırmaları.* Istanbul: Edebiyat Fakultesi Basimevi.

Caneva, C. and Palmieri, A.,1983. Metalwork at Arslantepe in Late Chalcolithic and Early Bronze Age I: The Evidence of Metal Analysis. *Origin*i, XII(2), pp.637-654.

Çiftçi, E., 2019. Volcanogenic Massive Sulfide (VMS) Deposits of Turkey. In: F. Pirajno, T. Ünlü, C. Dönmez and M.B. Şahin, eds. 2019. *Mineral Resources of Turkey, Modern Approaches*. Berlin, Heidelberg: Springer. pp.427-495.

Craddock, P., 1995. *Early Metal Mining and Production*. Edinburgh: Edinburgh University Press.

Craddock, P.T., 2013. Tarteso y la Explotatión Minera. Local Traditions and Foreign Contacts: Innovation in Tartessian Metallurgy. In: J. Alvar and J.M. Campos Carrasco, eds. 2013. *Acta Congreso Tartesso. Editores Tarteso. El emporio del metal. Almuzara.* Huelva, pp.231-268.

Çukur, A. and Kunç, Ş., 1989. Analyses of Tepecik and Tülintepe Metal Artefacts. *Anatolian Studies,* 39, pp.113-120.

Di Nocera, G.M., 2013. Organization of production and social role of metallurgy in the prehistoric sequence of Arslantepe (Turkey). *Origini*, 35, pp.111-142.

Di Nocera, G.M., Hauptmann, A. and Palmieri, A., 2004. I metalli della Tomba Reale e la metallurgia agli albori del III millennio. In: M. Frangipane, ed. 2004. *Arslantepe. Alle origini del potere. Arslantepe, la collina die Leoni*. Milan: Electa. pp.122-143.

Esin, U., 1986. Doğu Anadolu'ya ait Bazı Prehistorik Cüruf ve Filiz Analizleri. *Anadolu Arastırmaları*, 10, pp.143-160.

Eugster, H.P. and Wones, D.R., 1962. Stability Relations of the Ferruginous Biotite, Annite. *Journal of Petrology,* 3, pp.82-125.

Frame, L.D., 2012. Reconstructing Ancient Technologies: Chalcolithic Crucible Smelting at Tal-Iblis, Iran. In: P. Jett, B. McCarthy and J.G. Douglas, eds. 2012. *Scientific research on ancient Asian metallurgy. Proceedings of the Fifth Forbes Symposium at the Freer Gallery of Art.* London: Archetype Publications in association with the Freer Gallery of Art, Smithsonian Institution. pp.181-202.

Frangipane, M., 1992. Dipinti murali in un edificio “palaziale” di Arslantepe –Malatya: aspetti ideologici nelle prime forme di centralizzazione economica. *Studi miceni ed Egeo Anatolici*, 30, pp.143-154.

Frangipane, M., 1993. The results of the 1991 campaign at Arslantepe – Malatya. In: T.C. Kültür Bakanlığı. Anıtlar ve Müzeler Genel Müdürlüğü, ed. 1991. *XIV. Kazı Sonuçları Toplantısı. Ankara, May 25–19, 1992.* Ankara: Ankara Üniversitesi Basımevi. pp.213-229.

Frangipane, M., 1994. Excavations at Arslantepe-Malatya, 1992. In: T.C. Kültür Bakanlığı. Anıtlar ve Müzeler Genel Müdürlüğü, ed. 1991. *XV. Kazı Sonuçları Toplantısı. Ankara, May 24–28, 1993.* Ankara: Ankara Üniversitesi Basımevi. pp.211-228.

Frangipane, M., 2010a. Arslantepe. Growth and collapse of an early centralised system: the archaeological evidence. In: M. Frangipane, ed. 2010. *Economic Centralisation in Formative States. The Archaeological Reconstruction of the Economic System in 4th Millennium Arslantepe*. Rome: Sapienza University of Rome, Arbor Sapientiae. pp.23-42.

Frangipane, M. ed., 2010b. *Economic Centralisation in Formative States. The Archaeological Reconstruction of the Economic System in 4th Millennium Arslantepe. Studi di Prehistoria Orientale, 3*. Roma: Sapienza Università di Roma.

Frangipane, M., 2017. The Role of Metallurgy in Different Types of Early Hierarchical Society in Mesopotamia and Eastern Anatolia. In: P.W. Stockhammer and J. Maran, eds. 2017. *Appropriating Innovations Entangled Knowledge in Eurasia, 5000-1500 BCE*. Oxford; Philadelphia: Oxbow Books. pp.171-183.

