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ORIGINAL PAPER

From desert ores to Middle Kingdom copper: elemental and lead isotope data from the RMAH collection, Belgium

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Abstract
This paper presents the first combined elemental composition and lead isotope (LI) ratio data for Middle Kingdom Egyptian copper alloy artefacts and significantly extends our knowledge on copper smelting remains from the Sinai Peninsula. It further provides the first precise LI ratio and trace element data for two Classic Kerma daggers. Forty-one samples have been analysed from artefacts housed at the Royal Museums of Art and History, Brussels. An important part of this assemblage consists of ore, "slag" and raw metal from workshops associated with 12th Dynasty mining expeditions in the southern Sinai Peninsula. These offer a unique insight into Middle Kingdom copper production chains and the associated waste materials, and form an essential reference group for provenance studies. The other part of the assemblage encompasses finished artefacts from different sites in Egypt—the first ever to be characterised for LI ratios for this period—as well as two daggers from Kerma, Nubia. This study illustrates the need for a careful approach to provenance research of early Egyptian metals, tailored to the particular technologies attested there. Based on the wide range of artefact LI ratios overlapping with those of arsenic-poor Sinai ores on the one hand, and the discrepancy in arsenic content between these ores and artefacts on the other hand, a two-step process for the production of arsenical copper alloys is identified. This suggests some technological continuity with respect to earlier pharaonic periods. The sources for primary copper production, however, likely changed over time: a narrower range of Sinai mines appears to have been exploited compared to preceding periods, and the recycling of circulating metal gained importance in the overall provisioning system.

Keywords Egyptian archaeology · Kerma · Copper smelting · Arsenical copper · Provenance · Archaeometallurgy

Introduction

Copper has played a key role in Pharaonic Egyptian material culture and its consumption is widely attested in ancient funerary, manufacturing and urban contexts. For many years, epigraphic and economic aspects have been investigated (e.g. Altenmüller 2015; Bloxam 2006; Bonnet and Valbelle 1995; Gardiner et al. 1952, 1956; Marcus 2007; Tallet 2012, 2015, 2018), but the underlying production technologies have remained relatively obscure as a result of limited specialised study of the subject. The systems of copper production and consumption in Egypt certainly changed significantly throughout the millennia. Egypt's exceptionally long history of copper metallurgy merits closer attention, as such detailed study can provide new perspectives on technological traditions in the Nile Valley. The latter, in turn, relate to broader socio-cultural and economic conditions changing through time on local to regional scales. The study of copper metallurgy thus plays an integral role in developing a holistic understanding of ancient Egyptian culture.

Egyptian metallurgy captured the attention of early archaeologists such as Petrie, who excavated mining and metallurgical camps in Sinai (Petrie 1906) on the basis of geological work by Bauerman (1869), while the first overviews of metallurgical technology were compiled by Garland and Bannister (1927), Lucas (1962) and Rothenberg (1970,

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1979). Further large-scale characterisations of Egyptian copper compositions were undertaken in the 1970s and the 1980s (e.g. Cowell 1987; Riederer 1988) outlining a general "evolution" of Egyptian copper alloy composition through time (cfr. Rademakers et al. 2018b and references therein). Of particular relevance to the Middle Kingdom period are the copper alloy artefact compositions reported from the settlements at Kahun (Gilmore 1986: 40 artefacts, NAA) and Tell el-Dab'a (Philip 2006: 43 quantitative (10 Middle Kingdom), 12 semi-quantitative (all Middle Kingdom) and 16 qualitative (6 Middle Kingdom) sample analyses, AAS and XRF), while smaller Middle Kingdom datasets are reported by Garenne-Marot (1984: 7 artefacts, AAS/AES (?) and PIXE), Vandier d'Abbadie and Michel (1972: 8 Middle Kingdom artefacts, AES) and Odler et al. (2018: 4 Middle Kingdom artefacts, 2 C-group artefacts: surface XRF). These illustrate the continued use of copper and arsenical copper, as well as the introduction of tin bronze. As previously discussed by Rademakers et al. (2018b), these trends stand to be evaluated and further explored, particularly with regard to copper provenance and production technology.

Recent studies have adopted a more detailed analytical methodology combining trace element and lead isotope ratio data to assess copper provenance. This has shed new light on the earliest occurrence of copper in Predynastic up to Old Kingdom times (ca. 4400–2130 BCE; e.g. Abdel-Motelib et al. 2012; Kmošek et al. 2018; Rademakers et al. 2018b; Rehren and Pernicka 2014), suggesting a highly different provisioning system compared to the New Kingdom (ca. 1550–1070 BCE; cfr. Rademakers et al. 2017 and Stos-Gale et al. 1995). However, these studies necessarily cover only a relatively small window of time and space, fragmentarily illuminating an ancient economy wherein millions of copper objects circulated. For Middle Kingdom (ca. 2030–1650 BCE) Egypt, the period of interest in this paper, no lead isotope data on copper alloys have yet been published[1].

This paper presents the results of archaeometallurgical research in the Nile Basin carried out by a team composed of Frederik Rademakers, in charge of the archaeometry, and Georges Verly, in charge of the (experimental) archaeology, as well as numerous Master students and *Maître d'art* Hugues Paridans. Dialogue and interdisciplinarity are the assets of this project, dictating equality between its members, representing the sum of ideas and debates, building all research protocols and publications.

In this study, we present the analytical results from elemental and lead isotopic analysis conducted on forty-one artefacts from the Royal Museums of Art and History (RMAH), Brussels, obtained within the EACOM project as part of a wider evaluation of copper alloy provenance and production technology throughout Pharaonic history. The artefacts to be analysed were selected after careful reconstruction of their archaeological find contexts: mostly excavated in the late nineteenth to early twentieth century, this archival study represents an important effort of which the results are only summarised here (cfr. Rademakers et al. 2018b). This contextual data is crucial in order to arrive at meaningful discussions of artefact provenance. The assemblage consists of ore fragments and primary production waste, but equally encompasses finished objects. This unique combination allows a particular focus on the underlying techniques for raw and alloyed copper production in Middle Kingdom Egypt for the first time. We further present the first precise LI ratio data for two Classic Kerma (ca. 1750–1480 BCE: Bonnet 2019) daggers held at the RMAH. Kerma was an independent state on the Nile at that time, contemporary to the Middle Kingdom to First Intermediate Period in Egypt, and in contact with the Egyptian state, thus representing an interesting point of comparison.

This research has benefited from recent archaeological discoveries at Ayn Soukhna, a harbour site transformed into a centre of concentration and metallurgy during the Middle Kingdom (2000–1930 BCE; Tallet 2018: 140–145). At this site on the Red Sea coast, shipments of Sinai copper ore were being smelted as part of large-scale state-organised expeditions (Abd el-Raziq et al. 2011; Tallet 2016-2017). A second detailed study of primary and secondary metallurgy at Ayn Soukhna, including excavation, experimentation and in situ archaeometric analysis, is currently being conducted and prepared for publication by the authors (Verly 2017, in preparation; Verly and Rademakers forthcoming; Verly et al. 2021, and references therein). The remains attested at Ayn Soukhna provide a technological anchoring point for the interpretation of Middle Kingdom artefacts presented in this paper. The detailed characterisation of potential changes in elemental and lead isotopic composition which may occur during smelting at Ayn Soukhna (Rademakers et al. 2020) is particularly important in this context.

Materials and methods

Compared to other Pharaonic periods, the RMAH collection houses relatively few metal artefacts from the Middle Kingdom. However, a lot from Petrie's (1906) Sinai assemblage allowed the detailed characterisation of production waste from Middle Kingdom metallurgical workshops, a central focus of this paper. This presents a rare opportunity to study ores intended for smelting in antiquity, from a dated archaeological context (as opposed to modern geological

[1] For the Middle Kingdom, Shortland (2006) provides LI ratio data for kohl (a cosmetic, mostly galena) only, which have no bearing on the copper alloy production chain discussed here. The only published lead isotope ratios for Kerma (modern day Sudan) copper alloys were acquired by Young (1996) for two daggers by Q-ICP-MS (Quadrupole-Inductively Coupled Plasma-Mass Spectrometry) and are insufficiently precise for provenance analysis.

samples). In addition, a choice was made to investigate within-object variability for a mirror and a dagger (E.03996 and E.06118), thereby maximising the information yield for the few contextualised artefacts.

It should be noted here that the term "slag" is employed for the discussion of heat-exposed ore fragments. To avoid confusion, this terminology is explained within the particular context of this publication. The analysis of Middle Kingdom metallurgy at Ayn Soukhna has shown that "heat-exposed ore" can represent the waste products of smelting (Rademakers et al. 2020; Verly 2017; Verly et al. 2021). These are indeed the remains of the ore charge after copper has been extracted, which have undergone chemical and mineralogical changes in the process (Rademakers et al. 2020), and as such "slag" offers the best terminology to describe them. The term "heat-exposed ore", on the other hand, may imply the accidental heating of ore or a roasting process. In the case of the finds presented here, close correspondence to the Ayn Soukhna type smelting waste suggests a similarity in its production chain. Given that liquid slag is often considered the norm (and even a defining feature) for Bronze Age metallurgy in wider archaeometallurgical literature, we insist on including this "type of slag" within the broader term here, to emphasise its metallurgical nature.

From the combined results of contextual and qualitative compositional analysis (handheld X-ray fluorescence spectrometry), a selection of forty-one samples was made. These are listed in Table 1, which includes essential contextual data, while for each artefact further details and photographs are provided in the Online Supplementary Materials (OSM). Figure 1 presents a map with find locations for all sampled artefacts (for period-specific maps, see OSM Figures 5–6 and 13–18), while Fig. 2 offers a more detailed overview of sites in Sinai. A selection of the artefacts is illustrated in Fig. 3.

Metal samples were either clipped using steel cutting pliers or drilled using a clean 1mm drill bit made from TiN-coated steel to obtain core material. Prior to sampling, all surface corrosion was mechanically removed (Dremel rotary tool (Bosch®), steel brush) to ensure a metallic sample. In two objects (E.00785.11 and E.02588) and copper prill EA-MR-171, little metallic copper alloy was preserved and important corrosion is present in the sample. Ore, "slag" and turquoise fragments were ground down in an agate mortar to a fine powder, from which homogenised samples were taken.

All samples were completely dissolved following a high-temperature acid digestion procedure. One aliquot was retained for elemental analysis by ICP-OES (inductively coupled plasma-optical emission spectroscopy), while the remainder was used for lead isolation and subsequent lead isotopic (LI) analysis by MC-ICP-MS (multi-collector inductively coupled plasma-mass spectrometry). The precision and accuracy of ICP-OES results are better than 5% for the reported elements (bias up to 20% for silver and gold). Lowered analytical totals for ore and "slag" reflect the important (hydr)oxide, carbonate, chloride and silicate bulk fraction, while lowered totals for metals are due to corrosion. Error values for LI ratios after correction for mass bias are better than 0.03% for ratios involving ^{204}Pb (up to 0.05% in four samples). Full details of laboratory procedures for sample preparation, elemental and LI analysis are provided by Rademakers et al. (2020).

The remaining powder for ore, "slag" and turquoise fragments was used for quantitative XRD (X-ray diffraction) analysis to identify mineral phases (cfr. Adriaens et al. 2018). An internal standard was added to "spike" the samples for quantification: 10 wt% zincite (ZnO) for all samples except turquoise to which 10 wt% corundum (Al_2O_3) was added. Measurement was performed on a Philips PW1830 diffractometer with Bragg/Brentano θ–2θ setup. Cu Kα radiation was used at 45 kV and 30 mA, scanned angle ranging from 3° to 75° 2θ with a step size of 0,02° 2θ and 1 s per step. ConvX software was used for file conversion, while mineral identification and quantification (calculated to 100 wt%) were performed using DiffracPlus (EVA) and Profex software (Döbelin and Kleeberg 2015). Given the small fragment sizes, the reported percentage values should be regarded as indicative—relative quantities of these minerals are expected to vary within the ores that were mined.

Results

The results of XRD analysis, performed for seventeen ore, two "slag" and two turquoise samples[2], are summarised in Table 2 (full results in OSM). These show that the dominant copper ore phase in the assemblage is clinoatacamite ($Cu_2(OH)_3Cl$), with variable malachite ($Cu_2(CO_3)(OH)_2$). This is in line with the ore mineralogy described by Abdel-Motelib et al. (2012), who further note atacamite (cfr. E.04449), paratacamite (another polymorph of atacamite, closely related to clinoatacamite), chrysocolla and pseudo-malachite as common copper minerals. Manganese-rich minerals could not be detected, except for sample EA-MR-177 (cfr. Old Kingdom Sinai Workshops). Quartz (SiO_2) and dickite ($Al_2(Si_2O_5)(OH)_4$) make up the major gangue minerals, alongside a variety of minerals in smaller quantities such as goethite (α-$Fe^{3+}O(OH)$), hematite (Fe_3O_3) and calcite ($CaCO_3$). Dickite is a phyllosilicate mineral (kaolinite polymorph) usually found in hydrothermal veins but equally in soils and shales. It explains, for this dataset, the high

[2] Furthermore, XRD results for six ore samples published by Rademakers et al. (2018b) are included, which were not previously published. Malachite is confirmed as the major copper ore mineral, alongside clinoatacamite. The sulphide ores are mainly galena, with cerussite and anglesite as well as sphalerite (in adherence with their elemental composition). No material was available for XRD analysis of sample EA-MR-101 (sulphide E.04269).

