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Early Bronze Age copper metallurgy at Shahr-i Sokhta (Iran), reconsidered

Summary

Between 2700 and 2500 BC, mixed sulphidic and oxidic copper ores were brought to the urban site of Shahr-i Sokhta in eastern Iran to be smelted in crucibles. The main ore component to be extracted was copper oxide with remnants of copper sulphide, following the co-smelting process. No deliberate attempt was made to roast the copper sulphide in order to exploit its copper content. After the smelt, the entire charge, comprising metal, matte and slag, was poured or tapped from the crucibles into a separate receptacle, where the metal / matte melt separated underneath the slag. The separation of copper metal was improved by its interaction with low-melting copper sulphides. Detailed analyses of texture and phase content of the slag provide information on the cooling process and the origin of various inclusions. The role of iron arsenide (speiss) from the site is discussed in the context of early arsenical copper. Lead isotope ratios of archaeometallurgical finds offer proof of a common, though probably complex origin of ores, slags, matte and copper, and indicate a possible provenance of ores from the Iranian Malik-i Siah Mountains west of Shahr-i Sokhta. The scale of production indicates a domestic type of industry, while the technology being used appears more developed than that used throughout the Middle East, and can be seen as the beginnings of full slagging operations.

Keywords:

Shahr-i Sokhta, Iran, Early Bronze Age, copper metallurgy, domestic mode production, matte, speiss, co-smelting, liquation, lead isotope abundance ratios.

Zusammenfassung

Zwischen 2700 und 2500 v. Chr. wurden von außerhalb gelegenen Lagerstätten sulfidische und oxidische Kupfererze in die Siedlung von Shahr-i Sokhta (Ostiran) gebracht und dort in kleinen Schmelztiegeln verhüttet. Es wurde nach dem Röstreaktions-Schmelzen gearbeitet, wobei hauptsächlich oxidische Kupfererze mit Restanteilen von Sulfiden geschmolzen wurden. Der entstehende Kupferstein wurde nicht geröstet, um das enthaltene Metall zu extrahieren. Die gesamte Charge (Schlacke, Stein, Metall) wurde nach beendetem Schmelzgang in eine Grube gegossen, wobei sich Stein und Kupfer als Regulus unter einem Schlackenküchlein trennten. Dies wurde durch den niedrigschmelzenden Stein deutlich begünstigt. Detaillierte Phasen- und Gefügeanalysen erbrachten wichtige Informationen zur Abkühlungsgeschichte der Schlacken. Der Fund eines Stück Speiss wird im Kontext der Arsenkupfer-Problematik der Bronzezeit diskutiert. Bleiisotopenanalysen deuten darauf hin, dass Kupfer und Stein wahrscheinlich aus den in Shahr-i Sokhta gefundenen Erzen geschmolzen wurden. Diese stammen vermutlich aus Lagerstätten in den Malik-i Siah Gebirgsketten westlich der Siedlung. Der Produktionsumfang entspricht einer Haushaltsmetallurgie. Die angewandten hüttenmännischen Techniken hatten einen für diese Zeit sehr hohen Stand erreicht und sind als Anfangsphase des Schlackenschmelzens zu verstehen.

Schlagwörter:

Shahr-i Sokhta, Iran, Frühbronzezeit, Kupfermetallurgie, Haushaltsmetallurgie, Kupferstein, Speiss, Röstreaktionsverfahren, Ausschmelzen, Bleiisotopie.

Résumé

Entre 2700 et 2500 av. J.-C., différents minerais de cuivre sulphidiques et oxidiques ont été transportés à Shahr-i-Sokhta (Est de l'Iran) pour y être fondu dans des petits creusets. On travaillait selon la méthode de grillage-réaction-fusion en fondant surtout des minerais oxidiques avec des restes de sulfides. La matte de cuivre produite n'était pas grillée pour en extraire le métal. L'ensemble (scorie, matte, métal) était versé après la fusion dans une fosse ou la matte et le cuivre se séparaient comme regulus sous un petit gâteau de scorie. Ce procédé était nettement favorisé par la matte fondant à basse température. Des analyses détaillées des phases et des structures ont fourni des informations importantes sur la phase de retroidisse-

ment des scories. Un morceau de speiss retrouvé a fait l'objet d'une discussion sur le problème du cuivre arsenic à l'âge du bronze. Des analyses d'isotopes de plomb indiquent que le cuivre et la matte étaient probablement fondus à partir des minerais trouvés à Shar-i Sokhta, qui proviennent probablement des gisements situés dans les montagnes à l'ouest de l'habitat. La quantité de production correspond à une métallurgie de ménage. Les techniques de traitement métallurgique utilisées avaient atteint un très haut niveau pour cette époque; elles doivent être considérées comme la phase initiale de la fonte des scories.

Mots-clés:

Shahr-i Sokhta, Iran, âge de bronze précoce, métallurgie du cuivre, métallurgie de ménage, matte de cuivre, speiss, méthode grillage-reaction, fonte, isotopie du plomb.

Introduction

During his 1970 excavation of the settlement of Shahr-i Sokhta, which lies on the border region of modern day Iran, Afghanistan and Pakistan, Professor Maurizio Tosi, then of the *Istituto Italiano per il Medio ed Estremo Oriente* (ISMEO), Rome, excavated several kilograms of archaeometallurgical finds such as slags, ores and crucible fragments. Shahr-i Sokhta was a relatively short-lived urban settlement in Sistan, situated on the banks of the Hilmend river, a seasonal stream. This habitation site flourished from the late Early Bronze Age (EBA) to the Middle Bronze Age. The majority of metallurgical finds date approximately to the period from 2700 to 2500 BC; they were mainly retrieved from level VII, period II (personal communication M. Tosi). Thus, they fall between the earliest, late Neolithic, very small-scale and localised phases of copper metallurgy in the Middle East and the Iranian Plateau, and the large-scale copper production of the Middle and Late Bronze Age which formed part of a highly organised international trade and exchange system. While the EBA phase of metallurgical development is characterised by small · scale metallurgical operation, an increasing reliance on long-distance transportation of goods and specialisation in craft is beginning to emerge. The finds from Shahr-i Sokhta provide further evidence for the increasing importance of copper metallurgy during the rise of urbanism in the Middle East, a period of considerable archaeological interest and anthropological significance.

The main aim of the current study is to investigate the relationship of ores, crucible fragments, slag, matte, speiss and metal from Shahr-i Sokhta to each other, in order to identify the nature of the metallurgical operations during the Early Bronze Age period: Smelting or melting? Casting, alloying or even refining?

In 1980, when the first selection of metallurgical finds from Shahr-i Sokhta was given to Gerd Weisgerber, Maurizio Tosi's friend and colleague, Hauptmann (1980) and Hauptmann & Weisgerber (1980) published the results of their initial investigation of a few typical slag cakes from the site, along with another slag sample from Tepe Mochi, a nearby settlement. They also presented a short description of ores from Shahr-i Sokhta, mostly copper sulphides such as covellite (CuS) and chalcocite "Cu_2S", embedded in quarzitic sandstone. According to the state of the art in archaeometallurgy of the early 1980s they outlined the following model for copper smelting, thought to be characteristic for EBA metal production in this region: The ores were smelted in a „bowl hearth" which had been sunk into the ground, producing a mixture of copper and matte, i.e. copper sulphide, which separated from the slag in the liquid state. The slag cakes would have solidified and cooled in the hearth. During a second, further step, the matte would have been treated by roasting and smelting to also transform it into copper. This model led the authors to conclude that domestic mode production was carried out within this habitation site. Parallels to this proposed model have been developed subsequently at numerous sites in the Levant and in eastern Anatolia (e.g., Hauptmann et al. 1993; Shalev 1994; Levy 1995). Heskel (1982) suggested that „*sulphide metallurgy*" was present at Shahr-i Sokhta at that time, and chalcocite would have been added to copper oxide and carbonate ore in a furnace in proportions that did not require roasting of the ore („*co-smelting*" after Rostoker et al. 1989).

The systematic investigation of ores, slags and copper objects from Shahr-i Sokhta was completed in subsequent studies by Helmig (1986) and Helmig et al. (1988). A pronounced compositional variety of metals and ores was noted, and the ores that had been analysed did not fully represent the material that was smelted to produce the arsenical copper found on site. The authors doubted that any roasting had been carried out, but suggested the use of iron-rich fluxes. Due to large variations of the trace elements within the ore, slag and metal samples, however, they concluded that any reconstructed smelting processes, even in this seemingly complete archaeological ensemble, must be treated with caution. In a related study, Rehren et al. (1988) investigated the metal finds from Shahr-i Sokhta, concentrating on the phase relations between intermetallic compounds rich in arsenic and antimony, and the copper matrix. All of the objects studied were still in their as-cast condition, and their metallography mirrored the wide range of compositions found by Helmig (1986). However, no directly archaeologically relevant information emerged from this purely materials-oriented approach.