Frangipane, M., 2018. Different Trajectories in State Formation in Greater Mesopotamia: A View from Arslantepe (Turkey). *Journal of Archaeological Research*, 26(1), pp.3-63.

Frangipane, M. and Palmieri, A., 1983. A Protourban centre of the Late Uruk Period. *Origini,* XII(2), pp.287-454.

Frangipane, M. and Palmieri, A.M., 1994-95. Un modello di ricostruzione della metallurgia antica: il sito di Arslantepe. *Scienze dell’Antichità*, 8-9, pp.59-78.

Frangipane, M. and Erdal, Y.S., 2020. Ritualisation of violence and instability at Arslantepe at a time of crisis and political disruption (3300-3000 BC) In: H. Meller, R. Risch, K.W. Alt, F. Bertemes and R. Mico, eds. 2020. *Rituelle Gewalt – Rituale der Gewalt, Ritual Violence – Rituals of Violence. 12. Mitteldeutscher Archäologentag, 10.-12. Oktober 2019, Halle (Saale). Tagungsbände des Landesmuseums für Vorgeschichte Halle,* 22. Berlin: Steinbeck. pp.467-495.

Frangipane, M., Hauptmann, H., Liverani, M., Matthiae, P. and Mellink, M. eds., 1993. *Between The Rivers And Over The Mountains. Archaeologia Anatolica Et Mesopotamic Alba Palmieri Dedicata.* Dipartimento di Scienze Archaeologiche e Antropologiche dell’ Antichità Università di Roma “La Sapienza”.

Frangipane, M., Di Nocera, G. M., Hauptmann, A., Morbidelli, P., Palmieri, A., Sadori, L., Schultz, M. and Schmidt-Schultz, T., 2001. New Symbols of a New Power in a “Royal” Tomb from 3000 BC Arslantepe, Malatya (Turkey). *Paléorient*, 27(2), pp.105-139.

Frangipane, M., Di Nocera, G.M. and Palumbi, G. 2005. L’interazione tra due universi socio-culturali nella piana di Malatya (Turchia) tra IV e III millennio: dati archaelogici e riconoscimento di identità. *Origini*, XXVII, pp.123-170.

Frangipane, M., Balossi-Restelli, F., Di Nocera, G.M., Erdal, Y.S., Manuelli, F. and Mori, L., 2019. Recent Late Chalcolithic and Iron Age Discoveries at Arslantepe: The 2017-2018 Campaigns. In: S.R. Steadman and G. McMahon, eds. 2019. *The Archaeology of Anatolia. Vol. III: Recent Discoveries (2017-2018).* Newcastle upon Tyne: Cambridge Scholars Publishing. pp.15-32.

Ganzelewski, M., 2000. Archäometallurgische Untersuchungen zur frühen Verhüttung von Raseneisenerzen am Kammberg bei Joldelund, Kreis Nordfriesland. In: A. Haffner, H. Jöns and J. Reichstein, eds. 2000. *Frühe Eisengewinnung in Joldelund, Kreis Nordfriesland. Ein Beitrag zur Siedlungs- und Technikgeschichte Schleswig-Holsteins. Universitätsforschungen zur Prähistorischen Archäologie,* 59. Bonn: Habelt. pp.3-100.

Gauß, R., 2016. *Zambujal und die Anfänge der Metallurgie in der Estremadura (Portugal). Technologie der Kupfergewinnung, Herkunft des Metalls und soziokulturelle Bedeutung der Innovation.* Früher Bergbau und Metallurgie auf der Iberischen Halbinsel, 1. Iberia Archaeologica, 15(1). Tübingen, Berlin: Wasmuth.

Glumac, P.D. and Todd, J.A., 1991. Eneolithic Copper Smelting Slags from the Middle Danubian Basin. In: E. Pernicka and G.A. Wagner, eds. 1991. *Archaeometry 90*. Basel, Boston, Berlin: Birkhäuser Verlag. pp.155-164.

Goldenberg, G., 1990. Die Schlacken und ihre Analysen - Relikte der Metallgewinnung und Metallverarbeitung. In: H. Steuer and H. Maus, eds. 1990. *Erze, Schlacken und Metalle - Früher Bergbau im Südschwarzwald. Freiburger Universitätsblätter,* 109. Freiburg: Rombach. pp.147-172.

Griffitts, W.R., Albers, J.P. and Öner, Ö., 1972. Massive Sulfide Copper Deposits of the Ergani Maden Area Southeastern Turkey. *Economic Geology*, 67(6), pp.701-716.