Table 1 Sample overview

RMAH number	Sampling label	Type	Site	Context	Dating	Period	Dynasty	Excavator
E.08445	EA-MR-090	Adze	Elkab	Tomb 48	± 3300–3200 BCE	Protodynastic	Nagada III-A1	RMAH
E.04449	EA-MR-193	Copper ore	Tarkhan	Tomb 1522	± 3200–3100 BCE	Protodynastic	0	Petrie
E.06137	EA-MR-173	Copper ore	Sinai-Wadi Maghara	Metallurgical workshop, zone A	± 3000–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.06137	EA-MR-177	"Slag"	Sinai-Wadi Maghara	Metallurgical workshop, zone A	± 3000–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.06137	EA-MR-172	Copper prill	Sinai-Wadi Maghara	Metallurgical workshop, zone A	± 3000–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.04793.03	EA-MR-183	Copper ore	Sinai-Seih Ba'ba	Metallurgical workshop	± 2544–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.04793.03	EA-MR-185	Copper ore	Sinai-Seih Ba'ba	Metallurgical workshop	± 2544–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.04793.03	EA-MR-186	Copper ore	Sinai-Seih Ba'ba	Metallurgical workshop	± 2544–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.04793.03	EA-MR-189	Copper ore	Sinai-Seih Ba'ba	Metallurgical workshop	± 2544–2250 BCE	Old Kingdom	5 (most likely)	Petrie
E.04793.01/02	EA-MR-166	Turquoise (green)	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-167	Turquoise (blue)	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-178	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-179	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-180	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-181	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-182	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-184	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-187	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-188	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-190	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-174	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-175	Copper ore	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-176	"Slag"	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-191	Copper prill	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-192	Copper prill	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-170	Copper prill	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-171	Copper prill	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-168	Copper alloy (scrap)	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04793.01/02	EA-MR-169	Copper alloy (scrap)	Sinai-Wadi Maghara or Wadi Nasb	Metallurgical workshops	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.00785.11	EA-MR-001	Mirror—disk	Dayr al-Barsha	Tomb of Abou	± 2045–1974 BCE	Middle Kingdom	11	Gayet
E.01969	EA-MR-116	Mirror—disk	Qift (Koptos)	Tomb	± 2045–1700 BCE	Middle Kingdom		Petrie
E.03996	EA-MR-118	Mirror—tang	Abydos		± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.03996	EA-MR-119	Mirror—disk	Abydos		± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.04267	EA-MR-120	Mirror—disk	Abydos	Tomb 45	± 1974–1781 BCE	Middle Kingdom	12	Petrie
E.06150-C	EA-MR-126	Miniature chisel	Beni Hassan	Tomb 2 (BH2)	± 1944–1900 BCE	Middle Kingdom	12	Garstang

Table 1 (continued)

RMAH number	Sampling label	Type	Site	Context	Dating	Period	Dynasty	Excavator
E.02588	EA-MR-089	Blade/file	Tell el-Yahudiyeh	Tomb 407	± 1944–1900 BCE	Middle Kingdom	12	Petrie
E.06118	EA-MR-112	Dagger—blade	Kerma (Sudan)	Tumulus of Western Cemetery	± 1750–1480 BCE	Classic Kerma		Reisner
E.06118	EA-MR-113	Dagger—handle	Kerma (Sudan)	Tumulus of Western Cemetery	± 1750–1480 BCE	Classic Kerma		Reisner
E.06118	EA-MR-114	Dagger—rivet	Kerma (Sudan)	Tumulus of Western Cemetery	± 1750–1480 BCE	Classic Kerma		Reisner
E.07391	EA-MR-115	Dagger—blade	Kerma (Sudan)	Tumulus K IV-B	± 1750–1480 BCE	Classic Kerma		Reisner
E.02151	EA-MR-129	Statuette	Egypt (not specified)	Unknown	± 2045–1700 BCE	Middle Kingdom		Unknown

alumina contents noted as typical for Sinai ores by Abdel-Motelib et al. (2012, p. 42).

Lead isotope (LI) and elemental analysis have been performed for a total of twenty metal samples, in addition to the abovementioned ore, "slag" and turquoise samples. Complete LI ratio data are provided in Table 3 and presented graphically in Figs. 4 and 5. All elemental composition data are provided in Table 4 (in μg/g—all % values refer to wt%), with selected elements presented in Figs. 6 and 7. Discussion of specific compositional characteristics is organised along the artefacts' find contexts and typology below, while a broader overview is presented in the discussion.

Following the rationale outlined by Rademakers et al. (2017, 2018b), the Sinai Peninsula and Eastern Desert are considered the most likely source of raw copper in the first instance (see Figs. 1 and 2 for sites mentioned below). This has indeed been verified for the Predynastic up to Old Kingdom periods by Kmošek et al. (2018) and Rademakers et al. (2018b). Therefore, their data and those from Abdel-Motelib et al. (2012), Hauptmann et al. (1999), Pfeiffer (2013) and Shortland (2006) form the baseline for comparisons to the Middle Kingdom material, with further comparisons being made to Arabah Valley ores and metals (Faynan: Hauptmann 2007, Hauptmann et al. 1992, 2015; Timna: Asael et al. 2012; Gale et al. 1990; Harlavan et al. 2017; Hauptmann 2007). The metal artefacts have further been compared to ore sources and metal artefacts in the wider Eastern Mediterranean in terms of LI ratios (cfr. Rademakers et al. 2018b, OSM Figures 51–54) and trace element composition. These comparisons are not elaborated here as they reveal poorer consistency with the Middle Kingdom and Kerma material than the interpretations presented below.

Note that Pfeiffer (2013) presents an overview of all published data for ancient Sinai copper production (52 copper artefacts, 45 ores; data from Abdel-Motelib et al. 2012; Bar-Yosef et al. 1977, 1986; Beit Arieh 2003; Hauptmann et al. 1999 and Segal et al. 2004). However, not all elements, such as arsenic, are consistently reported on by these sources. Pfeiffer (2013: Table 10) reports concentration values for iron, zinc and silver for most artefacts; those of nickel, tin and arsenic are less frequently reported, and those for bismuth and antimony even less frequently. Cobalt concentrations are reported for five samples only. Therefore, this dataset should be treated carefully: for example, some "un-alloyed" copper may in fact have a relevant arsenic content, and elevated lead contents may or may not be associated with other elevated element concentrations. Ore data (Pfeiffer 2013, Table 12) is relatively better overall. It should further be noted that LI ratio and elemental data are not consistently reported for each sample, making comparisons difficult for certain ores and artefacts. Overall, available archaeological evidence from mining regions is thus considered an important point of comparison

Fig. 1 Overview of sites mentioned in the text. Green: copper mines, brown: metallurgical workshops, purple: settlements (Map: G. Verly)

(Ben-Yosef 2018), but its quality is critically evaluated and the likelihood of missing evidence is taken into consideration.

For comparisons of ancient metal compositions to those of other metals and ores, process-related changes as part of various steps in the metallurgical production chain must be accounted for wherever possible. To assess the "maximum level" at which the content of a trace element could be reduced from an ore into raw copper, its abundance relative to copper in the ore is considered (cfr. Fig. 6). Certain elements, such as zinc or arsenic, may be substantially depleted in the raw copper with respect to the ore due to, e.g. volatilisation or partitioning into the slag phase. The particular conditions governing these processes can indeed obscure the relation between ore and metal composition, but this does not entirely impede meaningful insights on provenance and technology to be developed (Pernicka 1999, 2014).

In the particular case of Middle Kingdom Egypt, compositional changes between ore and raw copper have been investigated for the Ayn Soukhna process by Rademakers et al. (2020) on the basis of 53 protocoled restitutions carried out by Georges Verly, Frederik Rademakers, Hugues Paridans and the EACOM team to understand the complex smelting technology. Secondary processes, such as alloying, can further distort metal composition along the production chain, in terms of both elemental composition and LI ratios. Apart from raw metal, it is likely that existing metal, circulating within Egypt, was being recycled over time and contributed to the "metal stock" characterising copper alloys in circulation during the Middle Kingdom (Bray et al. 2015; Rademakers et al. 2017).

Therefore, the interpretation of ore, raw copper and copper alloy data differs. Comparisons of ore samples to existing ore

Fig. 2 Detailed overview of sites in Sinai mentioned in the text. Green: copper mines, brown: metallurgical workshops (Maps: G. Verly)

data can be made confidently. For "slag" and raw copper, one should take into account possible changes related to the smelting process (cfr. Rademakers et al. 2020), in terms of elemental composition and, at low lead concentrations, LI ratios. For copper alloys, the possibly skewing effect of secondary metallurgical operations should be considered.

As such, the interpretation of individual artefacts may only make sense when viewed as part of a broader technological system, in this case with Egyptian specificities in terms of both metallurgical techniques and the organisation of production and consumption. The authors therefore follow a careful approach to interpreting the results below (as previously discussed by Rademakers et al. (2017, 2018b, 2020) and references therein), further elaborated in the Discussion.

Protodynastic and Old Kingdom contexts

Some artefacts, previously identified as deriving from Middle Kingdom contexts, were re-evaluated and attributed to Protodynastic and Old Kingdom contexts on the basis of further literature study. As this was only discovered after the

Fig. 3 Selection of analysed artefacts and production waste

publication of contemporary materials from the RMAH collection by Rademakers et al. (2018b), these five artefacts are presented here.

Protodynastic Elkab

The chisel from Tomb 48 at Elkab (E.08445) consists of pure copper, with the exception of ca. 0.4% of arsenic and 0.5% of antimony. Iron, cobalt and nickel concentrations are extremely low. Its LI ratios are similar to those of a Prehistoric pin from the Fayoum (E.01960: Rademakers et al. 2018b), although it has much lower lead (< 5 µg/g as opposed to 140 µg/g in the Fayoum pin) and higher antimony content. They best match the available ore data for Wadi Semna III in the central Eastern Desert, which has elevated antimony content (Abdel-Motelib et al. 2012)—as opposed to the Fayoum pin, for which Wadi el-Regeita is considered a more likely origin. However, primary or secondary processes may have affected the LI ratios, given the very low lead concentration. Furthermore, the arsenic content is not explained by naturally occurring arsenic in the hitherto characterised Eastern Desert ores, and most likely represents intentional alloying (cfr. discussion by Rademakers et al. 2018b). If so, antimony may equally have been introduced at a secondary stage. As

Table 2 Results of XRD analysis. Identified ore, turquoise and "slag" minerals (in wt%): anglesite ($PbSO_4$), atacamite ($Cu_2(OH)_3Cl$), cerussite ($PbCO_3$), clinoatacamite ($Cu_2(OH)_3Cl$), crandallite ($CaAl_3(PO_4)(PO_3OH)(OH)_6$), cuprite ($Cu_2O$), galena (PbS), malachite ($Cu_2(CO_3)(OH)_2$), reichenbachite ($Cu_5(PO_4)_2(OH)_4$), sphalerite (ZnS), tenorite (CuO), turquoise ($CuAl_6(PO_4)_4(OH)_8{\cdot}4H_2O$). Full results reported in OSM

				Copper minerals						Turquoise		Sulphide minerals			
RMAH number	Sampling label	Type	Period	Clinoatacamite	Malachite	Atacamite	Reichenbachite	Tenorite	Cuprite	Turquoise	Crandallite	Galena	Cerussite	Anglesite	Sphalerite
E.04449	EA-MR-193	Copper ore	Protodynastic	49.1	11.3	16.3									
E.06137	EA-MR-173	Copper ore	Old Kingdom	11.0											
E.04793.03	EA-MR-183	Copper ore	Old Kingdom	31.2	1.7				1.2						
E.04793.03	EA-MR-185	Copper ore	Old Kingdom	22.7	4.4										
E.04793.03	EA-MR-186	Copper ore	Old Kingdom	49.7											
E.04793.03	EA-MR-189	Copper ore	Old Kingdom	24.2	2.9										
E.04793.01/02	EA-MR-166	Turquoise (green)	Middle Kingdom							33.9	14.5				
E.04793.01/02	EA-MR-167	Turquoise (blue)	Middle Kingdom							38.8	21.3				
E.04793.01/02	EA-MR-178	Copper ore	Middle Kingdom				8.7								
E.04793.01/02	EA-MR-179	Copper ore	Middle Kingdom	30.2											
E.04793.01/02	EA-MR-180	Copper ore	Middle Kingdom	43.3											
E.04793.01/02	EA-MR-181	Copper ore	Middle Kingdom	15.7	4.3										
E.04793.01/02	EA-MR-182	Copper ore	Middle Kingdom	28.2	4.8										
E.04793.01/02	EA-MR-184	Copper ore	Middle Kingdom			47.2									
E.04793.01/02	EA-MR-187	Copper ore	Middle Kingdom	44.4											
E.04793.01/02	EA-MR-188	Copper ore	Middle Kingdom	37.1	4.6										
E.04793.01/02	EA-MR-190	Copper ore	Middle Kingdom	76.5	12.5										
E.04793.01/02	EA-MR-174	Copper ore	Middle Kingdom	12.5											
E.04793.01/02	EA-MR-175	Copper ore	Middle Kingdom	9.6	22.8										
E.04793.01/02	EA-MR-176	"Slag"	Middle Kingdom					30.5							
E.04662	EA-MR-095	Copper ore	Predynastic/ protodynastic	4.9	93.4										
E.04662	EA-MR-094	Sulphide ore	Predynastic/ protodynastic									75.9	4.1		17.9

Table 2 (continued)

RMAH number	Sampling label	Type	Period	Copper minerals						Turquoise		Sulphide minerals			
				Clinoatacamite	Malachite	Atacamite	Reichenbachite	Tenorite	Cuprite	Turquoise	Crandallite	Galena	Cerussite	Anglesite	Sphalerite
E.04269	EA-MR-100	Copper ore	Protodynastic	12.2	59										
E.04921	EA-MR-102	Copper ore	Protodynastic	8.8	91.2										
E.04921	EA-MR-103	Sulphide ore	Protodynastic									94.4	5.6		
E.04921	EA-MR-104	Sulphide ore	Protodynastic					2.9				53.9	25.7	17.5	

such, the LI ratios of this copper tool may have shifted significantly compared to those of its base copper ore source.