In the meantime, the entire complex of archaeometallurgical finds from Shahr-i Sokhta has become available for further studies, and following improved knowledge about ancient metal smelting in general, and the determination

of a set of lead isotope abundance ratios of ores, metals and matte from the material in particular, it was decided that we should reconsider the evidence from Shahr-i Sokhta. This would allow us to more widely investigate aspects of EBA copper metallurgy in the Afghan-Sistan region in eastern Iran. Several elements were central to this new research, due to the overall development of archaeo-metallurgy over recent years. These include the issue of crucible smelting versus smelting in furnaces during the early periods of copper metallurgy (Heskel 1982; Craddock 2001; Golden et al. 2001; Rothenberg 2002), the nature of the ore supply and the issue of co-smelting oxidic and sulphidic ores (e.g., Rostoker et al. 1989), and the origin of the arsenic (and antimony) found in the metal (e.g. Budd & Ottaway 1989; Hook et al. 1991; Keesmann & Moreno Onorato 1999), within the wider context of the organisation of metallurgical production in the settlement at Shahr-i Sokhta.

Sampling and measurements

Over the years, a large number of ores, crucible fragments, slags, and metal objects have been analysed using both chemical and mineralogical methods. The majority of chemical analyses were carried out by Helmig (1986), and we refer to his study for further details. Sixteen samples of slag were analysed by X-ray fluorescence spectrometry in the Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum. Fifteen samples of ores and 21 copper objects (prills, lumps, ingots and small finished objects) were selected for chemical analyses (atomic absorption spectroscopy (AAS), wet chemical analysis); five of the copper lumps and ingots were sampled and analysed several times to check their homogeneity. In addition, a range of ore, slag, copper, matte and speiss samples were investigated using mineralogical methods (optical and electron microscopy and X-ray diffractometry, microanalysis combined with scanning electron microscopy, electron probe micro analysis). Lead isotope abundance ratios were subsequently measured from seven ores, ten metal samples, one sample of speiss and three samples of matte by thermal ionisation solid-source mass spectrometry (TIMS).

Below, we present an up-to-date summary of the results together with an archaeological interpretation of our finds within the framework of EBA copper metallurgy.

Results and discussion

The ores

The samples initially labelled as 'ore' comprised a number of different rock samples, ranging from green metamorphic rocks ('green stones') to siliceous rocks coloured green by an impregnation with varying amounts of copper salts, and massive dark blue copper sulphide lumps with just a thin green corrosion skin. Following the chemical and mineralogical investigation, and neglecting the range of other 'green stones' mentioned, two major copper ore groups emerged, namely oxidic and sulphidic ore.

The majority of samples studied contains significant amounts of sulphides and / or sulphates with one exception; the ratio of sulphur to copper in the bulk analyses

Table 1 Chemical analyses of copper ores excavated at Shahr-i Sokhta (from Helmig 1986). Values are indicated in weight % (%) and in parts per million (ppm).

|		SS 96	SS 101/3	SS 109	SS 120	SS 133	SS 137	SS 145	SS 156 A	SS 156 B	SS 156 C	SS 160	SS 161	SS 212	SS 4	SS 176
SiO$_2$	(%)	28.3	41.3	32.3	39.6	37.9	39.1	43.5	36.0	42.2	37.7	23.6	30.3	38.7	3.2	4.3
TiO$_2$	(%)	0.18	0.58	0.44	0.05	0.45	0.16	0.03	0.02	0.04	0.43	0.16	0.54	0.43	0.02	0.07
Al$_2$O$_3$	(%)	5.8	6.9	10.8	2.8	10.9	3.7	0.84	4.0	1.6	10.6	3.1	12.5	12.2	0.55	0.74
FeO	(%)	9.3	3.6	2.5	10.0	5.8	8.1	6.3	17.9	3.8	5.3	9.9	1.9	7.1	27.3	1.7
MnO	(%)	0.18	0.26	0.35	0.33	0.60	0.05	0.18	0.28	0.35	0.58	0.20	0.17	0.66	<0.01	<0.01
MgO	(%)	1.37	1.26	1.64	0.56	3.49	0.78	0.58	1.74	1.11	3.71	1.04	2.49	2.35	0.01	0.30
CaO	(%)	16.3	12.1	14.5	27.1	28.2	1.0	35.3	30.2	31.1	27.1	16.1	11.3	30.4	<0.01	<0.01
P O	(%)	0.15	0.16	0.15	0.08	0.14	0.12	0.04	0.03	0.07	0.12	0.13	0.20	0.10	0.12	0.15
S	(%)	3.2	1.8	1.8	3.0	1.3	12.0	2.3	1.5	3.7	2.3	6.5	7.9	1.4	2.4	0.1
Cu	(%)	21.0	15.4	18.8	12.0	4.4	26.7	7.5	5.0	13.8	8.0	26.5	28.8	4.3	36.3	48.9
Zn	(ppm)	800	1200	500	300	100	500	100	200	200	200	400	500	100	260	800
Pb	(ppm)	2.2%	2.1%	55	12	4	60	9	<5	9	4	75	4	<5	0.58%	0.75%
Ni	(ppm)	25	13	28	12	34	47	5.5	75	9.0	31	26	35	21	280	13
As	(ppm)	60	0.95%	24	31	35	15	36	62	18	22	75	12	29	36	52
Sb	(ppm)	1.5	36	<0.4	1.0	1.6	<0.4	0.3	<0.4	1.3	0.8	<0.4	<0.4	0.5	3.0	6.0
Co	(ppm)	48	95	110	4	48	22	8	79	14	25	120	65	130	800	83
Bi	(ppm)	240	51	190	150	84	35	80	87	200	140	160	290	85	<1.2	6
Ag	(ppm)	16	12	<4	24	13	170	17	13	23	10	22	38	12	120	260
Cd	(ppm)	2.0	15	<0.3	1.7	0.2	0.8	1.4	0.7	1.4	<0.3	<0.3	1.0	<0.3	0.6	<0.3
Total	(%)	88.2	86.7	83.2	95.4	93.2	91.9	96.5	96.6	97.7	95.8	87.2	96.2	97.7	70.8	57.2
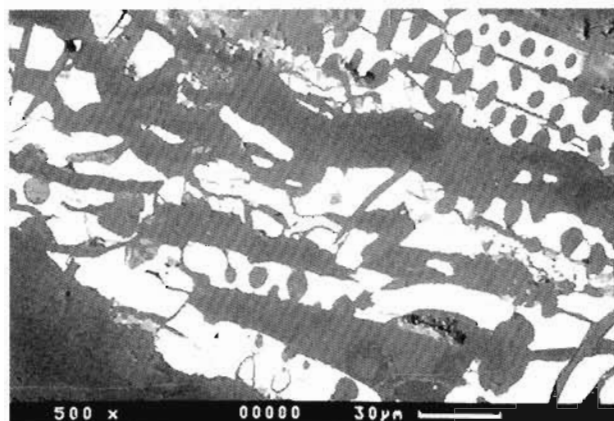
Fig. 1: Sample SS 30: Electron micrograph of the corroded speiss from Shahr-i Sokhta, showing cracked iron arsenide (white plates) in a matrix of iron hydroxides (dark). The oval shapes represent spaces initially taken up by arsenical iron, most of which is now corroded. At the bottom centre are a few surviving inclusions visible, enabling the identification of this phenomenon.

scatters from 1 : 2 to 1 : 15, with copper concentrations in the range from 4 to 50 wt% (table 1). It was argued that the primary ore minerals would hold more information regarding the nature of the ore deposit(s) exploited than the secondary minerals; thus, the investigation concentrated on the sulphidic parts of the ore. The dominating copper phases in these samples are chalcocite / digenite ('Cu_2S'), covellite (CuS) and bornite (Cu_5FeS_4). They occur as interstitials in garnet- and feldspar-bearing felsic rocks, forming massive clusters and aggregates of up to several centimetres in diameter. Minor phases in the more massive copper sulphide aggregates include magnetite (Fe_3O_4), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and graphite (C); very rarely were inclusions of other sulphides such as molybdenite (MoS_2) found. Of the three main ore minerals, only chalcocite and bornite are primary phases, while covellite is a weathering product of the other two. Chalcopyrite appears mostly as exsolution lamellae in bornite; this is typical for the disintegration of the high-temperature solid-solution phase in the ternary system iron-copper-sulphur.

The texture as well as the overall mineral association indicate that this is a skarn ore, formed from the reaction of very hot fluids with a calcareous or siliceous host rock (Einaudi et al. 1981). Typically, these reactions occur when a highly differentiated igneous body, rich in ore-bearing fluids, intrudes sedimentary or metamorphic rock units in the upper crust. The chemistry of the resulting skarn is determined by the composition of both the initial rock and the penetrating fluids which act as the carriers of the ore minerals.

The grade of the ore varies depending on the ratio of copper minerals to silicate rock; among the samples studied were several walnut-sized ones which were composed almost of pure copper sulphide, while others were merely

stained green with less than one percent of copper minerals being present.

The oxidic ore is most probably the direct in situ weathering product of the primary ore, consisting of malachite and similar secondary copper minerals closely intergrown with limonite / goethite and other iron hydroxide phases. The iron-rich phases are concentrated in veins and clusters, probably following the former complex intergrowths of iron and copper sulphides.

With a single exception the ore samples have less than 100 ppm arsenic, typically less then 50 ppm. Only sample SS 101/3 has just under one percent arsenic, together with 15 percent copper, under four percent iron and about two percent lead.