Hanilçi, N., Öztürk, H. and Kasapçı, C., 2019. Carbonate-Hosted Pb-Zn-Deposits of Turkey. In: F. Pirajno, T. Ünlü, C. Dönmez and M.B. Şahin, eds. 2019. *Mineral Resources of Turkey, Modern Approaches*. Berlin, Heidelberg: Springer, pp.497-533.

Hauptmann, A., 1985. *5000 Jahre Kupfer in Oman. Die Entwicklung der Kupfermetallurgie vom 3. Jahrtausend bis zur Neuzeit.* Der Anschnitt, Beiheft, 4. Bochum: Deutsches Bergbau-Museum. pp.1-137.

Hauptmann, A., 2003. Rationales of liquefaction and metal separation in earliest copper smelting: basics for reconstructing Chalcolithic and Early Bronze Age smelting processes. In: Associazione Italiana di metallurgia, ed. 2003. *Archaeometallurgy in Europe. International conference, 24-25-26 September 2003, Milan, Italy. Proceedings*. Milan: Associazione Italiana di Metallurgia. pp.459-468.

Hauptmann, A., 2007. *The Early Metallurgy of Copper. Evidence from Faynan. Jordan*. Berlin, Heidelberg, New York: Springer.

Hauptmann, A., 2020. *Archaeometallurgy. Material Science Aspects*. Berlin, Heidelberg, New York: Springer.

Hauptmann and Weisgerber, 1980. Third millenium BC copper production in Oman. *Revue d'Archaeometrie,* 3, pp.131-138.

Hauptmann, A. and Weisgerber, G., 1996. The Early Production of Metal in the Near East. In: B. Bagolini and F. LoSchiavo, eds. 1996. *The Copper Age in the Near East and Europe. 13th Congress of the International Union of Prehistoric and Protohistoric Sciences, Forli*. Forli: Abaco Edizioni. pp.95-101.

Hauptmann, A. and Wagner, I., 2007. Prehistoric Copper Production at Timna: TL-dating and Evidence from the East. In: S. La Niece, D. Hook and P. Craddock, eds. 2007. *Metals and Mines. Studies in Archaeometallurgy*. London: British Museum; Archetype Publications. pp.67-75.

Hauptmann, A. and Löffler, I., 2013. Technological Innovations and Organisational Structures of Prehistoric Mining and Metal Production – Examples from Faynan, Jordan. In: S. Burmeister, S. Hansen, M. Kunst and N. Müller-Scheeßel, eds. 2013. *Metal Matters. Innovative Technologies and Social Change in Prehistory and Antiquity.* Deutsches Archäologisches Institut. Menschen-Kulturen-Traditionen 12. Rahden/Westfalen: Marie Leidorf. pp.65-90.

Hauptmann, A., Lutz, J., Pernicka, E. and Yalçın, Ü., 1993. Zur Technologie der frühesten Kupferverhüttung im östlichen Mittelmeerraum. In: M. Frangipane, H. Hauptmann, M. Liverani, P. Matthiae and M. Mellink, eds. 1993. *Between the Rivers and Over the Mountains. Archaeologica Anatolica et Mesopotamica Alba Palmieri Dedicata.* Rome: Sapienza University of Rome. pp.541-572.

Hauptmann, A., Schmitt-Strecker, S., Begemann, F. and Palmieri, A., 2002. Chemical Composition and Lead Isotopy of Metal Objects from the „Royal" Tomb and Other Related Finds at Arslantepe. Eastern Anatolia. *Paléorient*, 28(2), pp.43-70.

Hauptmann, A., Rehren, T. and Schmitt-Strecker, S., 2003. Early Bronze Age copper metallurgy at Shahr-i Sokhta, reconsidered. In: Th. Stöllner, G. Körlin, G. Steffens and J. Cierny, eds. 2003. *Man and Mining. Studies in honour of Gerd Weisgerber on occasion of his 65th birthday. Der Anschnitt, Beiheft,* 16. Bochum: Deutsches Bergbau-Museum. pp.197-213.

Hauptmann, A. et al. How to handle crucibles: News from Arslantepe VII, in prep.

Heil, N., Hauptmann, A., Di Nocera, G.M. and Stöllner, Th., 2022. The Dawn of Metallurgy at Chalcolithic Arslantepe: Metal Finds and Other Metallurgical Remains from Level VII. *Metalla*, 26.2, pp.87-112.

Heimann, R.B. and Maggetti, M., 2014. *Ancient and Historical Ceramics. Materials, Technology, Art, and Culinary Traditions*. Stuttgart: Schweizerbart Science Publishers.