Protodynastic Tharkan

The copper ore from Tomb 1522 Tharkan (E.04449, Dynasty 0) consists of clinoatacamite, malachite and atacamite. It is characterised by very low trace element concentrations, with the exception of 1100 μg/g of lead. This is quite similar to the Pre- or Protodynastic Tharkan copper ore (E.04662: Rademakers et al. 2018b), with slightly lower sulphur and zinc contents. Its LI ratios are highly similar to those of Pre- and Protodynastic copper and lead ores from Tharkan, Abydos and Gizeh (E.04662, E.04269, E.04921: Rademakers et al. 2018b), matching data for previously published kohl/galena identified as representing Eastern Desert ores sources[3] (Masson-Berghoff et al. 2018; Shortland 2006).

Old Kingdom Sinai workshops

Amidst Petrie's (1906) Sinai assemblage at the RMAH, which mainly encompasses Middle Kingdom material, two small groups of Old Kingdom ore and production waste were identified (samples from each context were separated into envelopes and marked by Petrie). These derive from two metallurgical workshop contexts in Wadi Maghara and Seih Ba'ba, Southern Sinai, where ore was smelted into raw metal (E.06137 and E.04793.03). Ore was gathered here from different mines in the area and brought to these centralised workshop areas. One copper ore, one "slag" and one copper prill from assemblage E.06137 and four ore fragments from assemblage E.04793.03 were analysed.

E.06137 The copper ore (EA-MR-173) is relatively rich in iron (rusty-red hematite veins intersperse green atacamite). It has ca. 10% copper and low trace element concentrations except for ca. 500 μg/g of lead.

The associated non-vitrified "slag" fragment (EA-MR-177) has a markedly different composition: ca. 14% of copper, 34% of manganese, higher cobalt and nickel concentrations (ca. 400 μg/g) and an elevated zinc level (ca. 0.5%). Qualitative XRD assessment revealed a high amount of amorphous material, quartz, magnetite (Fe_3O_4) and braunite ($Mn^{2+}Mn^{3+}{}_6(SiO_4)O_8$); some peaks could not be identified (no quantification, cfr. Table 2). Note that this fragment does not represent a "liquid slag", but rather a blackened, heat-impacted ore (similar to the type of reduced ore blocks encountered at Ayn Soukhna: Verly 2017). It thus reflects the metallurgical treatment of a different, manganese-rich ore

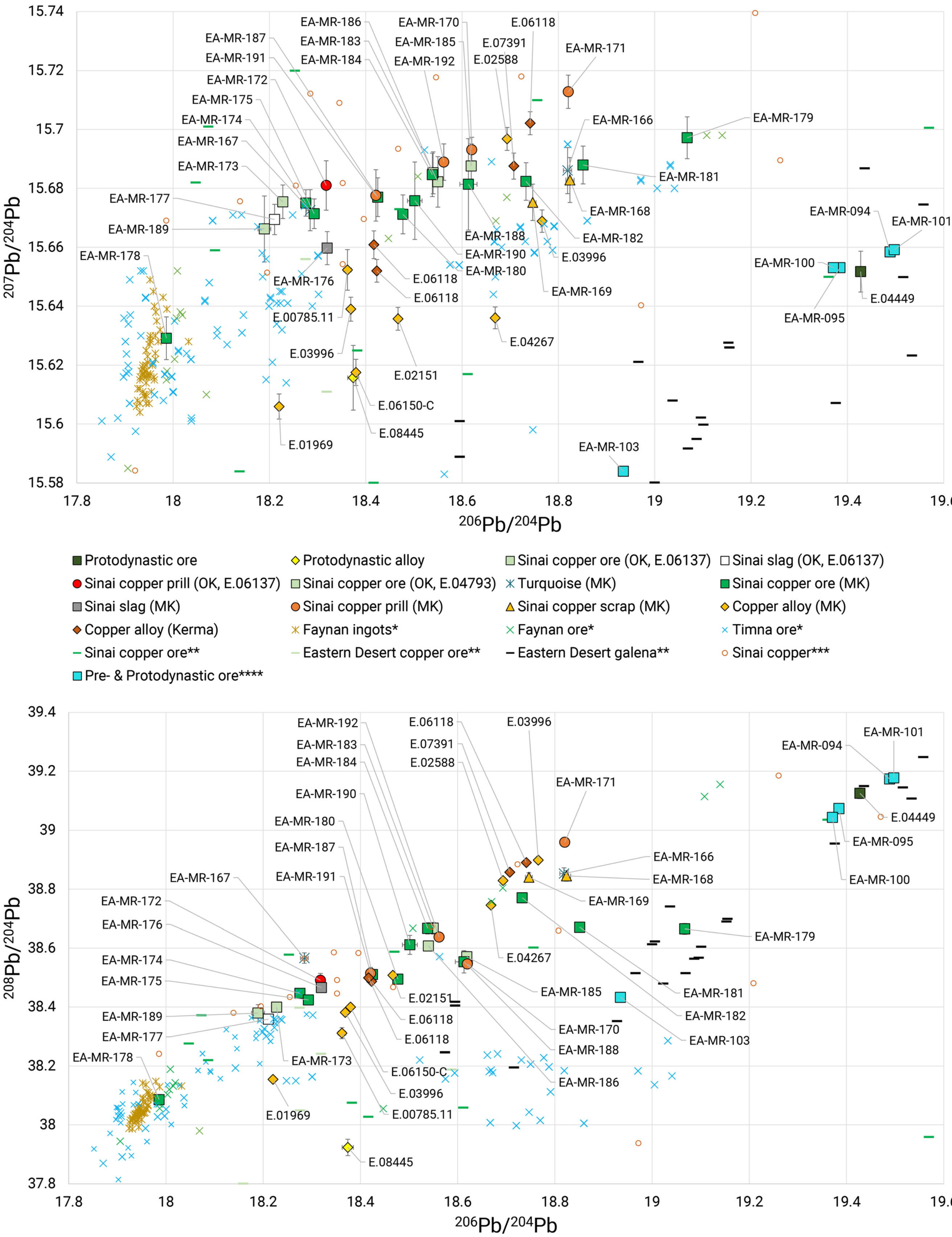
[3] Its LI ratios equally match an Umm Bogma ore sample (Southern Sinai, mining area 45: Abdel-Motelib et al. 2012). This has, however, far lower lead content, making an Eastern Desert origin more likely.

Table 3 Pb isotope ratios for sampled artefacts

kmkg name	Sampling label	Type	Period	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$\sigma^{206}Pb/^{204}Pb$	$\sigma^{207}Pb/^{204}Pb$	$\sigma^{208}Pb/^{204}Pb$	$\sigma^{207}Pb/^{206}Pb$	$\sigma^{208}Pb/^{206}Pb$
E.08445	EA-MR-090	Adze	Protodynastic	18.374	15.616	37.923	0.84988	2.06395	0.006	0.006	0.014	0.00008	0.00022
E.04449	EA-MR-193	Copper ore	Protodynastic	19.428	15.652	39.125	0.80565	2.01391	0.004	0.003	0.009	0.00004	0.00010
E.06137	EA-MR-173	Copper ore	Old Kingdom	18.228	15.675	38.399	0.85997	2.10662	0.003	0.003	0.008	0.00005	0.00015
E.06137	EA-MR-177	"Slag"	Old Kingdom	18.211	15.669	38.358	0.86044	2.10637	0.003	0.003	0.008	0.00004	0.00014
E.06137	EA-MR-172	Copper prill	Old Kingdom	18.318	15.681	38.491	0.85604	2.10123	0.004	0.004	0.012	0.00007	0.00026
E.04793	EA-MR-183	Copper ore	Old Kingdom	18.550	15.682	38.667	0.84532	2.08429	0.004	0.004	0.010	0.00009	0.00014
E.04793	EA-MR-185	Copper ore	Old Kingdom	18.619	15.688	38.571	0.84257	2.07160	0.004	0.004	0.009	0.00008	0.00013
E.04793	EA-MR-186	Copper ore	Old Kingdom	18.540	15.685	38.607	0.84602	2.08240	0.004	0.004	0.008	0.00005	0.00011
E.04793	EA-MR-189	Copper ore	Old Kingdom	18.189	15.666	38.379	0.86129	2.10994	0.007	0.006	0.014	0.00011	0.00021
E.04793	EA-MR-166	Turquoise (green)	Middle Kingdom	18.819	15.686	38.853	0.83352	2.06453	0.004	0.004	0.010	0.00005	0.00013
E.04793	EA-MR-167	Turquoise (blue)	Middle Kingdom	18.285	15.673	38.566	0.85715	2.10922	0.004	0.003	0.009	0.00005	0.00012
E.04793	EA-MR-178	Copper ore	Middle Kingdom	17.986	15.629	38.085	0.86897	2.11750	0.004	0.004	0.009	0.00005	0.00013
E.04793	EA-MR-179	Copper ore	Middle Kingdom	19.067	15.697	38.665	0.82327	2.02789	0.004	0.004	0.009	0.00006	0.00012
E.04793	EA-MR-180	Copper ore	Middle Kingdom	18.477	15.671	38.495	0.84814	2.08334	0.004	0.003	0.008	0.00005	0.00011
E.04793	EA-MR-181	Copper ore	Middle Kingdom	18.851	15.688	38.670	0.83220	2.05136	0.004	0.003	0.008	0.00004	0.00011
E.04793	EA-MR-182	Copper ore	Middle Kingdom	18.733	15.682	38.770	0.83716	2.06964	0.004	0.003	0.008	0.00005	0.00012
E.04793	EA-MR-184	Copper ore	Middle Kingdom	18.538	15.685	38.667	0.84604	2.08571	0.005	0.004	0.009	0.00005	0.00012
E.04793	EA-MR-187	Copper ore	Middle Kingdom	18.425	15.677	38.510	0.85086	2.09013	0.004	0.003	0.008	0.00008	0.00013
E.04793	EA-MR-188	Copper ore	Middle Kingdom	18.613	15.681	38.554	0.84247	2.07126	0.009	0.008	0.019	0.00008	0.00017
E.04793	EA-MR-190	Copper ore	Middle Kingdom	18.502	15.676	38.611	0.84724	2.08688	0.008	0.007	0.016	0.00010	0.00018
E.04793	EA-MR-174	Copper ore	Middle Kingdom	18.276	15.675	38.446	0.85771	2.10370	0.003	0.002	0.007	0.00006	0.00020
E.04793	EA-MR-175	Copper ore	Middle Kingdom	18.293	15.671	38.423	0.85668	2.10043	0.002	0.003	0.008	0.00004	0.00018
E.04793	EA-MR-176	"Slag"	Middle Kingdom	18.320	15.660	38.466	0.85479	2.09966	0.003	0.003	0.008	0.00004	0.00015

Table 3 (continued)

kmkg name	Sampling label	Type	Period	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$\sigma^{206}Pb/^{204}Pb$	$\sigma^{207}Pb/^{204}Pb$	$\sigma^{208}Pb/^{204}Pb$	$\sigma^{207}Pb/^{206}Pb$	$\sigma^{208}Pb/^{206}Pb$
E.04793	EA-MR-191	Copper prill	Middle Kingdom	18.421	15.678	38.514	0.85106	2.09075	0.005	0.004	0.010	0.00007	0.00016
E.04793	EA-MR-192	Copper prill	Middle Kingdom	18.562	15.689	38.638	0.84522	2.08159	0.003	0.003	0.008	0.00005	0.00012
E.04793	EA-MR-170	Copper prill	Middle Kingdom	18.620	15.693	38.546	0.84281	2.07018	0.003	0.002	0.006	0.00006	0.00013
E.04793	EA-MR-171	Copper prill	Middle Kingdom	18.820	15.713	38.959	0.83488	2.07003	0.003	0.003	0.008	0.00004	0.00015
E.04793	EA-MR-168	Copper alloy (scrap)	Middle Kingdom	18.824	15.683	38.845	0.83312	2.06356	0.004	0.004	0.009	0.00005	0.00013
E.04793	EA-MR-169	Copper alloy (scrap)	Middle Kingdom	18.747	15.675	38.840	0.83617	2.07186	0.003	0.003	0.008	0.00006	0.00012
E.00785.11	EA-MR-001	Mirror—disk	Middle Kingdom	18.362	15.652	38.311	0.85244	2.08639	0.004	0.003	0.009	0.00006	0.00018
E.01969	EA-MR-116	Mirror—disk	Middle Kingdom	18.220	15.606	38.155	0.85652	2.09411	0.003	0.002	0.005	0.00003	0.00009
E.03996	EA-MR-118	Mirror—tang	Middle Kingdom	18.369	15.639	38.381	0.85139	2.08949	0.002	0.002	0.005	0.00003	0.00007
E.03996	EA-MR-119	Mirror—disk	Middle Kingdom	18.766	15.669	38.898	0.83496	2.07279	0.002	0.002	0.005	0.00003	0.00007
E.04267	EA-MR-120	Mirror—disk	Middle Kingdom	18.669	15.636	38.745	0.83755	2.07540	0.002	0.002	0.004	0.00003	0.00009
E.06150-C	EA-MR-126	Miniature chisel	Middle Kingdom	18.380	15.618	38.400	0.84972	2.08927	0.002	0.002	0.006	0.00003	0.00009
E.02588	EA-MR-089	Blade/file	Middle Kingdom	18.693	15.697	38.829	0.83970	2.07716	0.002	0.002	0.005	0.00003	0.00013
E.06118	EA-MR-112	Dagger—blade	Classic Kerma	18.423	15.652	38.487	0.84959	2.08905	0.002	0.002	0.005	0.00003	0.00008
E.06118	EA-MR-113	Dagger—handle	Classic Kerma	18.417	15.661	38.499	0.85035	2.09043	0.002	0.002	0.006	0.00004	0.00009
E.06118	EA-MR-114	Dagger—rivet	Classic Kerma	18.741	15.702	38.890	0.83782	2.07508	0.002	0.002	0.005	0.00003	0.00011
E.07391	EA-MR-115	Dagger—blade	Classic Kerma	18.707	15.688	38.857	0.83858	2.07711	0.002	0.002	0.006	0.00003	0.00008
E.02151	EA-MR-129	Statuette	Middle Kingdom	18.467	15.636	38.508	0.84669	2.08526	0.002	0.002	0.005	0.00004	0.00008