Significantly, there is every degree of intermediate ores, with both sulphidic and oxidic copper minerals being present. This ranges from an outer layer of secondary minerals surrounding a hardly affected core of sulphides, to almost completely weathered ore with just a few specks of primary mineral left. The ratio of copper to iron is broadly similar in both ore types, with a certain enrichment of iron in the secondary minerals, probably due to the lower geochemical mobility of the oxidised iron salts when compared to the copper salts.

There was remarkably little deviation from this pattern of ore paragenesis among the studied samples, indicating a rather stable source of ore supply over the period of copper production at Shahr-i Sokhta. According to the available geological literature, such as Abdullah & Chmyriov (1977), Taghizadeh & Mallakpour (1977), Wolfart & Wittekindt (1980) and several Records of the Geological Survey of Pakistan from the early 1970s, such skarn deposits are frequent in the mountain ranges surrounding the Sistan depression. The nearest sources are in a distance of ca. 100 km from Shahr-i Sokhta in the northwest.

Note should be taken of the abundance of other 'green stones' among the metallurgical material sent to Bochum for analysis; they were mostly metamorphic rocks of serpentinitic or amphibolitic composition. Whether their presence in the assemblage reflects a purely colour-based sampling strategy of the EBA smelters or that of the modern field archaeologist is set to remain an unanswered question, at least for the present.

The speiss

A few samples stood out from the copper-dominated material as being very friable, dark brown and rusty in colour, and responding to a hand-held magnet. The study of one of these fragments (SS 30) identified iron and arsenic to be the dominating components in a strongly weathered matrix (bulk analysis 41 wt% Fe, 18 wt% As, 0.5 wt% Sb,

0.15 wt% Cu. The low total is due to the corrosion of the material.). Within the predominant corrosion products, some areas survived, comprised primarily of long lathes of iron arsenide (Fe_2As), with small (10 to 100 µm) oval inclusions of metallic iron with up to eight percent arsenic, and some iron sulphide (fig. 1). Clearly, this is an artificial product, speiss, rather than a natural mineral aggregate. The metallic iron is most strongly affected by weathering, followed by the iron arsenide, while the sulphide seems to have remained unaffected. Due to the severity of corrosion, it is difficult to estimate the original ratio of metallic iron to iron arsenide; our impression is that the latter dominated by far. No copper phase was identified, matching the low overall copper content found by bulk chemical analysis.

The close similarity in isotopic composition of the speiss (SS 30) and the copper lump SS 101/2 (see below) is of special interest. It is often a problem in Chalcolithic or EBA archaeometallurgy to find copper ores high enough in arsenic to make them suitable as a source for artefacts (Schmitt-Strecker et al. 1992; Begemann et al. 1994; Hauptmann et al. 2003). This metal lump contains 5.8 wt%, the highest amount of arsenic found in any of the metal objects analysed from Shahr-i Sokhta. Despite this, we do not see this as convincing proof for the intentional mixing of copper and iron arsenide to produce arsenical copper. If speiss such as the sample SS 30 would have been added to molten copper, we should find the metal to be enriched in iron too. This is not the case: the iron concentrations in many of the copper objects are at the same level (see table 4). In addition, the three finished objects do not show any consistency in their arsenic contents: it varies between 70 ppm and 2.4%. We therefore argue that the arsenical copper was produced by smelting copper ores higher in arsenic than typically discovered at Shahr-i Sokhta; the identification of one such arsenic-rich ore underlines the plausibility of this assumption. The speiss may have its origin in the erroneous heat treatment of an odd piece of arsenopyrite; a direct origin from the copper-dominated ore seems unlikely in view of the almost non-existent copper content of the sample.

In view of the ongoing discussion regarding the origin of the arsenic in some of the metal objects, these findings generated considerable interest as a possible source of arsenic. In order to discuss the role of this material within the wider chaîne d'opératoire at Shahr-i Sokhta, it is necessary to discuss whether it is more likely to be a by-product of the copper metallurgy, or whether it is a possible raw material or additive. The occurrence of speiss in base metal metallurgy is well known, and a number of examples have been published in the past. The most pertinent one, in terms of their iron dominance, is a Hittite find from Boğazköy (Muhly et al. 1985). Here, a very similar complex mixture of metallic arsenical iron, intergrown with iron arsenide and iron sulphide, was interpreted as evidence for the smelting of an arsenical iron ore such as arsenopy-
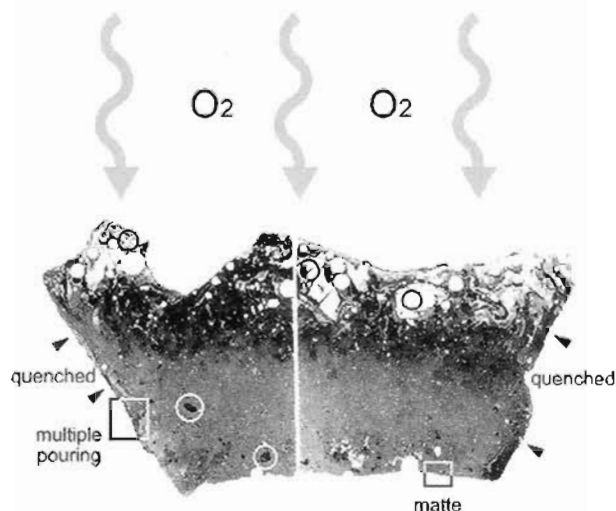

Fig. 2: Sample SS 141: Section of a typical slag cake from Shahr-i Sokhta, composed of two thin sections. The internal structure shows a horizontal division into two parts. The upper part is rich in white inclusions of gangue/ore (O) and gas bubbles embedded in a dark matrix. It is enriched in magnetite and glass that formed under the access of air during cooling. Note the streaks of glass. The lower part is almost fully crystallized, it contains predominantly hedenbergite and a ferroan wollastonite and reveals inclusions of ore (O). The side surface is quenched and indicates that the slag was poured into an irregularly formed cold ground. Multiple layering of magnetite may result from multiple pouring. The rim at the bottom shows the size of the original regulus of matte and copper that could not be fully separated from the slag, as remains of matte at the bottom show. Upper diameter of the slag: 8 cm.

rite. However, the resulting iron metal must have been useless, due to the extreme brittleness of the alloy. At present, no positive interpretation is available as to the reason for the existence of this find. It has been described in the context of a number of iron ingots found together in the same room, but no direct evidence relates the speiss to the primary production of this metal.

Other examples of archaeological speiss are predominantly from base metal contexts (Keesmann 1999; Rehren et al. 1999). In these cases, however, the speiss invariably contains considerable amounts of base metals, either copper and / or lead, both as mechanically incorporated particles of discrete phases and as solid solution in the iron arsenide. None of this has been observed from Shahr-i Sokhta, making it unlikely that the speiss had formed as a by-product of copper metallurgy. Thus, it can only be interpreted as a material in its own right; whether as a raw material for the production of arsenical copper or completely independent of copper metallurgy. The archaeological documentation, unfortunately, does not provide enough information to discuss the direct context in which the material was found.

In conclusion, the material is most likely smelted arsenopyrite. The almost complete absence of copper makes it highly unlikely that this has formed as a layer of

floating speiss between copper metal and matte or slag of a solidifying complex smelt. It could theoretically have served as a raw material to be added to copper to produce arsenical copper; this will be discussed further below.

The slags

Macroscopic

The most frequent and characteristic type of slag found at Shahr-i Sokhta consists of cakes with a height of ca. 2 cm, a diameter of 8-12 cm at the top surface and ca. 6 cm at the bottom (fig. 2). The upper surface is rough and highly irregular with coarse porosity and fuel impressions, while at the lower surface, the side forms a rim that juts out a few millimetres over the flat and smooth bottom. It marks out the impression of a matte regulus that separated from the overlying slag in the liquid state. As shown by several finds, these reguli formed flat buttons consisting of copper and matte (with a composition of nearly pure copper sulphide, "Cu_2S") in roughly equal amounts. Typically, the two copper-rich phases separated into two layers, following their different densities, and only one such button was found to consist of almost pure copper oxide. We can not currently decide of whether these finds are representative for the relative proportions of sulphide and metal produced in each smelt, or were considered failures and hence discarded. Occasionally we observed un-decomposed relics of the raw materials in the slag. Their size indicates that

Fig. 3: Sample SS 89d: Droplet of ruby-red glassy slag. The streaks are caused by layers of copper and copper oxide inclusions. Width of the sample: 2.8 cm. Transmitting light.

the ore was typically crushed to less than ca. 5 mm; this must have led to the production of much finer material. Slags of comparable shape and design as those from Shahr-i Sokhta are known from other sites. For instance, Lutz (1987) reported small slag cakes from the 4th millennium BC site of Murgul on the southern Black Sea coast. These cakes show remains of Fe-rich matte at the bottom. Inclusions of such matte were also observed in hand-sized slag cakes from Nevali Çori in Eastern Anatolia (Hauptmann et al. 1993). Bamberger & Wincierz (1990) were successful in the experiments they conducted to achieve a

Table 2: Chemical analyses of Early Bronze Age copper smelting slags from Shahr-i Sokhta (from Helmig 1986). Values are given in weight %. n.d. = not detected.