Hess, K., 1998. *Zur frühen Metallurgie am oberen Euphrat: Untersuchungen an archäometallurgischen Funden vom Arslantepe aus dem 4. und 3. Jahrtausend v. Chr.* Ph. D. Johann Wolfgang Goethe University of Frankfurt a.M.

Keesmann, I., 1989. Chemische und mineralogische Detailuntersuchungen zur Interpretation eisenreicher Schlacken. In: R. Pleiner, ed. 1989. *Archaeometallurgy of Iron. International Symposium of the Comité pour la sidérurgie ancienne de l'UISPP, Liblice 5-9 October 1987.* Prague: Archaeolocigal Institute ČSAV. pp.17-34.

Keesmann, I., Kronz, A. and Maier, P., 1994. Zur Kupfertechnologie von Los Millares (Provinz Almeria, Südwest Spanien). *Berichte der Deutschen Mineralogischen Gesellschaft,* 1, p.134.

Klein, S., Lahaye, Y., Brey, G.P. and Von Kaenel, H.M. 2004. The Early Roman Imperial Aes Coinage II: Tracing Copper Sources by Lead- and Copper-Isotope Analysis – Copper Coins of Augustus and Tiberius. *Archaeometry,* 46(3), pp.469-480.

Kondoh, S., Kitamura, M. and Morimoto, N., 1985. Synthetic Laihunite, an Oxidation Product of Olivine. *American Mineralogist*, 70, pp.737-746.

Kraeff, A., 1963., Geology and Mineral Deposits of the Hopa-Murgul Region (Western Part of the Province of Artvin, NE Turkey). *Bulletin of the Mineral Research and Exploration,* 60, pp.45-60.

Kronz, A. and Keesmann, I., 2005. Fayalitische Schmelzsysteme – Ein Beitrag zur vorneuzeitlichen Eisen- und Buntmetalltechnologie im Dietzhölztal (Lahn-Dill-Gebiet, Hessen). In: A. Jockenhövel and C. Willms, eds. 2005. *Das Dietzhölzetal-Projekt. Archäometallurgische Untersuchungen zur Geschichte und Struktur der mittelalterlichen Eisengewinnung im Lahn-Dill-Gebiet (Hessen).* Münster: Beiträge zur ur- und frühgeschichtlichen Archäologie. pp.403-499.

Kuşcu, I., Tosdal, R. and Gençalioğlu-Kuşcu, G., 2019. Porphyry-Cu Deposits of Turkey. In: F. Pirajno, T. Ünlü, C. Dönmez and M.B. Şahin, eds. 2019. *Mineral Resources of Turkey, Modern Approaches*. Berlin; Heidelberg: Springer. pp.337-425.

Laschimke, R. and Burger, M., 2018. Die Herstellung von kupferzeitlichen Äxten mit Schaftloch – archäometallurgische Experimente. *Metall,* 6, pp.239-243.

Laschimke, R. and Burger, M., 2020. Archäometallurgische Experimente zur Herstellung von kupferzeitlichen Schaftlochäxten. *Experimentelle Archäologie in Europa,* 19, pp.26-34.

Lehner, J.W. and Yener, K.A., 2014. Organization and Specialization of Early Mining and Metal Technology in Anatolia. In: B.W. Roberts and C.P. Thornton, eds. 2014. *Archaeometallurgy in Global Perspective. Methods and Syntheses.* New York: Springer. pp.529-558.

Leuzinger, U., 1997. Die jungsteinzeitlichen Kupferfunde aus dem Kanton Thurgau. *Archäologie der Schweiz*, 20, pp.51-53.

Lowell, J.D. and *Guilbert,* J.M., *1970.* Lateral and Vertical Alteration-Mineralization Zoning in Porphyry Ore Deposits. *Economic Geology,* 65, pp.373-408.

Lutz, J., 1990. *Geochemische und mineralogische Aspekte der frühen Kupferverhüttung in Murgul/Nordost-Türkei.* Ph. D. University Heidelberg.

Lutz, J., Wagner, G.A. and Pernicka, E., 1994. Chalkolithische Kupferverhüttung in Murgul, Ostanatolien. In: R.B. Wartke, ed. 1994. *Handwerk und Technologie im Alten Orient*. Mainz: Philip v. Zabern. pp.60-66.

Maddin, R., Muhly, J.D. and Stech, T., 1999. Early Metalworking at Çayönü. In: A. Hauptmann, E. Pernicka, T. Rehren and Ü. Yalçın, eds. 1999. *The Beginnings of Metallurgy. Proceedings of the International Conference "The Beginnings of Metallurgy", Bochum, 1995. Der Anschnitt, Beiheft*, 9. Bochum: Deutsches Bergbau-Museum. pp.37-44.