$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
EA-MR-186
EA-MR-187
EA-MR-183
EA-MR-191
EA-MR-184
EA-MR-172
EA-MR-175
EA-MR-174
EA-MR-167
EA-MR-173
EA-MR-177
EA-MR-189
EA-MR-178
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EA-MR-185
EA-MR-192
E.06118
E.07391
E.02588
EA-MR-171
EA-MR-166
EA-MR-179
EA-MR-181
EA-MR-168
EA-MR-182
EA-MR-188
EA-MR-190
EA-MR-180
EA-MR-169
E.04267
E.02151
E.06150-C
E.08445
E.01969
EA-MR-103
EA-MR-094
EA-MR-101
EA-MR-100
EA-MR-095
E.04449
Protodynastic ore
Protodynastic alloy
Sinai copper ore (OK, E.06137)
Sinai slag (OK, E.06137)
Sinai copper prill (OK, E.06137)
Sinai copper ore (OK, E.04793)
Turquoise (MK)
Sinai copper ore (MK)
Sinai slag (MK)
Sinai copper prill (MK)
Sinai copper scrap (MK)
Copper alloy (MK)
Copper alloy (Kerma)
Faynan ingots*
Faynan ore*
Timna ore*
Sinai copper ore**
Eastern Desert copper ore**
Eastern Desert galena**
Sinai copper***
Pre- & Protodynastic ore****
$^{208}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$

◀ **Fig. 4** Overview of artefact Pb isotope ratios. *Arabah valley copper ore and ingot data (Faynan: Hauptmann 2007; Hauptmann et al. 1992, 2015; Timna: Asael et al. 2012, Gale et al. 1990, Harlavan et al. 2017, Hauptmann 2007), **Sinai and Eastern Desert copper ore and galena data (Abdel-Motelib et al. 2012, Brill et al. 1974, Shortland 2006, Stacey et al. 1980, Stos-Gale and Gale 1981), ***Sinai copper data (compiled by Pfeiffer 2013: presumably "raw" copper), ****Pre- and Protodynastic ore (Rademakers et al. 2018b)

type, although possibly deriving from the same geological deposit: its LI ratios are highly similar to those of the abovementioned copper ore and broadly consistent with Southern Sinai ore and slag, as well as a copper ore from Ayn Soukhna[4] characterised by Abdel-Motelib et al. (2012). The high manganese content does not constitute a separately added smelting flux, but appears naturally associated. This suggests Umm Bogma may be the most likely mining source (Abdel-Motelib et al. 2012, p. 42).

The associated copper prill (EA-MR-172) is made of highly pure copper and most likely represents a raw smelting product. It contains ca. 0.6% of sulphur, 500 μg/g of iron and only 13 μg/g of lead. Its LI ratios fall within the same Southern Sinai range as those of the ore and "slag", but do not match either exactly (slightly higher $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ values). It may, nonetheless, be considered compatible with either one of the ore types attested by the ore and slag samples (Rademakers et al. 2020). It should be considered an example of raw copper compositions available during the Old Kingdom for further processing into copper (alloy) artefacts. None of the hitherto analysed Old Kingdom artefacts (Kmošek et al. 2018; Rademakers et al. 2018b) have similar LI ratios, while all have elevated arsenic (and lead) concentrations relative to this raw copper prill.

E.04973.03 Three copper ore fragments (EA-MR-183/186/189) are characterised by low trace element concentrations overall, while the fourth (EA-MR-185) has slightly higher nickel and lead levels and significantly higher cobalt, manganese and zinc concentrations. In terms of LI ratios, these fragments are again consistent with Southern Sinai deposits: one ore fragment (EA-MR-189) is indistinguishable from the E.06137 "slag" and ore, while the other three display relatively higher $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ ratios—comparable to the Middle Kingdom workshop remains discussed below.

Middle Kingdom contexts

Sinai workshops

From the E.04793 lot at the RMAH, one part (E.047093.03, cfr. above) is associated with an Old Kingdom workshop described by Petrie (1906). The rest of this lot, however, was separately marked and derives from Middle Kingdom workshop contexts in the Southern Sinai (Petrie 1906): E.04793.01 and E.04793.02 (cfr. OSM). The first concerns a settlement near Wadi Maghara, most likely dated to the 12th Dynasty, where ore collected from mining expeditions was processed: Petrie notes abundant evidence for primary as well as secondary metallurgy. The second one concerns a similar settlement close to Wadi Nasb, Wadi Kharig, Serabit el-Khadim, Seih Ba'ba, Wadi Ba'ba and Wadi Ahmar. Sadly, fragments from both contexts were mixed and cannot be securely assigned to either—they are therefore discussed together.

Both settlements most likely acted as a centralised gathering point for ores obtained from nearby mines (Petrie notes no mineralisation present at the settlement locations) such as Bir Nasb, Wadi Kharig, Umm Bogma and Wadi Maghara (cfr. Fig. 2). Turquoise passed through these settlements as well, most likely mined at Wadi Maghara and Serabit el-Khadim.

Eleven ore fragments have been sampled for analysis, covering different mineralisations. Furthermore, two turquoise samples have been included for comparison. One ore fragment appears to have been heated and partially reduced (non-vitrified "slag", cfr. above). Amidst the ore fragments, four small copper prills were found and two tiny fragments of worked metal—possibly fragments of artefacts/scrap. As such, different steps of the production chain at these workshops are attested, even though a direct contextual relation between each of the samples remains tentative: they may derive from different production events taking place over time at these workshops.

Ore The ore fragments (all clinoatacamite-malachite) have 9 to 45% of copper (average 23%) and are characterised by overall low trace element concentrations: apart from iron, cobalt, manganese, sulphur and zinc[5], all elements are present at concentrations below 0.1% and mostly below 100 μg/g. This is in line with observations made for Sinai copper ore by Abdel-Motelib et al. (2012)—with zinc being notably higher at Umm Bogma area "45" and Serabit el-Khadim—and copper ore found at Kahun (Gilmore 1986). The only Sinai ore[6] with percentage levels of manganese sampled by Abdel-Motelib et al. (2012) derives from Umm Bogma area "45" (sample ET-55/4). Lead contents vary between ca. 40 and 500 μg/g, which is normal to relatively high compared to previously published Sinai ores.

The ore LI ratios overlap with the range of hitherto characterised Southern Sinai ore and slag. More specifically,

[4] Abdel-Motelib et al. (2012) list the ore as deriving "from archaeological contexts", without further details.

[5] Cobalt, manganese, nickel and zinc concentrations are loosely correlated.

[6] Although percentage levels of manganese are encountered in slag from Wadi Homr (ET-50/1), Bir Nasib (ET-51/1, ET-53/1), Wadi Nasib (ET-52/1), Wadi Ba'Ba (ET-57/1) and Wadi Nefoukh (ET-72/1).

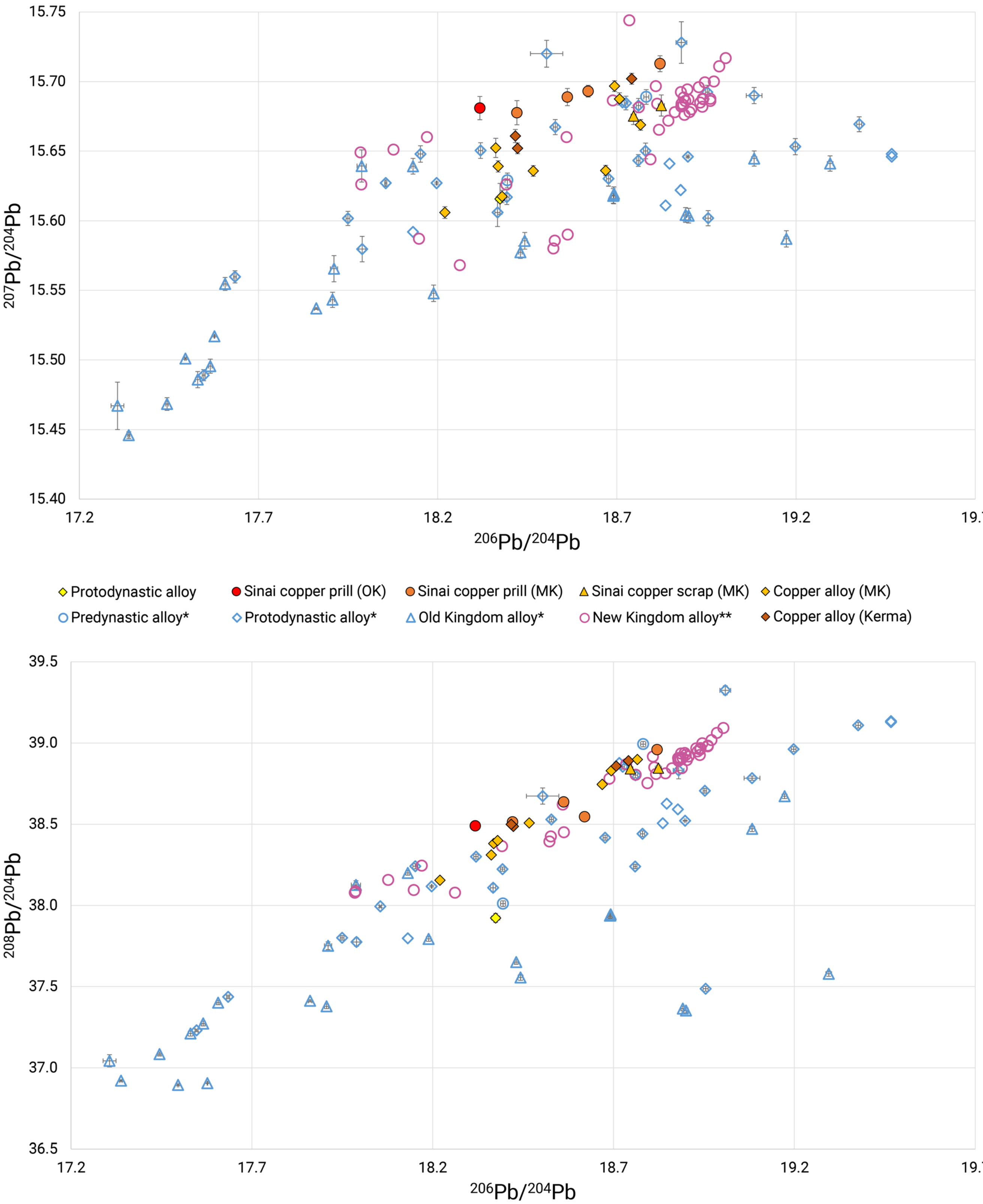

Fig. 5 Pb isotope ratios—comparison to *Predynastic, Protodynastic and Old Kingdom artefact data (various sites: Kmošek et al. 2018 (15 artefacts), Rademakers et al. 2018b (40 artefacts), Tell el-Farkha: Rehren and Pernicka 2014 (13 artefacts)) and **New Kingdom artefact data (Pi-Ramesse: Rademakers et al. 2017 (26 artefacts), Amarna: Stos-Gale et al. 1995 (16 artefacts))—radiogenic Pb isotope ratios not shown

Table 4 Element concentrations for sampled artefacts (all in µg/g, except for Cu in wt%) (*): Au content not quantified due to high Mn peak overlap; *n.d.* not determined