| Sample	SS 3	SS 5	SS 23	SS 31 a	SS 31 b	SS 31 c	SS 34	SS 40 a	SS 40 b	SS 41	SS 65	SS 84
SiO_2	37.5	38.0	39.1	44.7	43.6	41.4	43.8	32.5	37.9	38.5	41.5	42.3
TiO_2	0.16	0.17	0.17	0.14	0.19	0.23	0.22	0.29	0.31	0.19	0.27	0.22
Al_2O_3	3.45	3.11	3.45	3.39	4.71	5.01	5.14	6.44	7.43	3.16	6.17	4.62
Fe_2O_3	}25.3	14.3	19.8	}19.2	6.7	18.1	}27.3	}18.7	}23.0	26.7	}27.4	}24.5
FeO		21.6	10.3		13.0	10.8				11.8		
MnO	0.33	0.27	0.27	0.34	0.33	0.31	0.39	0.30	0.31	0.21	0.37	0.37
MgO	2.35	2.48	1.66	2.59	3.36	2.29	2.43	2.50	2.57	1.20	3.47	2.97
CaO	20.9	6.93	7.51	17.9	20.9	9.11	9.13	11.8	12.6	5.14	7.23	9.57
K_2O	0.85	0.77	0.75	0.88	1.16	0.92	1.33	0.92	0.88	0.66	1.73	1.21
Na_2O	1.24	1.01	1.53	1.17	1.36	2.48	1.18	1.71	1.52	0.87	1.81	1.13
P_2O_5	0.67	0.19	0.25	0.23	0.37	0.32	0.34	0.32	0.30	0.31	0.37	0.20
S	0.19	0.32	0.16	0.32	0.26	0.79	0.86	0.49	0.34	0.44	0.93	0.16
Ni	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.05	0.04	0.04
Cu	2.42	7.43	11.6	4.61	2.58	8.84	5.96	10.0	7.62	6.90	5.98	8.14
Zn	0.05	0.02	0.02	0.01	0.02	0.02	0.05	0.02	0.02	0.01	0.07	0.02
Pb	0.04	n.d.	0.01	0.02	0.03	0.01	0.17	n.d.	n.d.	0.01	0.41	n.d.
Sn	n.d	n.d	n.d	n.d.	n.d	n.d	n.d.	n.d	0.01	n.d	0.01	0.01
Total	95.7	99.0	100.7	98.1	98.7	98.7	98.5	88.9	97.1	98.6	98.7	98.1
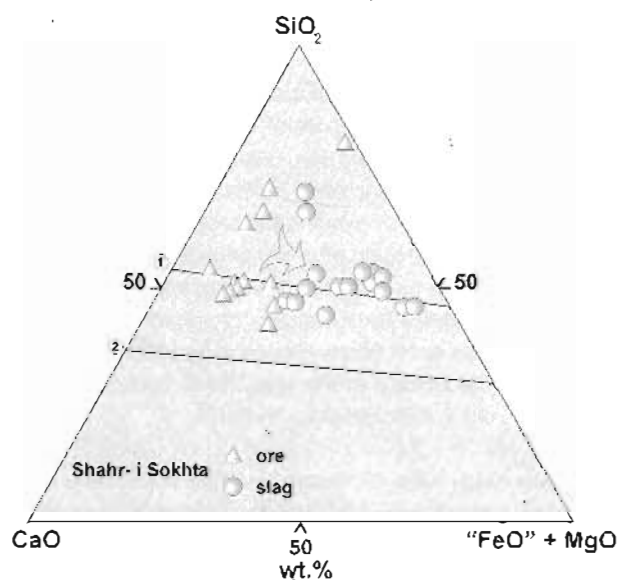
Fig. 4: Plots of ores and slags (reduced analyses) shown in the ternary system CaO - FeO(+MgO) - SiO_2. Note the shift of compositions of ores to Fe-rich slags. These are only approaching the low-melting area which is roughly in the right corner between the metasilicate (1) and the orthosilicate lines (2).

liquid-liquid separation between the metal-rich phase and slag, producing slag cakes extremely similar to those observed at Shahr-i Sokhta (Bamberger & Wincierz 1990: 133, Fig. 130 and 131).

Table 2ff.

Sample	SS 94	SS 107	SS 108	SS 157
SiO_2	47 0	39.3	41 0	31 5
TiO_2	0 47	0.12	0.30	0 12
Al_2O_3	9 95	3.02	7 29	2 3
Fe_2O_3	2 67	7.98	12 5	13 5
FeO	3 90	10.6	19 20	7.90
MnO	0.22	0 37	0.43	0 30
MgO	6.54	1.88	3.77	0 78
CaO	11.1	23.4	7.75	19 5
K_2O	2.73	0 46	1 44	0 41
Na_2O	5.83	0.80	1.16	0 63
P_2O_5	1.14	0.17	0.27	0.13
S	0.19	0.69	0.33	2 92
Ni	0.04	0.04	0.04	0.04
Cu	6.91	5.46	4 51	13 8
Zn	0.01	0 01	0.05	0.02
Pb	0.60	0.01	0 16	0.01
Sn	0.01	0 01	n d	n.d.
Total	99.4	98.3	101.3	94.3

In addition, a small amount of nut-sized slags was excavated. They show a heterogeneous texture characteristic of an incomplete smelting process. In contrast, a few elongated, striking red glassy slag droplets with pronounced flow structures measure little more than one centimetre in size (fig. 3).

Chemical composition
When compared with the bulk of copper slags, especially from later periods, the slag cakes from Shahr-i Sokhta only show a moderate content of iron oxide. Main components are silica and – notably – lime (up to 23 wt%, see table 2). The concentrations of MgO, MnO, Al_2O_3 and the alkalis are low and compatible with other archaeometallurgical slags. In general, the chemical composition of the slags reflects the gangue of the ores, being rich in quartz, feldspar and garnet (see above). The total iron oxide content varies from seven percent in the red slags up to 38 percent in the slag cakes. The arsenic content of the analysed slag samples appears to be very low. The initial XRF analysis of fused beads did not include arsenic due to the volatility of this element during the preparation of the beads; subsequent screening of cut slag samples by XRF indicated the presence of less than about 100 ppm arsenic in the cakes, matching the typically low arsenic content of the ore as found by AAS (see above).

The plots of bulk compositions (reduced to main components) of slags and ores in the ternary system SiO_2 - CaO - Fe-oxide (fig. 4) reveal a shift from the ores to slightly more iron rich compositions in the slags. We doubt that this is caused by a deliberate addition of fluxes to enhance the liquefaction of the slags. Based upon our observation of spots and clusters of iron hydroxides in the archaeological ore specimens, and of partly decomposed remains of iron-rich ore with copper and matte in the slags (see below), we assume that the raw material used by the ancient metallurgists at Shahr-i Sokhta was slightly more iron-rich than the samples analysed by us.

Obviously, when interpreting the composition of *archaeologically* excavated ore from a smelting site in relation to the slag one must bear in mind that the ore left behind by the ancient smelters is likely to reflect the basic type of ore processed; however, as the ore found its way into the archaeological record, it is also likely to have been discarded as being of sub-standard quality. We do not know the parameters used for quality control of the ore in the EBA. Judging from the nature of the ore specimens found on site, and the amount of slag produced, one may conclude that material too rich in copper sulphides was considered unsuitable, while the presence and nature of slag indicates that ores rich in slag-forming components such as iron (hydr)oxide were specifically selected for smelting.

If, however, iron oxide had been deliberately added to the smelted ore as a separate material to improve its lique-
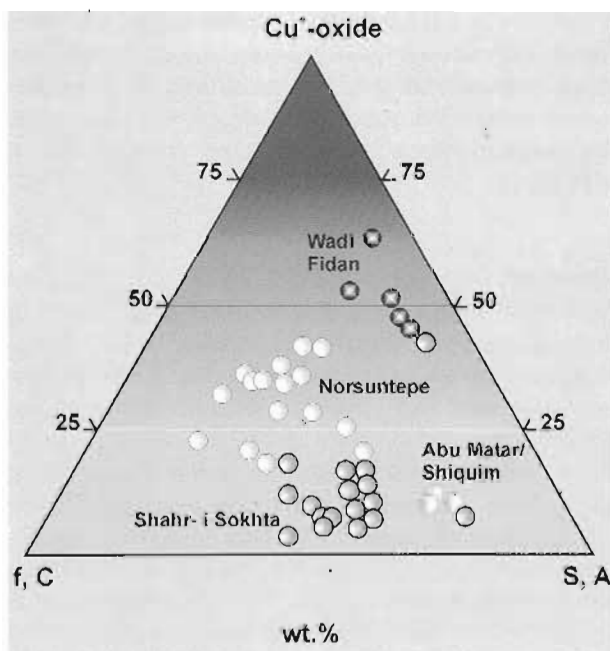
Fig. 5: Copper contents in Chalcolithic slags from several localities in the Near East and in slags from Shahr-i Sokhta shown in the ternary system Cu+-oxide - f, C - S, A (reduced analyses). Note the enormous high copper losses in these slags, and the decrease from chalcolithic samples to those of the Early Bronze Age. Abbrevations: f = Fe-oxide; C = CaO; S = SiO_2; A = Al_2O_3

faction, then we would expect better results, i.e., better low melting (eutectic) compositions than indicated by the archaeological record. Hence, we maintain our view that there is no current evidence to suggest deliberate fluxing in copper metallurgy in the Middle East before the Late Bronze Age (Hauptmann 2000).