Maresch, W., Schertl, H.P., Medenbach, O., 2014. *Gesteine. Systematik, Bestimmung, Entstehung.* Schweizerbart, Stuttgart.

Meier, D.M.P., 2015. *Traces of protohistorical metallurgical activities during the 3rd millennium BCE in East Iran with a special focus on the case of Shahdad in the Dasht-eh Lut (Kerman province).* Ph. D. Freie Universität Berlin.

Merkel, J. and Rothenberg, B., 1997. The earliest steps to copper metallurgy in the western Arabah. In: A. Hauptmann, E. Pernicka, T. Rehren and Ü. Yalçın, eds. 1999. *The Beginnings of Metallurgy. Proceedings of the International Conference "The Beginnings of Metallurgy", Bochum, 1995. Der Anschnitt, Beiheft*, 9. Bochum: Deutsches Bergbau-Museum. pp.149-165.

Metten, B., 2003. Beitrag zur spätbronzezeitlichen Kupfermetallurgie im Trentino (Südalpen) im Vergleich mit anderen prähistorischen Kupferschlacken aus dem Alpenrau. *Metalla,* 10(1-2), pp.1-122.

Migineishvili, R., 2005. Hybrid nature of the Madneuli Cu-Au deposit, Georgia. Au-Ag-Te-Se deposits. *Geochemistry, Mineralogy and Petrology*, 43, pp.128-132.

Moritz, R. and Baker, T., 2019. Metallogeny of the Tethyan Orogenic Belt: From Mesozoic Magmatic Arcs to Cenozoic Back-Arc and Postcollisional Settings in Southeast Europe, Anatolia, and the Lesser Caucasus: An Introduction. *Economic Geology,* 114(7), pp.1227-1235.

Muan, A., 1955. Phase Equilibria in the System FeO-Fe2O3-SiO2. *Journal of the Minerals, Metals & Materials Society,* pp.965-976.

Müller-Karpe, A., 1994. *Altanatolisches Metallhandwerk.* Offa-Bücher 75. Neumünster: Wachholtz-Verlag.

Neuninger, H., Pittioni, R. and Siegl, W., 1964. Frühkeramikzeitliche Kupfergewinnung in Anatolien. *Archaeologia Austriaca,* 35, pp.98-110.

Noll, W. and Heimann, R.B., 2016. *Ancient Old World Pottery. Materials, Technology, and Decoration*. Stutgart: Schweizerbart Science Publishers.

Oelsen, W., 1952. Die Desoxydation von Kupferschmelzen mit Eisen, mit Phosphor und mit Schwefel. *Giesserei, Technisch-wissenschaftliche Beihefte,* 618, pp.383-387.

Özbal, H., Adriaens, A.M. and Earl, B., 1999. Hacinebi Metal Production and Exchange. *Palèorient,* 25(1), pp.57-65.

Özdoĝan, M. and Özdoĝan, A., 1999. Archaeological evidence on the early metallurgy at Çayönü Tepesi. In: A. Hauptmann, E. Pernicka, T. Rehren and Ü. Yalçın, eds. 1999. *The Beginnings of Metallurgy. Proceedings of the International Conference "The Beginnings of Metallurgy", Bochum, 1995. Der Anschnitt, Beiheft*, 9. Bochum: Deutsches Bergbau-Museum. pp.13-22.

Palmieri, A., 1973. Scavi nell‘ area sud-occidentale d i Arslantepe - Ritrovamento di una struttura templare dell‘ antica eta del bronze. *Origini,* 7, pp.55-179.

Palmieri, A. and Morbidelli, P., 2003. Archaeometric Study on Crucibles from Arslantepe, Turkey (IV-II mill. BC). In: S. Di Pierro, V. Serneels and M. Maggetti, eds. 2003. *Ceramic in the Society, Proceedings of the 6th European Meeting on Ancient Ceramics, Fribourg Switzerland, 3-6 October 2001*. Fribourg: Department of Geosciences, Mineralogy and Petrography. pp.231-243.

Palmieri, A., Sertok, K. and Chernykh, E., 1993. From Arslantepe Metalwork to Arsenical Copper Technology in Eastern Anatolia. In: M. Frangipane, H. Hauptmann, M. Liverani, P. Matthiae and M. Mellink, eds. 1993. *Between the Rivers and Over the Mountains. Archaeologica Anatolica et Mesopotamica Alba Palmieri Dedicata.* Rome: Sapienza University of Rome. pp.573-599.