RMAH number	Sampling label	Type	Period	Cu (%)	Ag	As	Au	Ba	Bi	Co	Cr	Fe
E.08445	EA-MR-090	Adze	Protodynastic	80.0	45	3800	3	< 5	230	< 2	< 2	11
E.04449	EA-MR-193	Copper ore	Protodynastic	40.1	8	25	10	110	< 10	30	16	24000
E.06137	EA-MR-173	Copper ore	Old Kingdom	10.4	1	35	< 15	30	45	14	145	213000
E.06137	EA-MR-177	"Slag"	Old Kingdom	14.0	17	25	< 4200*	135	25	410	90	125000
E.06137	EA-MR-172	Copper prill	Old Kingdom	97.7	50	135	8	< 1	< 10	12	< 1	470
E.04793	EA-MR-183	Copper ore	Old Kingdom	21.7	< 2	16	< 2	45	< 10	7	90	10000
E.04793	EA-MR-185	Copper ore	Old Kingdom	19.0	< 2	25	< 350*	65	< 10	250	80	9300
E.04793	EA-MR-186	Copper ore	Old Kingdom	33.8	< 2	25	< 2	25	14	6	75	5500
E.04793	EA-MR-189	Copper ore	Old Kingdom	14.2	4	30	2	30	14	9	140	51000
E.04793	EA-MR-166	Turquoise (green)	Middle Kingdom	6.1	< 2	30	3	380	< 10	200	30	16000
E.04793	EA-MR-167	Turquoise (blue)	Middle Kingdom	6.8	10	50	3	500	< 10	75	20	8700
E.04793	EA-MR-178	Copper ore	Middle Kingdom	8.5	7	20	70	590	< 10	16	< 10	6900
E.04793	EA-MR-179	Copper ore	Middle Kingdom	22.3	< 2	115	4	25	16	135	85	28000
E.04793	EA-MR-180	Copper ore	Middle Kingdom	25.3	< 2	170	< 500*	90	15	1200	85	42000
E.04793	EA-MR-181	Copper ore	Middle Kingdom	21.5	3	115	< 500*	100	< 10	3400	90	31000
E.04793	EA-MR-182	Copper ore	Middle Kingdom	22.7	< 2	135	70	140	13	60	85	23000
E.04793	EA-MR-184	Copper ore	Middle Kingdom	32.5	10	16	< 2	16	20	5	390	13000
E.04793	EA-MR-187	Copper ore	Middle Kingdom	24.8	< 2	125	< 100*	130	< 10	680	75	22000
E.04793	EA-MR-188	Copper ore	Middle Kingdom	24.7	< 2	190	10	65	< 10	40	125	48000
E.04793	EA-MR-190	Copper ore	Middle Kingdom	44.9	< 2	13	< 2	15	< 10	4	150	1900
E.04793	EA-MR-174	Copper ore	Middle Kingdom	14.6	6	35	< 1000*	110	< 30	95	90	91000
E.04793	EA-MR-175	Copper ore	Middle Kingdom	15.0	6	19	< 1600*	60	< 25	390	85	159000
E.04793	EA-MR-176	"Slag"	Middle Kingdom	15.7	< 2	45	19	50	< 25	7	250	47000
E.04793	EA-MR-191	Copper prill	Middle Kingdom	60.9	< 2	390	3	25	< 10	190	13	2800
E.04793	EA-MR-192	Copper prill	Middle Kingdom	76.3	3	240	< 2	4	< 10	590	< 10	8200
E.04793	EA-MR-170	Copper prill	Middle Kingdom	60.5	1	100	16	35	< 25	440	30	7600
E.04793	EA-MR-171	Copper prill	Middle Kingdom	27.9	< 2	95	45	20	< 70	240	30	5400
E.04793	EA-MR-168	Copper alloy (scrap)	Middle Kingdom	73.1	610	2300	4	< 2	< 10	50	< 10	2700
E.04793	EA-MR-169	Copper alloy (scrap)	Middle Kingdom	72.3	60	6700	20	< 2	< 10	25	< 10	2700
E.00785.11	EA-MR-001	Mirror—disk	Middle Kingdom	76.7	1500	14000	40	2	60	6	2	1400
E.01969	EA-MR-116	Mirror—disk	Middle Kingdom	89.9	140	37000	< 4	< 2	90	170	< 3	2600
E.03996	EA-MR-118	Mirror—tang	Middle Kingdom	94.7	< 45	2400	< 4	< 2	< 5	180	8	3600
E.03996	EA-MR-119	Mirror—disk	Middle Kingdom	90.0	320	29000	85	< 1	< 40	4	< 1	1200
E.04267	EA-MR-120	Mirror—disk	Middle Kingdom	83.8	80	46000	< 4	< 5	< 50	150	10	3700
E.06150-C	EA-MR-126	Miniature chisel	Middle Kingdom	94.7	125	9200	15	< 1	< 50	370	< 2	4800
E.02588	EA-MR-089	Blade/file	Middle Kingdom	59.0	< 10	28000	5	10	< 60	40	5	65000
E.06118	EA-MR-112	Dagger—blade	Classic Kerma	88.9	160	4000	10	380	< 60	125	25	8600
E.06118	EA-MR-113	Dagger—handle	Classic Kerma	98.3	190	7100	10	105	< 80	130	15	440
E.06118	EA-MR-114	Dagger—rivet	Classic Kerma	96.1	65	650	20	1400	< 40	15	6	180
E.07391	EA-MR-115	Dagger—blade	Classic Kerma	92.7	180	5500	20	< 3	< 40	20	6	1500
E.02151	EA-MR-129	Statuette	Middle Kingdom	94.8	180	27000	50	< 3	75	15	6	2500

Table 4 (continued)

RMAH number	Mg	Mn	Ni	P	Pb	S	Sb	Se	Sn	Te	Ti	Zn	U	Sum (%)
E.08445	200	1	9	50	< 5	180	5100	22	60	95	< 2	< 10	*n.d.*	81.0
E.04449	4500	730	35	370	1100	330	< 10	19	< 25	55	2400	20	400	43.5
E.06137	2600	95	45	300	520	1000	85	< 10	< 15	40	2200	120	*n.d.*	32.4
E.06137	8000	337000	350	315	135	3600	< 25	280	< 25	45	1000	5400	*n.d.*	62.2
E.06137	8	80	155	< 4	13	6100	20	< 10	< 5	110	2	14	*n.d.*	98.4
E.04793	7600	30	20	240	40	320	< 10	< 15	45	30	2700	180	< 5	23.9
E.04793	5600	24000	85	850	410	1900	< 10	25	< 25	25	1400	2400	< 5	23.7
E.04793	4800	25	20	180	50	240	< 10	< 15	< 25	40	2400	280	< 5	35.2
E.04793	4400	40	20	210	100	420	< 10	< 15	< 25	19	2800	95	60	20.2
E.04793	710	280	53	210000	7	1800	<10	< 15	< 25	5	160	46000	35	33.7
E.04793	1500	160	4	200000	390	12000	< 10	< 15	< 25	3	1200	18000	< 5	31.0
E.04793	2400	5100	17	7000	530	1000	< 10	< 15	< 25	13	1300	50	10	11.0
E.04793	3200	310	135	130	130	270	< 10	< 15	< 25	40	2000	1700	1100	26.0
E.04793	3800	31000	670	190	190	690	< 10	30	< 25	35	2100	8800	280	34.4
E.04793	4200	32000	320	420	100	820	< 10	25	< 25	30	2100	850	760	29.1
E.04793	5000	5300	60	220	35	290	< 10	< 15	< 25	35	3700	1100	50	26.7
E.04793	2500	35	16	330	50	3000	< 10	< 15	< 25	45	1000	85	8	34.5
E.04793	4700	4900	130	190	130	540	< 10	< 15	< 25	30	2200	1100	75	28.5
E.04793	4500	7000	115	190	75	360	< 10	< 15	< 25	35	2300	4400	220	31.5
E.04793	8100	40	50	75	190	390	< 10	< 15	< 25	75	660	160	< 5	46.0
E.04793	1900	89000	65	480	310	6000	9	< 10	< 15	45	3100	630	*n.d.*	33.9
E.04793	3000	120000	80	180	195	2900	< 10	< 35	< 25	45	1300	1100	*n.d.*	43.8
E.04793	4500	70	17	250	45	980	20	< 35	< 25	30	2400	75	*n.d.*	21.3
E.04793	2900	220	440	125	90	7600	< 20	< 15	< 25	75	280	1200	< 5	62.6
E.04793	560	20	770	280	85	4500	< 20	< 15	< 25	105	120	1900	< 5	78.0
E.04793	26400	185	780	650	65	5400	< 10	< 15	< 10	95	2400	480	*n.d.*	65.0
E.04793	18000	280	360	400	30	7400	< 20	< 35	< 50	< 50	1700	130	*n.d.*	31.3
E.04793	720	25	160	420	40	410	< 30	< 15	540	100	90	40	< 5	73.9
E.04793	1200	< 5	250	55	430	1800	50	35	1200	90	30	12	< 5	73.7
E.00785.11	65	1	860	180	145	910	2200	50	100	120	< 1	10	*n.d.*	78.9
E.01969	< 35	2	710	< 70	910	1800	400	< 15	8200	125	6	45	*n.d.*	95.1
E.03996	< 150	< 2	430	< 100	350	840	< 110	< 2	2500	135	25	65	*n.d.*	95.7
E.03996	< 60	< 1	130	< 45	270	620	190	30	11000	120	5	< 10	*n.d.*	94.3
E.04267	< 150	10	340	790	1800	2700	190	20	< 600	85	125	140	*n.d.*	89.4
E.06150-C	< 15	< 1	520	< 50	1400	2300	230	50	520	125	4	150	*n.d.*	96.7
E.02588	140	45	170	2900	1200	1400	280	40	990	90	5	125	*n.d.*	69.0

Table 4 (continued)

E.06118	< 150	40	1500	130	720	3000	390	< 1	1600	105	35	250	*n.d.*	91.0
E.06118	< 150	10	1300	220	320	4100	380	40	< 750	140	80	50	*n.d.*	99.7
E.06118	< 35	2	730	210	55	680	180	45	< 400	130	30	20	*n.d.*	96.6
E.07391	< 35	< 1	330	200	970	3200	240	< 1	< 400	120	25	240	*n.d.*	94.0
E.02151	< 5	2	160	40	440	1300	360	75	370	145	3	20	*n.d.*	98.1

there is a good correspondence with samples from Umm Bogma and, to a lesser extent, Wadi Kharig (ET-55/1 and ET 54/1, respectively: Abdel-Motelib et al. 2012), while smelting slag samples from various Southern Sinai sites (e.g. Sheikh Mukhsen, Wadi Ba'Ba and Wadi Homr) have similar LI ratios (the three Sheikh Mukhsen copper ore samples are more radiogenic). One of the Ayn Soukhna ore samples[4] (ET-66/2: Abdel-Motelib et al. 2012) falls exactly within the range of ores presented here.

The highest LI ratios in the assemblage (sample EA-MR-179) are associated with elevated uranium content (ca. 0.1%), yet fall along the overall trend-line presented by the LI ratio data. This trend-line does not form an isochron and most likely covers multiple mineralisation events. Indeed, the data likely represents multiple mines, characterised by varying cobalt, nickel, zinc and uranium contents, belonging to the same broader ore range. The lowest LI ratios (sample EA-MR-178) sit slightly below this broad trend-line and may represent a distinct ore deposit.

"Slag" The fragment of heat-exposed ore is of the same type as the Old Kingdom material discussed above. It is dominated by tenorite (cfr. Rademakers et al. 2020) and likely derives from a larger "Ayn Soukhna type slag block". It is characterised by an elemental composition that is similar to that of the ore fragments, and its LI ratios fall within the broad range attested in the associated ore.

Copper prills The four copper prills are composed of fairly pure copper, similar to the Old Kingdom prill discussed above. Notable trace elements are arsenic (100–400 μg/g), cobalt (200–600 μg/g), nickel (400–800 μg/g), manganese[7] (20–300 μg/g) and zinc (100–1900 μg/g), while lead is present at lower concentrations (< 100 μg/g) and the level of iron varies between 0.3 and 0.8%. The copper ores EA-MR-174/179/180/181/187 from the same context have similar or higher abundances of these trace elements (relative to copper) and thus represent possible sources for the production of these prills.

In terms of LI ratios, three prills (EA-MR-170/191/192) fully overlap with the LI range of the ores, while one prill (EA-MR-171) has slightly elevated $^{207\text{-}208}Pb/^{204}Pb$ values. Compared to the five "chemically compatible ores", prill EA-MR-191 is isotopically indistinguishable from ore EA-MR-187, while the others have slightly elevated $^{207\text{-}208}Pb/^{204}Pb$ values. These prills are thus compatible with the associated ores, allowing for some further variability among the ores and relative shifts introduced during smelting.

[7] In contrast with iron, which may be partly reduced to its metallic state, manganese requires far more reducing conditions and its reduction into the metal phase is expected to be negligible (Hauptmann 2007). The slightly elevated trace contents observed in the raw copper prills may thus be attributed to minor MnO and/or MnS inclusions (which may be accompanied, i.a., by iron oxides or sulphides). Manganese concentrations are obviously much lower in the finished artefacts, as would be expected after removal (as dross) during crucible melting (and alloying).

Copper alloys The two copper alloy fragments are very small, making it difficult to ascertain their original shape (they may represent scrap fragments), but both derive from thinly worked (hammered, sheet) metal objects. Compared to the copper prills, they have far lower cobalt, nickel and zinc concentrations. The iron content is low but similar (0.3%), the lead content is similar in one and slightly higher in the other. In contrast, both fragments have relatively elevated arsenic (0.2–0.7%), silver (60–600 μg/g) and tin (0.05–0.12%) concentrations. None of these elements are known to occur at similar concentrations in the Southern Sinai ores characterised so far. The LI ratios of the two fragments fall within the range of the raw copper prills (and ore) at the workshop. However, on top of a possible shift introduced by smelting, alloying and mixing/recycling may have further skewed these LI ratios with respect to ore and raw copper LI ratios (cfr. discussion).

Turquoise One green and one blue turquoise fragment were analysed (crandallite accompanies turquoise). Elevated iron and zinc (substituting for aluminium and copper) explain the more green to yellow shade of the former. Their trace element composition falls within the range attested by the copper ores, with the exception of higher phosphorus and zinc (regular constituents of the mineral) levels and a lower tellurium concentration. Their LI ratios are consistent with those of the presented copper ores, with a slightly elevated $^{208}Pb/^{204}Pb$ ratio in the blue turquoise.