We found rather high concentrations of copper in the slags, present both in the metallic state and as copper sulphide in changing amounts. They reach more than 10 wt%, with an average of 7 wt% (table 2 and fig. 5). Copper concentrations of this sort, however, are not unusual in such early slags. Chalcolithic and EBA I slags from the Levant and eastern Anatolia contain up to 50 wt% copper oxide and are evidence that separating metal from slag was rather difficult (Hauptmann 2000). It is not before the rise of an „industrial" metal production in the Near East that such a separation was fully mastered. This development coincides with the consolidation of the earliest fortified sites during EBA II. The effort necessary to extract copper from slag is best exemplified at Khirbet Hamra Ifdan, Jordan (Levy et al. 2002). It is an EBA III/IV (2400-2200 BC) metal factory where multistage beneficiation of metal-rich slags was conducted as part of copper production.

Texture and mineralogical phase content
A fundamental goal of slag investigation in an archaeological context is the reconstruction of metallurgical tech-

niques and craftsmanship. This requires detailed analytical work using both chemical and mineralogical methods to understand the incomplete archaeological record. In our case, one of the most important questions concerns the origin and formation of the slag cakes. Were they smelted in a bowl hearth as suggested by Hauptmann (1980)? Or were they produced by pouring the smelting charge into a depression in the ground after the smelting operation was finished, enabling the separation of slag and metal / matte to take place outside the furnace or crucible? Because the two possibilities imply different cooling conditions which, in turn, affect the texture of the slag, these questions were addressed using mineralogical methods.

Since the slags were produced by small-scale metallurgical operations, it was possible to prepare thin sections which show a complete slag cake in section (fig. 2). They revealed what had already been observed by the naked eye: omnipresent inclusions of light and dark remains of ore embedded in an almost completely liquefied slag. The light inclusions are rich in quartz, often transformed to its high-temperature modification, cristobalite, frequently showing inclusions of copper sulphides. Furthermore, we identified, in almost every single specimen, mm-sized agglomerations of irregularly-shaped magnetite. These agglomerates were partly in sharp, non-reactive, contact to the slag matrix, partly they dissolve in the liquid and were dotted with droplets of copper and copper sulphides (fig. 6). Such inclusions are frequently observed in early copper slags, for instance in Late Bronze Age samples from northern Italy (Hohlmann 1997), or in EBA slags from the upper Euphrates area (Hess 1998), and they are interpreted as remains of limonitic ore intimately intergrown with copper minerals. Their ubiquitous distribution mirrors the occurrence of iron (hydr)oxides in the ores, and strongly

Fig. 6: Sample SS 53: Remnants of ore rich in iron oxide, with inclusions of copper and embedded in an almost fully liquified slag matrix of magnetite + pyroxene. Such inclusions are frequently to observe in the Early Bronze Age slags from Shahr-i Sokhta and are comparable to other numerous copper slags from other localities. Reflected light.
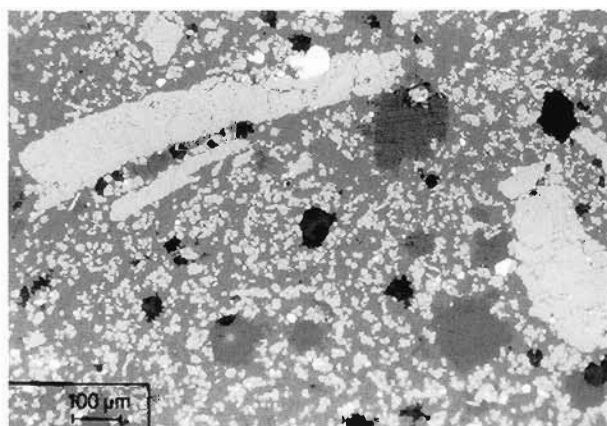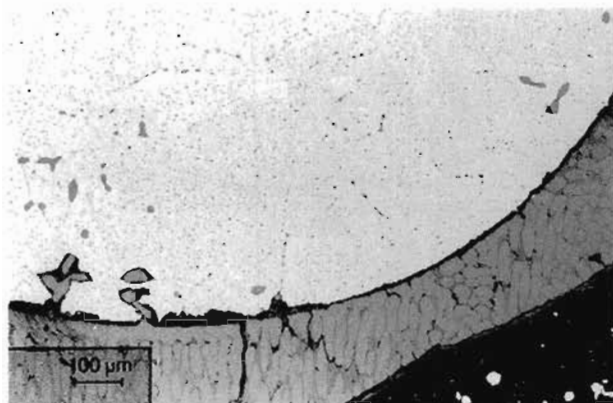
Fig. 7: Sample SS 141: Section of copper droplet embedded in a slag cake surrounded by a rim of copper sulfide ("Cu_2S"). The rim, in turn, is slightly desulphurised and consists of dendrites of "Cu_2S" embedded in a matrix of "Cu_2S" + Cu_2O (cuprite). Reflected light.

supports the hypothesis that ores with a high content of iron (hydr)oxide clusters were smelted at Shahr-i Sokhta.

Heterogeneities in the slag cakes are also caused by the siliceous matrix itself. The central and lower parts of the slag cakes consist of equigranular crystals of pyroxene (according to microprobe analysis hedenbergite, $CaFeSi_2O_6$), intergrown with acicular Fe-wollastonite (($CaFe)SiO_3$). The silicates are associated with magnetite, and interstices are filled with glass.

This phase assemblage changes towards the outer margins of the cakes. The association of magnetite and glass in the upper half demonstrates that the slag cooled under oxidising conditions, i.e., in contact with air (fig. 2). The side of the slag shows a columnar growth of the silicates perpendicular to the surface (the „spinifex-texture" of petrology), while thin crusts of magnetite agglomerations run parallel to the surface. This texture, highly indicative of rapid cooling of a melt in contact with a cold surface, definitely excludes a slow solidification of the slag cake within a furnace or a crucible.

We observed in the slag inclusions of copper sulphide and of copper, both as individual particles, and intergrown with each other. Such droplets exhibit eutectics of Cu - Cu_2S and a crescent shaped rim of sulphide surrounding the metal (fig. 7). They result from smelting mixed sulphidic and oxidic ores (co-smelting, Rostoker et al. 1989), and very similar structures have been found by Golden (1998) in a similar cultural and technological context. The inclusions of sulphides mainly are close in composition to chalcocite and digenite ($Cu_{1.8}S$) with small amounts of bornite, but a ubiquitous surplus of sulphur, in parts, has resulted in the formation of covellite, embedded in the inner part of the inclusions.

Weathered ore collected from the outcrops of sulphidic ore deposits typically contains both oxide and sulphide minerals, frequently resulting in the formation of copper sulphides in the slag. Covellite intergrown with chalcocite was observed in Chalcolithic slags from Tepe Sialk (Schreiner 2002), and with a variety of sulphur-enriched modifications of copper sulphide in Bronze Age slags from Oman (Hauptmann 1985).

It is worth mentioning that, according to the Cu-S phase diagram, the liquidus of such copper sulphides decreases if matte contains slightly higher sulphur than Cu_2S and drops steeply down to 813° C at a composition of 25 wt% sulphur, i.e., far lower than the composition of covellite with 33.5% sulphur (Kullerud & Yund 1960). Based upon this extremely low liquidus temperature we suggest that the sulphidic matte acted as a solvent and collector for copper metal during smelting, and as a lubricant that considerably enhanced the liquid-liquid separation of copper from the slag as it solidified. Such a liquation of (metal bearing) matte follows the basic principles of early metal smelting processes that can be seen as a progressive, but often incomplete, liquefaction of a batch of ore containing gangue (Hauptmann 1999). With increasing temperatures those components of the batch will melt first that *per se* have low melting points or form eutectic compositions in contact with other minerals. Consistently, refractory materials such as quartz, certain clays, or chromite melt last or stay behind unmelted, forming a „restite".

Redox conditions

As ores and gangues employed in ancient metallurgical processes used to be high in iron and copper, i.e., elements that occur in several valencies ($Fe^{2+,3+}$, $Cu^{1+,2+}$), the physico-chemical conditions of ancient (s)melting processes, in general, can be judged from the presence and relative proportions of these different species. These conditions were decisively controlled by the relative amount of charcoal used and air blown into the charcoal bed. This ratio had to match the thermodynamic conditions necessary to reduce the ore to metal and to melt it, i.e., the temperature and the composition of the gas atmosphere. Hence, at any given overall chemical composition, the composition of the mineralogical phases in the resulting slags reflects the ratio of CO/CO_2 as a measure of the redox conditions.