Palmieri, A.M., Hauptmann, A. and Sertok, K., 1996. Additional Data of Ores for East-Anatolian Metallurgy. In: T.C. Kültür Bakanlığı ed. 1996. *Anıtlar ve Müzeler Genel Müdürlüğü. XI. Arkeometri Sonuçları Toplantısı. Ankara, May 29–June 2, 1995.* Ankara: T.C. Kültür Bakanlığı Milli Kütüphane Basımevi. pp.167-180.

Palmieri, A.M., Hauptmann, A., Hess, K. and Sertok, K., 1996a. The composition of ores and slags found at Arslantepe, Malatya. In: Ş. Demirci, A.M. Ozer and G.D. Summers, eds. 1996. *Archaeometry 94. Proceedings of the 29th International Symposium on Archaeometry, Ankara, 9-14 May 1994*. Ankara: Tübitak. pp.447-449.

Palmieri, A., Frangipane, M., Hauptmann. A. and Hess, K., 1999. Early metallurgy at Arslantepe during the Late Chalcolithic and the Early Bronze Age IA-IB periods. In: A. Hauptmann, E. Pernicka, T. Rehren and Ü. Yalçın, eds. 1999. *The Beginnings of Metallurgy. Proceedings of the International Conference "The Beginnings of Metallurgy", Bochum, 1995. Der Anschnitt, Beiheft*, 9. Bochum: Deutsches Bergbau-Museum. pp.141-148.

Palumbi, G., 2021. The "Royal Tomb" at Arslantepe and the 3rd Millennium BC in Upper Mesopotamia. In: L. Giemsch and S. Hansen, eds. 2021. *The Caucasus / Der Kaukasus. Bridge between the urban centres in Mesopotamia and the Pontic steppes in the 4th and 3rd millennium BC. Brücke zwischen den urbanen Zentren Mesopotamiens und der pontischen Steppe im 4. und 3. Jahrtausend v. Chr. Proceedings of the Caucasus conference Frankfurt am Main, November 28 - December 1, 2018. Schriften des Archäologischen Museums,* 34. Frankfurt am Main. pp.235-249.

Palumbi, G. and Chataigner, C., 2014. The Kura-Araxes Culture from the Caucasus to Iran, Anatolia and the Levant. A synthesis. *Paléorient,* 40, pp.247-260.

Parvaz, D.B., 2014. *Oxidation Zones of Volcanogenic Massive Sulphide Deposits in the Troodos Ophiolite, Cyprus: Targeting Secondary Copper Deposits*. Ph. D. University of Exeter.

Pearce, M., Merkel, S., Hauptmann, A. and Nicolis, F., 2022. The smelting of copper in the third millennium cal BC Trentino, north-eastern Italy. *Archaeological and Anthropological Sciences*, 14(1), 10, pp.1-21.

Radivojevic, M., Rehren, T., Farid, S., Pernicka, E. and Camurcuoğlu, D., 2017. Repealing the Çatalhöyük extractive metallurgy: The green, the fire and the 'slag'. *Journal of Archaeological Science,* 86, pp.101-122.

Ramdohr, P. and Strunz, H., 1978. *Klockmanns Lehrbuch der Mineralogie*. Stuttgart: Ferdinand Enke Verlag.

Romieux, J., 1941. *Rapport d'ensemble géologique et miniére sur le gisements. The 5th report on Ergani Maden. Etibank no. 266*. unpublished.

Rose, D., Endlicher, G. and Mucke, A., 1990. The Occurrence of "Iscorite" in Medieval Iron Slags. *Historical Metallurgy,* 24(1), pp.27-32.

Rothenberg, B., 1973. *Timna. Das Tal der biblischen Kupferminen*. Bergisch Gladbach: Gustav Lübbe.

Rothenberg, B. ed., 1990. *The Ancient Metallurgy of Copper. Researches in the Arabah 1959-1984, 2.* London: Institute for Archaeo-Metallurgical Studies, University College London.

Rothenberg, B. and Blanco-Freijeiro, A., 1981. *Ancient Mining and Metallurgy in South-West Spain.* Institute of Archaeometallurgical Studies (IAMS), London.

Ryndina, N., Indenbaum, G. and Kolosova, V., 1999. Copper Production from Polymetallic Sulphide Ores in the Northeastern Balkan Eneolithic Culture. *Journal of Archaeological Science,* 26, pp.1059-1068.

Salkield, L.U., 1987. *A Technical History of the Rio Tinto Mines: some notes on exploitation from pre-Phoenician times to the 1950s.* Institute of Mining and Metallurgy, London.