Overall, this strengthens the hypothesis that both turquoise and copper ore were extracted in the same Sinai mining district, arriving at centralised Middle Kingdom workshops situated at the valley mouths during one or multiple campaigns.

Finished objects

With one exception, all the objects analysed consist of copper alloys: copper with concentrations of 0.3–4.6% arsenic (the main alloy component) and/or 0.05–1.1% tin. The two scrap finds from Sinai share these characteristics.

These objects are all relatively enriched in silver, arsenic, lead, antimony and tin when compared to the raw copper and ore presented above, while being relatively depleted in cobalt, iron, manganese and zinc (Fig. 6). Their LI ratios show an important overlap with those of Southern Sinai ores and raw copper, though shifted towards slightly lower values on average. These observations are fully compatible with changes that may occur during secondary metallurgy of copper produced from Sinai ores, which include oxidation, volatilisation and mixing during remelting and alloying.

Mirrors: Dayr al-Barsha area, Qift and Abydos Four mirrors from three different sites have been analysed: two consist of arsenical copper, while the other two are ternary bronzes (copper-arsenic-tin).

The mirror (E.00785.11) from the Tomb of Abou (11th Dynasty, Dayr-al Barsha area), consists of (entirely corroded) arsenical copper, with notable traces of antimony, nickel and silver, while mirror E.04267 from Abydos (ca. 4.5% arsenic) has traces of silver, cobalt, nickel, antimony and zinc, with almost 0.2% of lead and 0.4% of iron. The LI ratios of both mirrors differ significantly, but both fall within the range of Southern Sinai ore data, sitting slightly below the trend-line defined by Middle Kingdom ore and raw copper discussed above (particularly for $^{207}Pb/^{204}Pb$: E.04267).

The Qift (Koptos) mirror (E.01969) contains almost 3.7% of arsenic and 0.8% of tin, making it a ternary bronze—just like Abydos mirror E.03996 (2.9% arsenic and 1.1% tin). Silver, nickel, antimony and lead are present as trace elements at levels up to a few 100 μg/g (as is cobalt in E.01969 and 85 μg/g gold in E.03996), with 0.1–0.25% of iron. The lead concentration is slightly higher in E.01969. The two mirrors' LI ratios again fall within the range of Southern Sinai ore data. E.01969 sits furthest below the trend-line defined by the Sinai ores and raw copper discussed above, while E.03996 is characterised by relatively higher $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ values, similar to metal scrap discussed above.

For mirror E.03996, compositional variability between the mirror disk (following terminology by Lilyquist 1979) and tang (a folded sheet fragment, attached by three rivets) was noted by handheld XRF, prompting the sampling of both. While the mirror itself is composed of a ternary bronze, the tang contains only 0.25% of both arsenic and tin (indicative of recycling, cfr. Discussion). In terms of trace elements, the mirror disk shows slightly higher silver, gold and antimony levels, while the tang has slightly higher cobalt, nickel and zinc concentrations. The LI ratios differ significantly, with the tang's LI ratios being more similar to those of the Abou mirror. This indicates that two different copper sources were used for the manufacturing of this mirror—in one or multiple production events taking place at one or multiple locations over time.

The Middle Kingdom mirror compositions reported by Garenne-Marot (1984), Gilmore (1986) and Odler et al. (2018) show similar trace element patterns and arsenic contents (one 12th Dynasty mirror from Elkab has only 0.3–0.4% arsenic), but none of these reveal elevated tin contents. Vandier d'Abbadie and Michel (1972) report[8] pure copper, arsenical copper and tin bronze mirrors (some of the latter with up to 0.5% arsenic). They equally note a different composition in a mirror disk and its handle.

Chisel: Beni Hassan This miniature chisel (E.06150-C) consists of a low (ca. 0.9%) arsenical copper with traces of silver, cobalt, nickel, antimony and zinc, 0.14% of lead and ca. 0.5% of iron. Its LI ratios fall within the range of Southern Sinai ore

[8] The contextual information for these artefacts is not provided by Vandier d'Abbadie and Michel (1972).

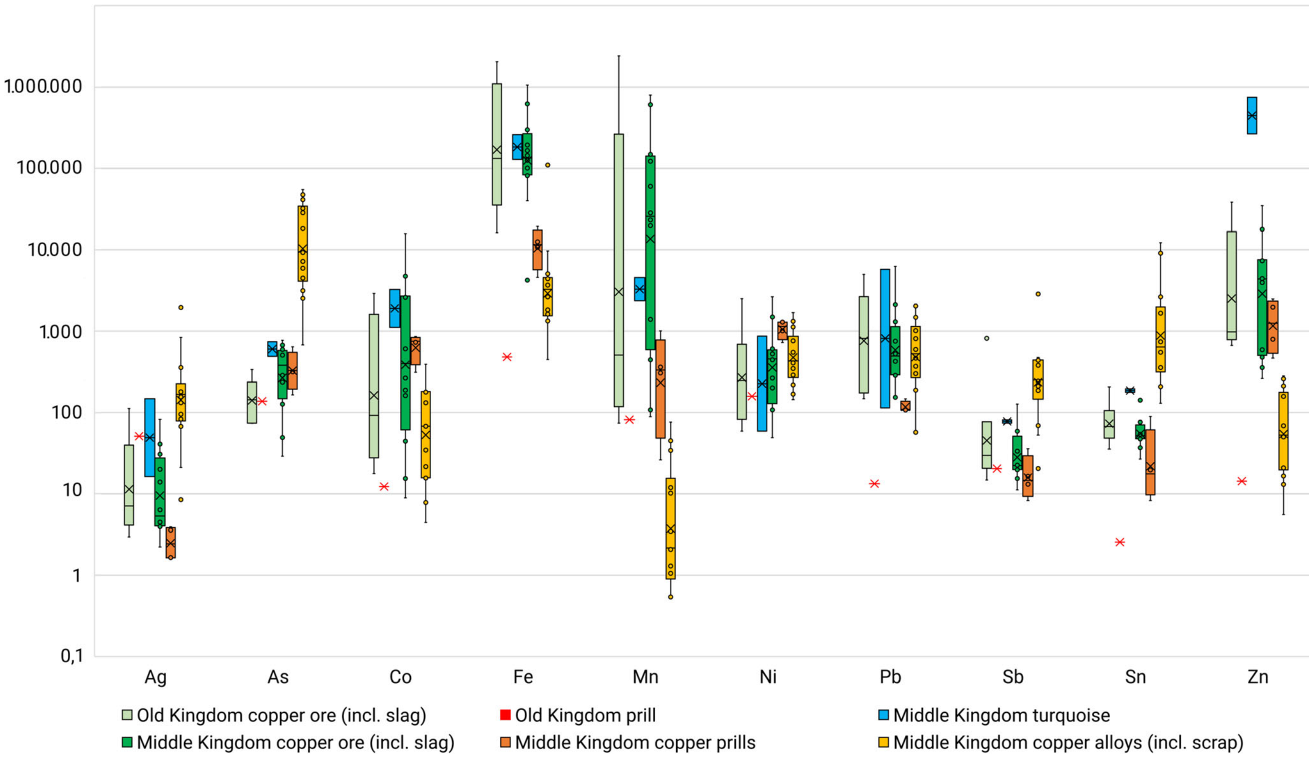

Fig. 6 Box blot of element concentrations (in µg/g) for artefact groups discussed in the text—normalised to copper

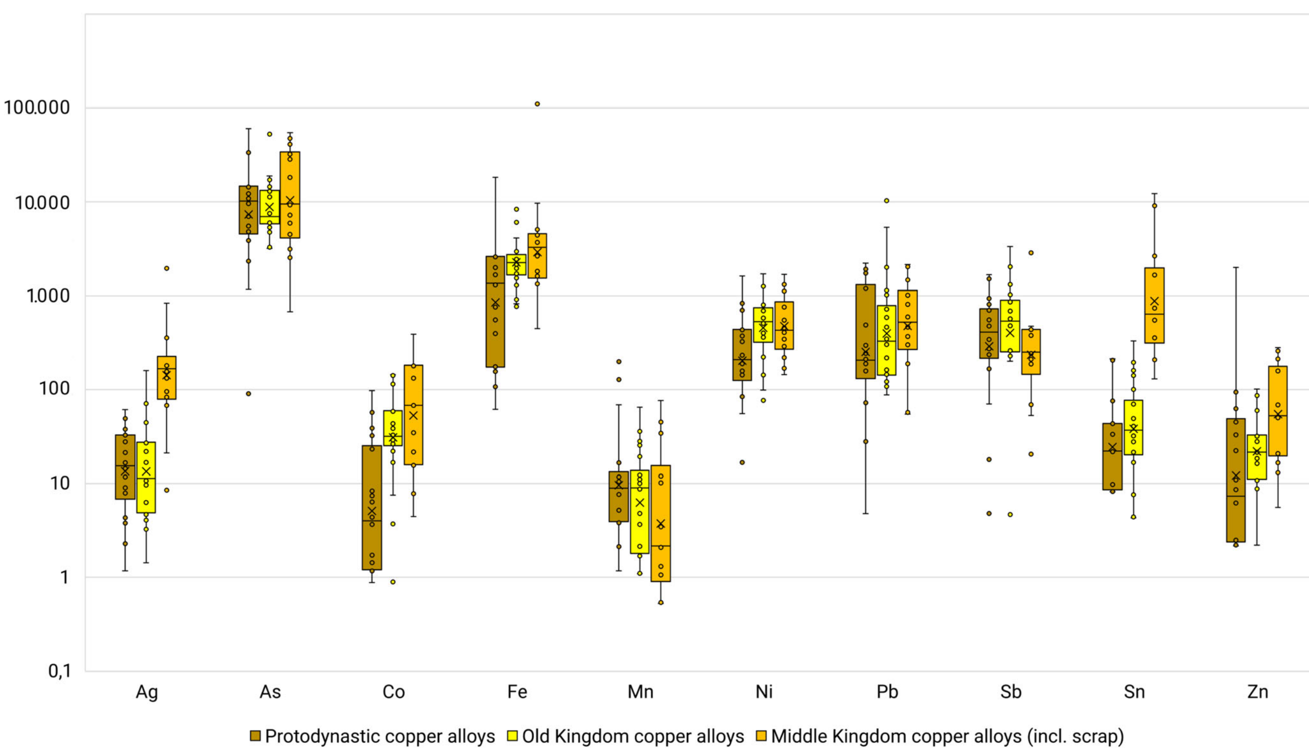

Fig. 7 Box plot comparing element concentrations (in µg/g) for copper alloys over time—normalised to copper (Protodynastic and Old Kingdom artefact data: Rademakers et al. 2018b)

data, but sit below the trend-line defined by the Sinai ores and raw copper presented above.

Blade: Tell el-Yahudiyeh The blade (E.02588) of what is most likely a file is made of arsenical copper with almost 3% of arsenic (indicative: the object is strongly corroded). The presence of nearly 0.1% of tin stands out, with notable traces of nickel, antimony and zinc. The remarkably high iron content (ca. 6.5%) can be attributed to corrosion/concretion rather than representing metallic iron or slag inclusions. Its LI ratios fall within the range of Southern Sinai ore data, including those for ore and raw copper presented above. They are very similar (though not identical) to the LI ratios of the Kerma dagger E.07391 (see below).

Statuette: unknown context The statuette of a walking man (E.02151, stylistically attributed to the Middle Kingdom) is made of arsenical copper (2.7% arsenic). It has notable traces of silver, nickel lead and tin, with 0.25% of iron.

Its LI ratios fall within the range of Southern Sinai ore data, but sit below the trend-line defined by the Sinai ores and raw copper presented above, particularly in terms of $^{207}Pb/^{204}Pb$.

Daggers: Kerma (Sudan) The two Kerma daggers, dated to the Classic Kerma period (contemporary to the Late Middle Kingdom and Second Intermediate Period in Egypt), have low arsenical copper blades (ca. 0.4–0.6% of arsenic). Both blades have fairly similar silver, lead, antimony and zinc contents, while cobalt, nickel and tin concentrations are notably higher in blade E.06118 (as is iron). The LI ratios of the two blades differ as well, with E.07931 having relatively higher $^{206\text{-}207\text{-}208}Pb/^{204}Pb$. Both fall within the overall range of Southern Sinai ores and Egyptian artefacts discussed above.

For dagger E.06118, the metallic part of the handle (running through and along the sides of the ivory pommel) and one of the metal rivets were sampled too[9]. Both the blade and the handle consist of arsenical copper, with slightly higher arsenic content in the handle, whereas the rivet has only traces of arsenic (650 μg/g). The trace element composition of the blade and handle are highly similar, with the exception of slightly elevated tin, zinc (and lead) and higher iron levels in the blade. Their LI ratios are furthermore indistinguishable, suggesting the use of the same copper alloy in the (simultaneous) manufacture of both parts. The rivet, in contrast, is made of unalloyed copper with different trace element concentrations and strongly different LI ratios from those of the blade and handle. The LI ratios for all parts are consistent with Southern Sinai ores, with the blade/handle having relatively lower $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ values compared to the rivet, which is consistent with raw Sinai copper presented above.