The slags from Shahr-i Sokhta are composed mainly of pyroxene, wollastonite, magnetite and glass. Magnetite is one of the most characteristic phases that is formed during a smelting process under just slightly reducing conditions, i.e., under a low cover of charcoal and allowing for the access of air. This is consistent with the entire assemblage of finds, especially the crucible fragments (see below) that suggest that smelting took place in small reaction vessels. Fayalite or related orthosilicates were identified only rarely.
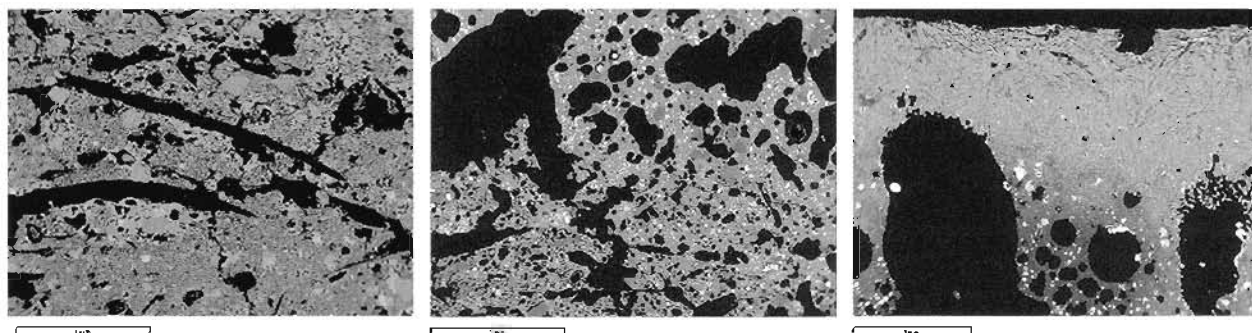
Fig. 8: Sample SS 32: Series of three electron micrographs covering the crucible fabric (left) with little heat impact and well preserved remains of organic temper (elongated voids) in a matrix of ceramic and mineral inclusions (different shades of grey). The central micrograph shows the vitrified and bloated inner part of the fabric, with some residual mineral grains in the glassy matrix and a much rounded, often closed, porosity. The right micrograph covers the inner layer of smelting slag above the vitrified and bloated ceramic, with a dense and well crystallised matrix dominated by elongated crystals of hedenbergite and other silicates.

In addition, we often found inclusions of primary cuprite, i.e., cuprite that was directly precipitated from the melt (as opposed to cuprite that formed during weathering), and of metallic copper. These inclusions are mixed with the silicate matrix and apparently result from an incomplete reduction of oxidic copper ore. They are mm- down to μm-sized, contributing to colouring larger parts of slags an orange to ruby red. The unique regulus that consisted of cuprite instead of matte and copper metal (see above) probably results from an accident, but still fits the model of smelting under low redox conditions.

The copper sulphides were also affected by the presence of oxygen in the melt. Occasionally the sulphidic rims around the copper are composed not of pure copper sulphide, but of dendrites of "Cu_2S" embedded in a eutectic of "Cu_2S" + Cu_2O (fig. 7). This was already observed previously in EBA slags from Çayönü Tepesi (Hauptmann et al. 1993). This texture results from a partial desulphurisation of matte. At high temperatures, matte high in copper is able to absorb a certain amount of oxygen (Schlegel & Schüller 1952). This is exsolved as cuprite (Cu_2O) during cooling. In the case of a matte rich in iron, it will first exsolve magnetite, embedded in the CuFe-sulphidic matrix.

The crucibles

The crucible fragments are generally rather small, in average a few cm^2, and allow no reliable reconstruction of their original shape. The majority of fragments are concave-convex, indicating an approximately bowl-shaped, probably open profile, and heavily slagged on the concave, inner, side. The thickness of these fragments is around from one centimetre, but may initially have been greater: the outer surfaces are rich in traces of organic temper, and are rather crumbly and may have been partly eroded due to insufficient firing of the outer part of the fabric. Towards the concave side the fabric turns black and eventually be-

comes heavily bloated, followed by a layer of dense slaggy material of varying thickness (fig. 8).

The ceramic is rich in calcium oxide and magnesia, and has a ratio of alumina to silica near 1 : 4. Thus, the ceramic is not particularly refractory, as is also indicated by the average levels of alkali oxides and iron oxide present (table 3). The high amount of organic temper will have made it thermally insulating, i.e. containing the heat within the vessel and ensuring sufficient mechanical strength from the outer part of the fabric even when the inner part is bloating and vitrifying. This aspect makes the ceramic material very much typical of early technical ceramics from elsewhere in the Near and Middle East (Rehren 1997).

Table 3: Chemical analyses of crucible ceramic, vitrified crucible ceramic and crucible slag from Shahr-i Sokhta (sample SS 32 in comparison with slag SS 31 a). Values are normalised semi-quantitative SEM-EDX data, given in weight %. bdl = below detection limit.

Sample	SS 32 ceramic	SS 32 vitr. cer.	SS 32 slag	SS 31 a
SiO_2	52	56	45	44.7
TiO_2	0.6	0.6	0.2	0.14
Al_2O_3	14	13	4.1	3.39
FeO	5.0	4.8	22	19.2
MnO	bdl	bdl	0.3	0.34
MgO	8.5	6.5	2.8	2.59
CaO	18	14	22	17.9
K_2O	0.6	3.4	0.8	0.88
Na_2O	1.4	1.3	0.7	1.17
P_2O_5	0.3	0.3	0.2	0.23
Cu	0.1	0.2	1.5	4.61

Of particular importance for this study is the nature of the slag within these crucible fragments, and a number of SEM-EDS analyses were done to clarify whether it is similar enough to the slag cakes to link the two technologically to each other. A typical example is given in table 3, indicating that the bulk composition is indeed very much within the range of compositions found for the slag cakes (see above, and note the intentional avoidance of copper inclu-sions in the SEM area analyses in the crucible slags, which thus appear much 'leaner' than the cakes). The dominant phase is a calcium- and iron-rich silicate, probably hedenbergite, followed by ferroan wollastonite. A comparison of the bulk slag chemistry to the composition of the underlying ceramic further corroborates the likelihood that the crucible slag is indeed a 'proper' smelting slag; both the vitrified and the original ceramic are clearly different in

Table 4: Chemical analyses of metal objects from Shahr-i Sokhta (from Helmig 1986). Note that copper prills listed under SS 100/6 and 211 are individual samples, while those numbers listed under SS 130, 142, 143, 152, 210 are drillings in one and the same sample to check homogeneity. The distinction between lumps and ingots was not clear in every case. Values are given in weight % (%), and in parts per million (ppm).

Sample-No.	Description	Cu (%)	Fe (%)	Pb (%)	Ag	As	Bi	Cd	Co	Ni	Sb
SS 98/1	Cu-prill	97.3	< 0 12	0.30	350	0.3%	240	< 3.6	27	81	160
SS 100/3	Cu-prill	93.1	1.05	0.12	670	2.4%	390	< 3.6	< 30	54	900
SS 100/5	Cu-prill	93.9	< 0.12	1.37	720	610	1000	11	< 30	110	15
SS 100/6. a	Cu-prill	89.7	1.41	6.56	260	55	780	3.0	380	230	6.3
b	Cu-prill	93.0	0.91	0.05	140	82	330	< 3.6	290	420	10
c	Cu-prill	92.1	0.67	1 01	210	0.2%	250	< 3.6	29	130	640
SS 101/2	Cu-lump	92 1	1 98	< 0.06	250	5.8%	60	< 3 6	18	45	7900
SS 111	Cu-prill	93.4	1 05	0 28	100	0.1%	68	12	920	1730	21
SS 119/1	Cu-prill	92.1	0 22	3 98	300	61	280	9.4	520	570	37
SS 130, a	Cu-lump	95.1	2 30	0.21	220	25	53	< 3.6	610	500	2 8
b		94 3	2 34	0.20	430	41	63	< 3.6	640	510	1 7
c		93.8	2.06	0.22	500	12	61	< 3 6	660	510	1.0
d		93.5	1.93	1.16	200	29	120	< 3.6	590	500	3.2
SS 142, a	Cu-ingot(?)	96.6	2.09	0.47	310	61	570	8.4	320	160	10
b		96 5	1.54	0.58	220	71	600	11	220	140	20
c		90.7	1 92	0.40	270	86	680	9.2	300	100	6.8
d		96.7	1.51	0.72	340	71	630	9.0	290	140	11
e		96 3	1 61	0.68	70	53	590	11	240	130	10
SS 143, a	Cu-ingot(?)	97.1	2.40	0.53	410	44	320	12	350	270	7.0
b		96.8	2.19	0.26	430	60	340	9.0	390	240	1.9
c		97.4	2.07	0.23	420	51	290	8.6	350	290	7.0
d		93.8	2.23	0.45	330	57	420	9.3	320	250	13
e		96.0	2.58	0.65	440	65	400	14	340	220	4.8
f		95.5	2 64	0.85	180	51	350	10	340	240	6.6
g		94 6	2.42	0.53	230	210	340	9.3	320	280	9.8
h		96 5	2.31	0.47	420	55	290	10	320	270	6 4
SS 152, a	Cu-lump	93.4	2.99	0.03	790	0.7%	35	< 3 6	100	1050	150
b		92.1	2.59	0.03	830	1.2%	20	< 3.6	83	1180	170
c		94.2	3.06	0.03	510	1 2%	30	< 3.6	120	1580	150
SS 165	Cu-needle	99.7	< 0.12	0.15	230	69	160	< 3.6	230	240	3 4
SS 187	Cu- needle	96.1	0 30	0.04	550	800	130	3.6	< 30	47	42
SS 204	Cu- needle	96.9	< 0.12	0.29	2500	2.4%	< 36	< 3 6	< 30	480	24
SS 209	Cu-prill	96 2	< 0 12	0.04	350	250	1400	< 36	27	35	46
SS 210, a	Cu-lump	91.8	< 0.12	< 0.06	360	3.8%	30	< 3.6	< 30	< 36	190
b		92.6	< 0.12	< 0.06	590	3.7%	25	< 3.6	< 30	< 36	79
c		92.5	< 0 12	< 0 06	1110	1.6%	22	< 3.6	< 18	< 36	51
SS 211, a	Cu-prill	91.9	< 0.12	0.03	120	77	22	< 3 6	< 30	19	< 1.8
b	Cu-prill	99.0	< 0.12	0.04	260	94	36	< 3.6	< 30	< 36	3.9
SS 212	Cu-prill	83.4	< 0.12	12.3	250	1.4%	470	< 3.6	58	240	120