Salzmann, E., 2019. *Silver, Copper and Bronze in Early Dynastic Ur, Mesopotamia. A High-Resolution Analysis Approach.* Der Anschnitt, Beiheft, 41. Rahden/Westfalen: VML, Bochum: Deutsches Bergbau-Museum.

Sayre, E.V., Yener, A. and Joel, E.C., 1992. Statistical Evaluation of the Presently Accumulated Lead Isotope Data from Anatolia and Surrounding Regions. *Archaeometry,* 34(1), pp.73-105.

Sayre, E.V., Joel, E.C. and Blackman, M.J., 2001. Stable Lead Isotope Studies of Black Sea Anatolian Ore Sources and Related Bronze Age and Phrygian Artefacts from Nearby Archaeological Sites. Appendix: New Central Taurus Ore Data. *Archaeometry,* 43(1), pp.77-115.

Schäfer, M.W., 1983. Measurements of iron (III)-rich fayalites. *Nature,* 303, pp.325-327.

Schneider, H.J., Özgür, N. and Palacios, C.M., 1988. Relationship between Alteration, Rare Earth Element Distribution, and Mineralization of the Murgul Copper Deposits, Northeastern Turkey. *Economic Geology,* 83, pp.1238-1246.

Seeliger, T., Pernicka, E., Wagner, G.A., Begemann, F., Schmitt-Strecker, S., Eibner, C. and Öztunali, Ö., 1985. Archäometallurgische Untersuchungen in Nord- und Ostanatolien. *Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz,* 3, pp.597-659.

Shalev, S., 1994. The Change in Metal Production from the Chalcolithic Period to the Early Bronze Age in Israel and Jordan. *Antiquity,* 68, pp.630-637.

Smirnov, S.S., 1954. *Die Oxidationszone sulfidischer Lagerstätten*. Berlin: Akademie-Verlag.

Smuts, J., Steyn, J.G.D. and Boeyens, J.C.A., 1969. The Crystal Structure of an Iron Silicate, Iscorite. *Acta Crystallographica*, 25(7), pp.1251-1255.

Stanton, R.L., 1972. *Ore Petrology.* New York: McGraw-Hill.

Stöllner, T., 2018. What is an Ore Deposit? Approaches from Geoscience and Archaeology in Understanding the Usage of Deposits. *Metalla,* 24(2), pp.87-110.

Stöllner, T., 2021. Sakdrisi and the Gold of the Transcaucasus. In: L. Giemsch and S. Hansen, eds. 2021. *The Caucasus / Der Kaukasus. Bridge between the urban centres in Mesopotamia and the Pontic steppes in the 4th and 3rd millennium BC. Brücke zwischen den urbanen Zentren Mesopotamiens und der pontischen Steppe im 4. und 3. Jahrtausend v. Chr. Proceedings of the Caucasus conference Frankfurt am Main, November 28 - December 1, 2018. Schriften des Archäologischen Museums,* 34. Frankfurt am Main. pp.101-118.

Stos-Gale, S., Maliotis, G. and Gale, N., 1998. A preliminary survey of the Cypriot slag heaps and their contribution to the reconstruction of copper production on Cyprus. In: T. Rehren, A. Hauptmann and J.D. Muhly, eds. 1998. *Metallurgica Antiqua. In honour of Hans Gert Bachmann and Robert Maddin. Der Anschnitt, Beiheft,* 8. Bochum: Deutsches Bergbau-Museum. pp.235-262.

Taylor, R., 2009. *Ore Textures. Recognition and Interpretation*. Berin, Heidelberg, New York: Springer.

Taylor, R., 2011. *Gossans and Leached Cappings. Field Assessment.* Berin, Heidelberg, New York: Springer.

Temur, S., 1991. Bolkardaği (Ulukişla-Niğde) Yöresi Çinko-Kurșun Yataklarinin Petrografik Incelemesi. *Maden Tetkik ve Arama Dergisi,* 112, pp.71-84.

Ucurum, A., Demir C.S., Otlu, N., Erturk, M., Ekici, T., Kirk, J., Ruiz, J., Mathur, R. and Arehart, G.B., 2021. Re-Os Age and Stable Isotope (O-H-S-Cu) Geochemistry of North Eastern Turkey's Kuroko-Type Volcanogenic Massive Sulfide Deposits: An Example from Cerattepe-Artvin. *Minerals,* 11(2), pp.1-23.

Vignola, C., Marzaioli, F., Balossi Restelli, F., Di Nocera, G.M., Frangipane, M., Masi, A., Passiarello, I., Sadori, L. and Terrasi, F., 2019. Changes in the Near Eastern chronology between the 5th and the 3rd millennium BC: New AMS ^{14}C dates from Arslantepe (Turkey). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* 456, pp.276-282.