The study of two Kerma daggers by Young (1996) similarly compared the composition of blades and rivets, equally revealing a difference in alloy composition[10] between the blades (ca. 1.1–1.7% arsenic) and the rivets (0–0.4% arsenic). Their trace element patterns are not as similar, however, and the LI ratios of the blades and rivets appear distinct too. Trace element concentrations (Q-ICP-MS) are overall similar to those reported here, with the notable exception of significantly higher selenium and zinc reported by Young (1996). The LI ratio data reported by Young (1996) are too imprecise for meaningful comparisons in terms of ^{204}Pb ratios. ^{206}Pb ratios for the short rivet seem comparable to those for the E.06118 rivet, but LI consistency cannot be reliably evaluated without precise ^{204}Pb ratios.

Discussion

Discussions of copper provenance are intimately linked with metallurgical technology. The discussion is therefore organised by the different materials presented here: ores, "slag", raw copper and copper alloys. A final section discusses broader perspectives on Middle Kingdom Egyptian metal technology.

Ore

The interpretation of ore data is fairly straightforward: compositions reflect geological processes and can be compared directly to existing ore data. An important issue in the Egyptian context, however, is the relative scarcity of such data, which does not yet allow a clear distinction between the Eastern Desert and Sinai (which may not exist; yet the available data reveal a marginally better distinction in terms of uranogenic ($^{207}Pb/^{204}Pb$) than thorogenic lead ($^{208}Pb/^{204}Pb$)), nor between different mining zones within Southern Sinai (cfr. Rademakers et al. 2017, 2018b).

The ore analysed was almost certainly mined in the Southern Sinai, given its find context. In terms of LI ratios and overall elemental composition, these ores match earlier published data (Abdel-Motelib et al. 2012; Gilmore 1986; Pfeiffer 2013). In particular, the exploitation of copper ore (and turquoise[11]) at Bir Nasb, Wadi Kharig, Umm Bogma and/or Wadi Maghara is indicated both by the ores'

[9] For all three samples, an elevated barium concentration is measured. Notable Ba (and Sr, Ca and Mn) was already detected by HH-XRF—on the metal parts as well as the ivory. This suggests a barium contamination of the entire object, rather than barium being present in the metal. Barium was likely a component of the plaster used in the consolidation of the ivory handle, but unfortunately, no documentation of the artefact's conservation history exists. Barium hydroxide is most commonly used in the consolidation of plaster and stone (e.g., Sierra-Fernández et al. 2017 and references therein), and sometimes iron; its application to organics or copper alloys is uncommon.

[10] Vercoutter et al. (1960) report the results of (qualitative) spectroscopy and metallography of another Kerma dagger, revealing a similar distinction between an alloyed (tin bronze) blade and unalloyed rivet.

[11] Although exploited for its intrinsic value (Lucas 1962), the possible use of turquoise as a copper ore in antiquity remains poorly explored. Future smelting experiments of turquoise in Ayn Soukhna type furnaces (cfr. Verly 2017; Verly et al. 2021) may illuminate this possibility.

geochemical fingerprint and by the workshops' locations. These deposits are all located in the same Sinai area (part of the Wadi Sidri, Serabit el-Khadim and Wadi Ba'Ba systems, surrounding Gebel Umm Bogma), for which Middle Kingdom mining activity has been well documented (Beit-Arieh 1985; Petrie 1906; Tallet 2016-2017). Sadly, it is not possible to directly link this new data to specific mines, due to their particular find context (ores from different mines arrived at centralised workshops) and the lack of exhaustive geological reference data. Nonetheless, the geochemical correspondence between these ores and one of the Ayn Soukhna ore samples characterised by Abdel-Motelib et al. (2012) further validates the link between the Red Sea harbour workshops at Ayn Soukhna and the Southern Sinai mines.

Copper ores from Timna and Faynan (Arabah Valley) have markedly different LI ratios from those presented here, as do the copper artefacts and ingots produced at those sites. The only Faynan ores with comparable LI ratios derive from the Massive Brown Sandstone formation, which was exploited only during the Chalcolithic, Early Bronze Age I and Roman periods[12] (Hauptmann 2007). It can be noted, however, that one ore sample (EA-MR-178) has LI ratios indistinguishable from either Timna or Faynan (Dolomite-Limestone-Shale) ores, while some samples (EA-MR-177/189) border the Arabah Valley LI range. Indeed, some overlap is to be expected given the existence of similar mineralisation conditions at Umm Bogma and the Arabah Valley (although ores may be petrographically distinguished: Abdel-Motelib et al. 2012).

The Tharkan copper ore enlarges the provenance signature for ores extracted during the earliest period of Pharaonic history. Rademakers et al. (2018b) previously noted that these Eastern Desert ores were mined for use as minerals (along with galena: Stos-Gale and Gale 1981), as is apparent here, even though there are (later) indications for their metallurgical exploitation. The Old and Middle Kingdom assemblages, in contrast, strongly expand the current database of well-contextualised Sinai ores mined for metallurgical purposes, adding mineralogical data, a larger suite of determined elements and more accurate LI ratios than hitherto available. Variable trace element concentrations (e.g. cobalt, manganese and zinc) indicate the exploitation of multiple mineralisations in the (wide) vicinity of the metallurgical workshops, some of which may not have been previously analysed and/or located.

It is worth noting here that beyond this well-known activity in Sinai, (poorly documented) evidence for Middle Kingdom copper mining in the Eastern Desert exists too at, e.g. Abu Seyal (Klemm and Klemm 2008), Kuban/Wadi Allaqi (Emery and Kirwan 1936: 26–69; possibly only secondary metallurgy?), Umm Balad (Castel et al. 1998; Klemm and Klemm 2013), Umm Fahm I (Klemm and Klemm 2013), Umm Semiuki (Klemm and Klemm 2008; Pfeiffer 2013) and Umm Soleimat (Klemm and Klemm 1994, 2008, 2013).

[12] Exploitation at other periods cannot be excluded, however, as later activities may have obliterated earlier mining evidence. Nonetheless, currently available evidence does not suggest this.

Raw copper and slag

The interpretation of raw copper and slag data needs to take into account the smelting process. Trace elements in the Sinai workshops' raw copper are fully consistent with (Southern) Sinai copper ore (here and Pfeiffer 2013), as they are more abundantly present (relative to copper) in the ores, allowing for relative depletion in the metal phase during smelting.

Arsenic does not appear as minor or major constituent in the raw copper prills, as would be expected from the smelting of arsenic-poor Sinai ores. This is equally observed at Middle Kingdom Ayn Soukhna (qualitative XRF analysis of raw copper prills: Verly and Rademakers forthcoming).

Iron concentrations in the raw copper are indicative of relatively reducing conditions or the inclusion of impurities from the smelting process. They are consistent with those obtained from experimental copper smelting in Middle Kingdom furnaces, but not diagnostic for the use of any particular technology or fuel type (Rademakers et al. 2020). While high sulphur and phosphorus concentrations in the prills are consistent with their relative abundance in the corresponding ores, some (surface) fuel contamination may exist (as suggested by elevated magnesium and titanium contents for some prills).

Lead contents do not exceed 100 μg/g in the four Middle Kingdom (and one Old Kingdom) prills. Similar levels are encountered in many unalloyed copper artefacts and prills from Sinai, as summarised by Pfeiffer (2013: Table 10), although several have a few 100 μg/g lead (however, not all alloy components are consistently reported, cfr. above). These lead contents are consistent with Sinai copper ores too: the same range is attested at Serabit el-Khadim and Umm Bogma, while a much higher lead content is noted (although not consistently) at Wadi el-Regeita, Nabi Salah and the arsenic-rich ores of Wadi Tarr[13].

As far as LI ratios go, there is an overall good match with Sinai ores. It is, however, important to consider possible shifts due to contamination, given the relatively low lead content of the ores (Rademakers et al. 2020). As such, a comparison to "un-alloyed" copper from Sinai (Pfeiffer 2013) is most instructive (Fig. 4). This reveals a good correspondence to copper from Sheikh Awad, Sheikh Mukhsen, Bir Nasib I, Wadi

[13] In this manuscript, we have adopted the spelling "Wadi Tarr", although it is most commonly referred to as "Wadi Tar" in archaeological literature (e.g., Abdel-Motelib et al. 2012, Ilani and Rosenfeld 1994, Pfeiffer 2013, Rademakers et al. 2018b). Wadi Tarr lies in the southeastern part of the Sinai Peninsula (cfr. Fig. 1), as does Gebel Tarr. Gebel Tar, however, is situated in the western part of Sinai. To avoid confusion, the spelling used in the topographical maps published by The Survey of Egypt (1935), upon which the maps presented in this paper are based, is followed here.

Homr and Serabit el-Khadim[14]: these prills can thus be considered good representatives of raw copper produced from Southern Sinai ores. Again, their composition differs strongly from that of (older) copper ingots produced at Faynan during the Early Bronze Age (e.g. at Khirbet Hamra Ifdan: Hauptmann et al. 2015).

The two "slag" fragments consist of non-liquified, heat-exposed ore. This adheres to the typology encountered at Ayn Soukhna (Verly 2017; Verly et al. 2021), thus presenting a possible technological parallel from Sinai. This does not exclude, however, that different smelting technologies existed in Egypt at the time—an important issue requiring the study of primary workshops throughout Egypt (e.g. at Seh Nasb: Tallet et al. 2011; Tallet and Verly forthcoming). The "slag" is geochemically consistent with the associated ore from the same (Old and Middle Kingdom) workshop contexts. However, their compositions may have shifted relative to the original ore during smelting (Rademakers et al. 2020). As such, these samples present a reference for comparison with other smelting slag, comprising a separate category for provenance research.

Copper alloys

Copper alloys represent the final category for provenance research. In addition to the smelting step to produce raw copper, a secondary metallurgical operation is essential for copper alloy production[15] (unless co-smelting of copper and arsenic or tin minerals is directly achieved). This step is extremely poorly documented for ancient Egypt. Rademakers et al. (2017, 2018a) present the only detailed analytical study of tin bronze production in Egypt, dated to the New Kingdom (thirteenth century BCE). Many crucibles from earlier periods exist (e.g. Abd el-Raziq et al. 2011; Claes et al. 2020; Davey and Edwards 2007), but their metallurgical residues have not been characterised. Therefore, alloy manufacture can only be assessed indirectly for now, through the study of artefacts as presented here. Based on such data, Rademakers et al. (2018b) have already argued for active alloy selection from the onset of metallurgy in Egypt— through either specific ore selection (resulting in alloyed copper directly after smelting) or (more likely) secondary alloying. This perspective is expanded for the Middle Kingdom on the basis of new data presented here.

It is important to emphasise at the outset that Middle Kingdom copper alloys, like alloys from earlier periods in Egypt, are compatible with Sinai copper ore and raw copper in terms of LI ratios and trace element patterns (cfr. above)—with the critical exception of arsenic and tin. If Sinai copper was used for the production of copper alloys, the relative depletion in cobalt, iron, manganese and zinc in copper alloys most likely reflects partitioning into the crucible slag through oxidation and zinc volatilisation during in-crucible melting (cfr. Rademakers et al. 2018a). Such remelting of raw copper is a mandatory step in artefact production; however, it does not imply an alloying operation.

While antimony and silver contents in the raw copper prills are low, consistent with Sinai ores, nearly all copper alloy objects analysed have antimony contents of 200–400 μg/g and silver contents of 50–600 μg/g (ca. 900 and 1500 μg/g, respectively, in the strongly corroded Dayr-al Barsha mirror). Furthermore, arsenic contents are consistently elevated to 0.2–4.6% (the majority over 0.5%), with the exception of the unalloyed Kerma dagger's rivet[16]. This is 10- to 100-fold higher than the average arsenic content in the presented copper ores (ca. 75 μg/g; or 300 μg/g normalised to copper) and previously characterised Sinai (and Eastern Desert) ores (ca. 85 μg/g; excluding Wadi Tarr ore: up to ca. 30%). Furthermore, raw copper from Sinai and Ayn Soukhna smelting workshops (this publication, Pfeiffer 2013; Verly and Rademakers forthcoming) has consistently low arsenic levels—in line with the primary production of unalloyed copper from these ores. A similar qualitative relation between arsenic and antimony was previously noted by Rademakers et al. (2018b) in Predynastic to Old Kingdom copper. The same trend is apparent for Kmošek et al.'s (2018) data and for copper encountered in Sinai (Pfeiffer 2013)[17]. Silver weakly correlates to antimony and arsenic concentrations.[18]

The compositional discrepancy observed between raw and alloyed copper (cfr. Finished objects and Fig. 6) strongly suggests a production process involving at least two steps: the primary

[14] More specifically samples 225 (Sheikh Awad), ET-1/6, ET-1/7, ET-1/8 (Sheikh Mukhsen), ET- 51/1, ET-53/1 (Bir Nasib I), ET-50/1 (Homr) and ET-59/3 (Serabit el-Khadim). Note that analysis methods vary and dating is not consistently specified for these samples, cfr. Pfeiffer 2013.

[15] With respect to the Kahun material, Gilmore (1986) notes that "If these particular ore samples are indeed representative of the local copper ores we would have to conclude either that the metals were not made from local ores or that arsenic was deliberately added in some way. Alternatively we can suggest that these items were indeed imported from areas where arsenic is a natural companion of copper".

[16] For this Kerma blade, the lowest lead and sulphur contents are associated with the lowest arsenic content. This may suggest the use of the same copper for the different parts, but alloyed for specific parts, whereby the alloying introduced an important shift in LI ratios. On the other hand, the use of different copper sources may be attested, either in a single workshop or as a result of repair elsewhere, perhaps at a later time.

[17] Antimony contents exceeding 100 μg/g are not measured in pure copper, whereas elevated antimony contents (200 up to 1000 μg/g) are associated with percentage levels of arsenic (not all artefacts are well dated and trace elements are not reported for each artefact).