composition (table 3). Significant oxides here are magnesia and alumina which are both much lower in the slag than in the vitrified ceramic, and calcium and especially iron oxide which are much increased in the slag. Thus, the inner slag layer is clearly not derived from a simple fusion of the vitrified ceramic, contaminated by some copper from the metal charge. Similarly, the increase in calcium oxide and the much different ratio of silica to alumina strongly argue against an origin of the slag from the refining of an iron-rich raw copper; in the latter case, only the iron oxide content of the slag should be increased when compared to the vitrified ceramic. Furthermore, one would expect much more oxidising conditions to have prevailed under such a refining scenario, which would have resulted in the presence of much higher copper oxide levels than actually present. The arsenic content in these slags is below the detection limit of the SEM-EDX system, estimated to about 0.2 wt% arsenic, in keeping with the available analyses of the slag cakes. The opaque phases present are mainly magnetite clusters and a scatter of copper prills containing up to a few percent iron, and arsenic at or below the detection limit. Some of them are surrounded by copper sulphide layers. In contrast, copper oxide was only rarely observed, indicating that the conditions were not oxidising enough to interpret the slag as the result of remelting collected copper prills and primary smelting slag rich in trapped copper metal, as suggested for some fayalitic crucible slags from the New Kingdom site of Timna (Rothenberg 1999).

Rapid solidification of the slag cakes in a hearth or other receptacle mentioned above would have required some sort of pouring of the crucible charge. Due to the very fragmentary nature of the surviving fragments, no spout has been identified so far. The apparent pouring of the charge from the crucibles is a unique feature in early crucible smelting, and requires further explanation. It would have assisted in the (relative) homogenisation of the melt, probably facilitating the collection of isolated small copper prills in the more abundant and more fluid sulphidic melt, thus 'washing' the copper more effectively from the slag during the casting. The increased presence of oxygen during this process might have further increased the yield of copper metal at the expense of matte. There may have been further, as yet un-identified, benefits in the pouring of the charge. Importantly, this paves the way for the proper slag-producing copper smelting technologies of the following periods, allowing dramatically increased production.

The metal

Table 4 presents the minor and trace element concentrations in metal objects from Shahr-i Sokhta. The objects seem to originate from different stages of copper processing: Helmig (1986) analysed what he classified as raw copper, i.e. copper prills and larger batches (lumps of a few hundred grams, bars or ingots up to more than one

kilogram), and finished artefacts such as needles. They vary considerably in their elemental composition. A systematic decrease of certain elements, as one would expect from the refining of raw copper to the final object as outlined by Pernicka (1987), is not visible here. There are copper objects that are very pure even according to modern standards (SS 165, SS 211b). Other objects are high in impurities. This concerns mainly lead, which may reach several percent (SS 100/6,a: >6 wt%; SS 119: 4 wt%; SS 212: 12 wt%). Such high concentrations in lead are rare in early copper in the Old World. They are, however, to some extent paralleled by copper from Feinan that too can contain up to several percent of lead (Hauptmann 2000). Iron may reach the lower percentage level. The complete digestion of the samples with HNO_3 showed that in the metal objects the tin concentrations did not exceed a few ppm at most, i.e. that tin bronzes were not known at Shahr-i Sokhta.

In nine of the twenty-one metal objects, the arsenic concentrations are in the range of tens of ppm, in others they may reach the lower percentage level (1 - 6 wt%). Antimony is often below 10 ppm and only sporadically reaches

Fig. 9: Lead isotope abundance ratios of archaeometallurgical finds from Shahr-i Sokhta (except for two ores from this site that plot off the graph to the lower left). Also shown are ores from Qaleh Zari and Chechel Kureh in the Iranian Malik-i Siah Mountains west of the settlement, which qualify as potential sources for some of the Cu metal objects and one of the excavated „archaeological" ores. Note the agreement of the speiss sample with one copper metal SS 101/2.
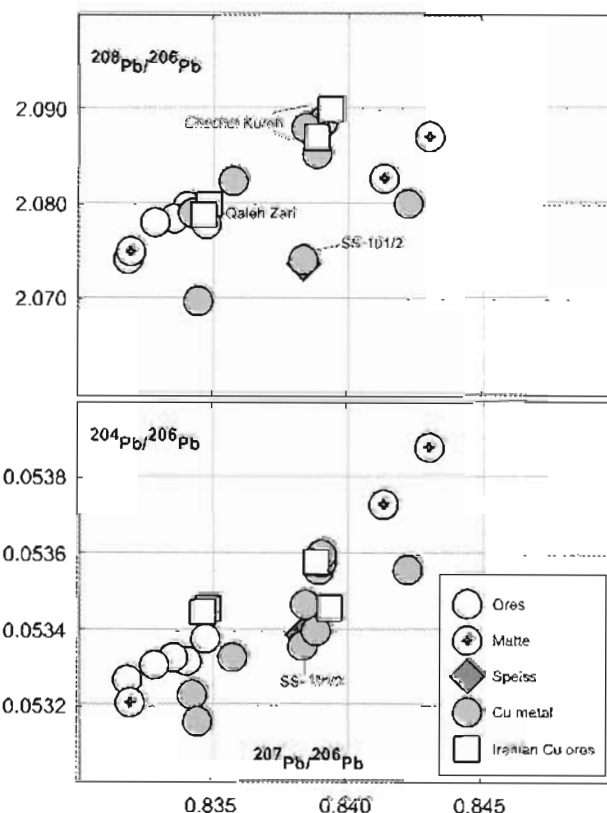
Table 5: Lead isotope abundance ratios of ores, matte. metal objects and a sample of speiss from Shahr-i Sokhta, and of ores from Chechel Kureh and Qaleh Zari, Iran. Experimental uncertainties are 0.1 percent or less.

Sample no.	Description	Pb (ppm)	$\dfrac{^{208}Pb}{^{206}Pb}$	$\dfrac{^{207}Pb}{^{206}Pb}$	$\dfrac{^{204}Pb}{^{206}Pb}$
Shahr-i Sokhta					
SS 96	ore	12	2.0779	0.8348	0.05338
SS 101/1	ore	40	2.0798	0.8341	0.05332
SS 137	ore	35	2.0785	0.8336	0.05333
SS 145	ore	2	2.0187	0.8120	0.05185
SS 148	ore	40	2.0742	0.8319	0.05327
SS 156 A	ore	2	2.0399	0.8193	0 05233
SS 161	ore	6	2.0781	0.8329	0.05331
SS 62	matte	6	2.0872	0.8432	0.05388
SS 98/2	matte	20	2.0828	0.8414	0.05373
SS 149/2	matte	7	2 0750	0.8320	0.05321
SS 30	speiss	510	2.0737	0.8384	0 05339
SS 101/2	Cu-prill	110	2.0741	0.8384	0.05336
SS 111	Cu-prill	1250	2.0854	0.8389	0.05340
SS 119/1	Cu-prill	22400	2.0886	0.8390	0.05356
SS 130	Cu-lump	3900	2.0886	0.8391	0 05358
SS 143	Cu-ingot(?)	1500	2.0887	0.8391	0.05360
SS 152	Cu-lump(?)	120	2.0791	0.8343	0.05323
SS 165	Cu-needle	710	2.0881	0.8385	0.05347
SS 187	Cu-needle	200	2.0698	0.8345	0 05316
SS 204	Cu-needle	5170	2.0825	0.8358	0.05333
SS 210	Cu-lump	20	2.0801	0.8423	0.05356
Iran					
Chechel Kureh					
E 127/4111	atacamite.	6700	2.0900	0.8394	0.05346
E 128/4112	atacamite.	2900	2.0871	0.8389	0.05358
Qaleh Zari					
E 128/4286	atacamite,	3100	2.0800	0.8349	0 05346
E 130/4661	malachite/ atacamite	300	2.0789	0.8347	0.05345

several hundred ppm. Sample SS 101/2 contains 6 wt% As and 0.79 wt% Sb. There is nothing to suggest that the level of arsenic, in a sequence from copper prill (extracted from slags) to final objects, would increase due to an intentional alloying of copper with speiss or other materials rich in arsenic. When normalised to Cu = 100%, the copper ores excavated at Shahr-i Sokhta not only cover the range of arsenic concentrations in the metal objects, but also show a As/Sb-ratio with the same variation as the metals. We have to note, however, that only one of the fifteen ore samples analysed is rich enough in arsenic to match the lower percentage range observed in eight of the metal objects. This could indicate that either the arsenic was derived from a further additive, such as the speiss discussed above, or that the assemblage of ores from the site is not fully representative of the material actually processed in antiquity.