Wagner, G.A., Pernicka, E., Seeliger T., Lorenz, I., Begemann, F., Schmitt-Strecker, S., Eibner, C., Öztunali, Ö., 1986. Geochemische und isotopische Charakteristika früher Rohstoffquellen für Kupfer, Blei, Silber und Gold in der Türkei. *Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz*, 33, pp.723-752.

Wagner, G.A., Begemann, F., Eibner, C., Lutz, J., Öztunali, Ö., Pernicka, E. and Schmitt-Strecker, S., 1989. Archäometallurgische Untersuchungen an Rohstoffquellen des frühen Kupfers Ostanatoliens. *Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz,* 36, pp.637-686.

Wagner, G.A. and Öztunali, Ö., 2000. Prähistorische Kupferquellen in der Türkei. In: Ü. Yalçin, ed. 2000. *Anatolian Metal I. Der Anschnitt, Beiheft*, 13. Bochum: Deutsches Bergbau-Museum. pp.31-67.

Yalçın, Ü. ed., 2000. *Anatolian Metal I. Der Anschnitt, Beiheft*, 13. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2002. *Anatolian Metal II. Der Anschnitt, Beiheft*, 15. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2005. *Anatolian Metal III. Der Anschnitt, Beiheft*, 18. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2008. *Anatolian Metal IV. Der Anschnitt, Beiheft*, 21. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2011. *Anatolian Metal V. Der Anschnitt, Beiheft*, 24. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2013. *Anatolian Metal VI. Der Anschnitt, Beiheft*, 25. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü. ed., 2016. *Anatolian Metal VII. Anatolien und seine Nachbarn vor 10.000 Jahren. Anatolia and neighbours 10.000 years ago. Der Anschnitt, Beiheft*, 31. Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü., 2017. The Beginnings of Metal Use in West Asia. In: A. Tsuneki, K. Hisada and S. Yamada, eds. 2017. *Ancient West Asian Civilization. Geoenvironment and Society in the Pre Islamic Middle East.* Berlin; Heidelberg; New York: Springer. pp.115-132.

Yalçın, Ü. ed., 2018. *Anatolian Metal VIII. Eliten – Handwerk – Prestigegüter. Der Anschnitt, Beiheft*, 39. Rahden/Westfalen: VML, Bochum: Deutsches Bergbau-Museum.

Yalçın, Ü., Hauptmann, A., Hauptmann, H. and Pernicka, E., 1992. Norsuntepe Geç Kalkolitik Qagi Bakir Madenciligi üzerine Arkeometallurjik Arastirmalar, VIII. *Arkeometrie Sonuclari Toplantisi*, pp.381-389.

Yazar, E.A., Arslan, M., Kadir, S. and Temizel, I., 2015. Alteration mineralogy, lithochemistry and stable isotope geochemistry of the Murgul (Artvin, NE Turkey) volcanic hosted massive sulfide deposit: Implications for the alteration age and ore forming fluids. *Ore Geology Reviews,* 66, pp.219-242.

Yener, K.A., 2021. *Göltepe Excavations: Tin Production at an Early Bronze Age Mining Town in the Central Taurus Mountains, Turkey*. Philadelphia: Instap Publication.

Yiğit, O., 2009. Mineral Deposits of Turkey in Relation to Tethyan Metallogeny: Implications for Future Mineral Exploration. *Economic Geology,* 104, pp.19-31.

Authors

Andreas Hauptmann (Corresponding author)
Deutsches Bergbau-Museum Bochum
Research Division
Archaeometallurgy
Am Bergbaumuseum 31
D-44791 Bochum
andreas.hauptmann@bergbaumuseum.de

Nikolas Heil
Ruhr University Bochum /
Deutsches Bergbau-Museum Bochum
Institute of Archaeological Studies / Research Division
Archaeometallurgy
Am Bergbaumuseum 31
D-44791 Bochum
nikolas.heil@ruhr-uni-bochum.de

Gian Maria di Nocera
Department of Humanities, Communication and Tourism (DISUCOM) University of Tuscia Largo dell'Università s.n.c. (loc. Riello)
01100-Viterbo
gm.dinocera@unitus.it

Thomas Stöllner
Ruhr University Bochum /
Deutsches Bergbau-Museum Bochum
Institute of Archaeological Studies / Research Division
Mining Archaeology
Am Bergbaumuseum 31
D-44791 Bochum
thomas.stoellner@bergbaumuseum.de
thomas.stoellner@ruhr-uni-bochum.de