Lead isotope analyses

Results of the lead isotope analyses are compiled in table 5 and shown in fig. 9. The copper ores, the matte samples and the metal objects excavated at Shahr-i Sokhta are almost all grouped between $^{208}Pb/^{206}Pb$ = 2.070 and 2.090. Two ores are outliers and have no correspondence to any other archaeometallurgical find from the site.

When looking more closely at the data, there is only little correspondence between ores and metallurgical products like slag, matte, speiss, or metal. There is just one instance each where the isotopic fingerprint of an ore (SS 148) agrees with that of a matte (SS 149/2), that of an ore (SS 101/1) with a copper lump (SS 152), and that of a speiss (SS 30) with that of a copper prill (SS 101/2). Otherwise, ores are different in their isotopy from metal and, vice versa, the isotopic composition of the lead in matte and metal does not occur among the ores. It would appear that there was a complex, multistage ore deposit (such as it might be the case with skarn deposits), or a multiplicity of ore sources that served the needs of Shahr-I-Sokhta and that, presumably, this lack of correspondence reflects the incomplete sampling of the artefacts from the site.

Shahr-i Sokhta is situated on a flood plain with no local ore deposits. To the east, the environment opens out into a large, rather monotonous, basin of western Afghanistan. It is surrounded by a range of cupriferous mountain ranges, but the distances are large (see above, The Ores). Closer by are ore deposits in the Iranian Malik-i Siah Mountains immediately to the west and north-west of Shahr-i Sokhta. Bazin & Hübner (1969) report, inter alia, on two copper deposits at Chehel Kureh, some 200 km to the west, and at Qaleh Zari, some 300 km to the north-west, of Shahr-i Sokhta where (pre-)historic mining activities were described by Berthoud et al. (1976). There are two pieces of evidence in our data which suggest that indeed these sites might have served to fill, at least in part, the needs of Shahr-i Sokhta. One piece of evidence is a group of four artefacts (SS 119/1; 130; 143; 165) where the isotope abundance ratios agree within the experimental uncertainties of ± 0.1% (95 % confidence level) with outcropping ores at Chehel Kureh. The second hint that ore deposits from the Malik-i Siah mountains might have served the needs of Shahr-i Sokhta is the agreement in the lead isotope fingerprint between an excavated ore (SS 96) with two outcropping ores from Qaleh Zari.

Conclusions

The analyses demonstrate that at late EBA Shahr-i Sokhta complex copper ores were smelted for copper and arsenical copper. Both types of metal were found as irregular lumps and prills, presumably raw copper from the smelting operation, but also possibly as ingots, and as finished objects such as pins and needles. The investigation of ore, crucible fragments and slag samples shows that this smelting took place within crucibles, but that at the end of the operation the charge was poured from these vessels into some kind of hearth or mould. This allowed for a complete separation of slag and metal. Significantly, the necessary raw materials were obtained from ore deposits at a considerable distance from the site, in keeping with earlier practice known from elsewhere in the Middle East. Some aspects of this will be discussed below.

Domestic mode production

The small-scale metallurgical operations carried out at Shahr-i Sokhta to extract metal from copper ores constitute a domestic mode production in an urban settlement. Thus, the traditional pattern of metal production found earlier at numerous 4th and 3rd millennium BC sites all over the Near and Middle East is kept alive here (Shalev 1994; Pigott 1999; Hauptmann 2000). The region east of the desert of Dasht-e Lut apparently persisted in this tradition well into a period when, on the western part of the Iranian plateau and in the eastern Mediterranean, an explosion of copper production was taking place, resulting in the earliest larger slag heaps. It is the same time (first half of the 3rd millennium BC), when at Veshnoveh/Arisman in western Iran (Pigott 1999; personal communication Th. Stöllner) and at Feinan in Jordan copper was already produced in large quantities. Slag heaps with several thousand tons of slag are witness to this, located outside of the villages, and wind-powered furnaces with a volume of 0.5 - 0.7 m³ were already used to smelt the ore (Kölschbach et al. 2000). However, the presence at Shahr-i Sohkta of a relatively large quantity of relatively copper-poor slag in relation to the smallish metal reguli produced in each smelt puts this metallurgy in a more advanced stage when compared to the earlier crucible smelting technology which produced much less, and much richer, slag relative to the amount of metal smelted.

Crucible smelting

It appears that the ore was smelted in crucibles by heating the charge from above, using either blowpipes or bellows. No tuyere fragments were among the finds sent to Bochum, but this does not exclude the possibility that they may have been existed initially. The relatively high fluidity visible from the slag, enabling to pour the entire charge at the end of the process, possibly indicates the use of bellows, generating a higher process temperature. Despite the production of a considerable amount of slag relative to metal, we see no indication for intentional fluxing. If this had been the case, the composition of the slag would have reached a much better eutectic composition.

It is impossible for us to suggest a reconstruction of the crucibles' shapes or volumes based upon the archaeological record, and, hence, we can not confirm the statement of Heskel (1982) that the crucibles from Shahr-i Sokhta would have formed the bowl within a smelting furnace. According to the average slag volume and weight of the cakes (calculated to ca. 200 cm³ and 400 g, see also Hauptmann 1980), and the low thickness of the crucible ceramic, the reaction vessels were probably relatively small.

For comparison, we refer to contemporary finds from two sites in eastern Anatolia where slag cakes and better preserved crucible fragments were found in EBA levels, dating to ca. 3000 BC. The lower part of a crucible from Nevali Çori has a diameter of 16.5 cm (Hauptmann et al. 1993), and the remains of a crucible with similar dimensions from Arslantepe (personal communication M. Frangipane and A. Palmieri, Rome) enable us to calculate its initial volume to ca. three litres.

The irregular and relatively rough outer shapes of the slags indicate that they were poured (or tapped) into a hearth or simple hole in the ground rather than into a ceramic mould. Each smelting operation produced a regulus of ca. 150 g of copper sulphide and copper that separated underneath the slag. There is no evidence in the archaeological record at Shahr-i Sokhta for the further processing of matte or of copper-rich slag. Helmig (1986) suggested that smaller droplets and reguli of copper were probably remelted to form larger batches, and that small objects were used, and possibly manufactured, on site. However, there are no indications that the copper sulphide was further processed, e.g., by roasting, to be smelted then to metal. To the contrary, the matte cakes formed underneath the slag were obviously discarded as worthless material. Similarly, there is no evidence for the systematic crushing of slag to mechanically extract copper (or matte) prills. There is also no direct evidence of alloying practices, neither with arsenic nor tin, but the issue of the arsenic content remains to be discussed.

Co-smelting of sulphidic and oxidic ore

Even if the large amount of copper sulphide inclusions in the slags, and the finds of matte cakes suggest a „sulphide smelting" or „matte smelting", we believe that the aim of the smelting operations at Shahr-i Sokhta was not to produce matte, not even as an intermediate product, but to directly produce metal. Hereby, the „incidental" co-smelting of mixed ores (Rostoker et al. 1989) benefited from the chemo-physical properties of the copper sulphide. This separated from the silicate slag in its liquid state, acting as a collector for copper. During the smelting operation, carried out under only slightly reducing conditions, copper was reduced from the oxidic ore, finely distributed in the slag, while the sulphidic component remained mostly unchanged. Due to its low melting point and high fluidity the matte (including the copper) separated much easier from the cooling silicate melt than the metal would have done alone.

The poor homogeneity of these slags, indicated by plenty of remains of ore and gangue, is a typical result of brief smelting processes. In general, such operations are connected with small reaction vessels, such as crucibles, in which a consistent and complete liquefaction of the charge was difficult to achieve.

The arsenic content of ore, slag and metal

The arsenic content of the metal, reaching up to six percent and averaging one to two percent for the arsenical copper, contrasts with the typically low arsenic content of the ore and slag. There is one ore sample rich enough in arsenic to allow the production of arsenical copper to be based on it. Indeed, the direct smelting of complex ore to arsenical copper is archaeologically well known, but it results in arsenic-rich slag as well as arsenical copper (Hess 1998; Palmieri et al. 1999; Müller 2002). At present, we have roughly half of the metal finds being arsenical copper with the other half having less than 0.1 wt% arsenic. Of the ore samples, only one out of the total of fifteen samples has a significant arsenic concentration, while none of the slag cakes or crucible slags appear to have more than trace amounts of arsenic. However, there is some iron arsenide speiss which clearly is not a by-product of copper smelting, but was most likely made by treating arsenopyrite under smelting conditions sufficient to reduce some of the material to metallic iron. According to the lead isotope study, most of these materials originate from the same geological context. At the same time, there is no indication for an increased iron content of the arsenical copper when compared to the other copper, making a direct addition of speiss less likely. Clearly, there is enough reason to continue with the study of these – and other – finds in order to better understand the changing pattern of the production of arsenical copper during the Early Bronze Age.

Acknowledgement

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