[18] Rademakers et al. (2018b) report silver levels mostly below 50 μg/g (with the exception of one Protodynastic artefact from Faras (55 μg/g) and two Old Kingdom artefacts from Qau el-Kebir (55–145 μg/g)), while Kmošek et al. (2018) report higher silver contents for these earlier periods (50–1200 μg/g). This may be due to minor silver loss during digestion (less than 20%, cfr. analytical procedure in Rademakers et al. (2020: Online Supplementary Materials)) for ICP-OES (vs. NAA) and, probably more importantly, variable silver concentrations in these early artefacts. In each dataset, a weak Ag-As-Sb correlation can be noted.

production of raw, unalloyed copper, followed by the production of arsenical copper. Based on currently available data, there appears to be a small average increase in antimony (and silver?) concentrations accompanying the arsenic alloys. The otherwise similar trace element patterns, broadly similar LI ratios and contextual co-occurrence of raw and arsenical copper in early Egyptian workshops, indicate that arsenical copper was produced by adding arsenic (in some form) to raw copper from Sinai (and the Eastern Desert) during a secondary process. This was already advocated for earlier periods by Rademakers et al. (2018b) (Kmošek et al. (2018) offer no explanation for the noteworthy presence of arsenic in their assemblage), and this hypothesis is now corroborated more strongly for the Middle Kingdom period.

Three alternatives to explain these alloys without a secondary metallurgical step can be suggested. Firstly, the import of arsenical copper from other regions, where it is produced directly through co-smelting of arsenic-bearing ores (or otherwise). As already discussed by Rademakers et al. (2018b), contemporary arsenic alloys in surrounding regions, such as the Levant, have different trace element compositions and LI ratios, making such an interpretation less likely. Indeed, a survey of published LI ratios and trace element data for EBA-MBA copper alloys (and ores) in the Eastern Mediterranean does not reveal any strong matches. Even if a reasonable match could be found, the hypothesis that (all?) arsenical copper attested in Egypt from the Predynastic up to Middle Kingdom times was imported calls for much stronger supporting evidence. The fact that LI ratios and element concentrations for Sinai copper match those of Egyptian copper alloys (with the exception of arsenic and, to a lesser extent, silver and antimony) over the broad range of (hitherto characterised) Sinai deposits makes the hypothesis of secondary alloying of Sinai copper far more likely. It cannot be excluded formally that arsenic-rich metal (e.g. Anatolian metal traded across the Levant: Hauptmann 2007) was imported (as is occasionally attested, e.g. Kmošek et al. 2018—yet of different elemental composition), and that such metal was added to pure ("Egyptian") copper as a "master alloy", resulting in diluted arsenic alloys. However, there are no indications[19] for this in the resulting alloys' compositions. Furthermore, this would represent an alloying technology strongly reliant on steady imports over time—a scenario that appears less likely in light of the continuity witnessed in Egyptian alloys over centuries and the scarcity of attested Anatolian/Levantine alloy imports so far.

As a second alternative, the targeted (co-)smelting of arsenic-rich copper ores from Sinai for direct production of arsenical copper could be envisaged as a "parallel production chain" next to that of pure copper. This, however, raises several problems. As Pfeiffer (2013) notes, currently available geological data suggests that arsenic occurs in few, restricted Sinai deposits only—contrary to Rüppell's (1829) suggestion of its widespread occurrence. While this may be a sampling issue and more arsenic-rich copper deposits could exist, the currently known major Pharaonic mining zones exploited rather pure copper deposits. Furthermore, the LI ratios of Egyptian copper alloys cover a wide range, suggesting a range of ores were exploited for their production, rather than a few, relatively rare arsenic-rich copper deposits.

A third alternative explanation would be the accidental production of (low) arsenic copper and tin bronze through the smelting of ores with somewhat enriched As-Sb-Sn contents, such as hydrothermal vein ores with sulphosalts and stannite group minerals. The widespread occurrence of such alloys (from the Predynastic period onwards), alongside pure copper as well as alloys with higher arsenic concentrations (in tandem with the exploitation of a wide range of arsenic- and tin-free copper deposits, cfr. above), suggests that ancient Egyptian metallurgists did actively (rather than accidentally) select for certain materials and argues against this explanation. While it is likely that recycling plays a role in explaining low arsenic and tin concentrations in artefacts (cfr. Rademakers et al. 2018b and below), active alloying remains a necessary step in the overall production system.

A secondary alloying step in the production chain is thus the best explanation for the results observed. Therefore, Eaton and McKerrell's (1976) suggestion (on the basis of qualitative surface XRF analysis) that the Egyptians recognised only natural alloys during the Old and Middle Kingdom and did not know the principle of "artificial" alloying should be revised. Furthermore, their assertion that no "confusion" between tin and arsenical bronzes took place (i.e. the addition of tin to extant high-arsenic metal and vice versa) is refuted by the ternary alloy attested by mirror E.03996 (similar compositions: e.g. Cowell 1987; Gilmore 1986; Philip 2006). Rather than confusion, this most likely exemplifies flexibility in alloy production, with recycling playing an important role. The best way to test this hypothesis would be to analyse archaeological waste associated with alloy production: crucibles. The most direct proof for active alloying can be found in crucibles and associated raw materials found in workshop contexts.

Current limitations on sampling and analysis impede a wider assessment of secondary metallurgical technology, but sites such as Ayn Soukhna—where the authors have studied

[19] It is not possible to exclude formally Anatolia as a potential source of imported metal for all samples, although the majority fall outside of the ranges defined for Anatolian ores (Hirao et al. 1995; Sayre et al. 2001; Seeliger et al. 1985; Wagner et al. 1985, 1986, 2003; Yener et al. 1991), in particular with respect to their $^{207}Pb/^{204}Pb$ ratio. Of course, there are some LI ratio overlaps between the assemblage presented here and those ores (more specifically, for the samples with relatively higher $^{206}Pb/^{204}Pb$ ratios). However, these mainly concern the ore samples (which were mined in Sinai beyond any reasonable doubt) and four copper alloys which closely resemble those ores (two are scrap from the same workshops). Furthermore, the distribution of this Middle Kingdom assemblage cross-cuts the LI ranges defined by different Anatolian ore deposits, rather than overlapping with one particular deposit. All of these factors indicate that the (majority of) finds presented here are unlikely related to an Anatolian ore deposit. Even if an Anatolian origin cannot be formally excluded for one or two copper alloys, their consistency with the rest of the presented material argues against this.

crucible remains in terms of typology, production techniques and metallurgical use (2019 field season, with the aid of handheld XRF analysis: Verly and Rademakers forthcoming)—are key towards understanding the full production chain. For example, Pi-Ramesse crucible analysis has provided the first strong arguments for bronze alloying through cassiterite cementation (alongside metal mixing) as a relevant practice in ancient Egypt (Rademakers et al. 2018a). Such a tradition may have been imported, but was most likely a local adaptation, drawing on the use of local raw materials such as Eastern Desert cassiterite. This then might have been rooted in older traditions related to the manufacture of arsenical copper, whereby arsenic-rich minerals were added to unalloyed copper—such questions of technological traditions can only be addressed by far more extensive analysis of metallurgical workshop remains. Detailed micro-analysis of crucible remains (cfr. Rademakers and Rehren 2016) could reveal the "smoking gun" for active arsenical copper alloying in the form of high-arsenic prills (with γ- (Cu_3As) or αAs phase: Subramanian and Laughlin 1988), residual arsenic-rich minerals or speiss embedded in the crucible slag or dross (following the same reasoning as for tin/cassiterite alloying identification, cfr. Rademakers et al. 2018a).

Beyond the issue of technology, these secondary operations play an important role towards interpreting metal provenance. The addition of arsenic in mineral form[20] or as speiss could introduce various trace elements. The best known example for speiss, smelted as an intermediate product in arsenical copper production, comes from Early Bronze Age Iran (Rehren et al. 2012). Likely examples of alloying speiss with copper exist, however, for example at Early Cycladic Dhaskalio (Georgakopoulou 2018), Early Bronze Age Poros Katsambas (Doonan et al. 2007) and Late Minoan Mochlos (Soles and Giumlia-Mair 2018)—roughly equivalent to the Old Kingdom up to New Kingdom in Egypt. While no evidence for speiss as an import commodity (Rehren et al. 2012) or its production is currently known from Predynastic up to Middle Kingdom Egyptian contexts, its absence in ancient Egypt cannot be assumed, given the little attention attributed to slag-like materials in past Egyptian archaeology. Noteworthy exceptions may be tentatively identified speiss/matte (Object 1330) dated to the Hyksos period (stratum D/3) at Tell el-Dab'a (Philip 2006, pp. 170–171) and the (obscure) find of a "ferruginous material" at House P46.33 in Amarna, with ca. 60% of iron, 17% of arsenic, 2% of antimony and 0.3% of lead (Charles 1995). This was likely associated with arsenical copper production, as suggested by Charles (and by the presence of arsenical copper at Amarna during the New Kingdom, alongside tin bronze: Rademakers in preparation). Trace element data for speiss is not currently available but based on its general characteristics (Hauptmann et al. 2003; Rehren et al. 2012; Thornton et al. 2009 and references therein), elevated concentrations of antimony, nickel, cobalt and copper (and silver and gold) may be expected. The specific trace element data of speiss of course would strongly depend on the characteristics of the ore and conditions of the metallurgical process from which it was produced.

Arsenic-rich minerals present another, perhaps more likely source of arsenic in early Egypt. The existence of such minerals at Wadi Tarr in Southern Sinai (Ilani and Rosenfeld 1994) presents a realistic opportunity for ancient Egyptian metallurgists to have acquired a raw source of arsenic[21]—possibly under the form of copper arsenides. As discussed already at length by Rademakers et al. (2018b), this infamous deposit is poorly studied and its importance difficult to assess. It is possible that other arsenic-enriched (copper) ore deposits exist in Sinai, although strongly doubted by Hauptmann (2000). Indeed, Wadi Tarr remains the only known deposit of copper arsenides in the region (Hauptmann 2007; Hauptmann et al. 1999). While Segal et al. (2004) dismiss Wadi Tarr as a possible source for arsenical copper at Ashqelon due to different LI ratios, the little available data suggests important internal variability for Wadi Tarr ores. More importantly, even if those samples were representative, alloying arsenic-rich minerals with raw copper would result in

[20] Petrie (1890, p. 38) notes the occurrence of orpiment (As_2S_3) at Gurob during the New Kingdom, where the presence of copper ore and slag in a crucible leads him to suggest that "smelting was done in the town". The listing of other minerals such as hematite and green feldspar along with orpiment (it is unclear whether they belong to the same context) does not allow for a conclusion as to its possible use as a pigment or within a metallurgical context. Orpiment is indeed considered a common pigment used during the New Kingdom, but has been discovered already in Middle Kingdom contexts (e.g., Lee and Quirke 2000), and was traded as a raw material during the Late Bronze Age (e.g., Uluburun cargo: Bass 1986). Other arsenic sulphide minerals include realgar (As_4S_4) and arsenopyrite (FeAsS). Arsenic-rich minerals noted at Wadi Tarr include koutekite (Cu_5As_2) and domeykite (Cu_3As) (Ilani and Rosenfeld 1994).

[21] Umm Semiuki in the Eastern Desert might have presented an alternative source. Mainly considered to be a silver source from modern geological perspective (Shalaby et al. 2004), secondary deposits in the upper oxidation zone appear to have been exploited for copper production at some point in antiquity (El Shazly and Afia 1958; Hume 1937; Lucas 1962; Pfeiffer 2013), but evidence has been destroyed by modern mining according to Klemm and Klemm (2008). Lucas (1962, p. 236— referring to Hume (1937, pp. 837–842)) describes it as an important mining site for copper, with "extensive ancient workings with several shafts. At the surface, the ore is malachite and azurite, of which there is a thickness of about seven metres and below this are copper and zinc sulphides and lead ore … There are also ore crushers, pottery (possibly broken crucibles) and slag. These are the most important deposits of copper ore yet discovered in Egypt, some of the workings being 40 to 50 feet underground". While arsenic-bearing sulphides such as tennantite are described by Shalaby et al. (2004), it is unclear to which extent arsenic is present in the surface deposits. Silver, antimony, arsenic and particularly zinc might be present to some degree in the malachite/azurite, but no elemental or LI data are available (El Shazli and Afia mention only possible zinc enrichment—LI ratios determined for the primary Precambrian Cu/Pb/Zn ore by Stos-Fertner and Gale (1979) have expectedly low $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ ratios). Whether copper-arsenic alloys could be directly smelted from this deposit or an arsenic alloying agent was extracted is unclear but appears unlikely (rather, copper with high levels of zinc is expected: Afia 1985). As for Wadi Tarr, the extent and timing of ancient exploitation of this deposit cannot be assessed confidently.

mixed LI ratios[22] (cfr. discussion by Rademakers et al. 2018b). Indeed, the highest lead concentrations in any of the characterised Southern Sinai ores are noted for Wadi Tarr (antimony and silver are not associated). Note, however, that elemental analysis has been conducted for only two (!) Wadi Tarr ore samples so far (and four samples for their LI ratios). If an active alloying model is adopted, a shift from the raw copper signature towards the arsenic mineral's (or speiss's) LI ratios is expected, proportionate to its relative lead contribution. Some discrepancy between alloyed objects' LI ratios and those of raw copper prills can surely be attributed to variations in the primary copper ores used for their production. However, they might further indicate a general LI ratio shift towards arsenic-rich alloy components. As noted above, lead contents are indeed typically higher in Egyptian copper alloys than in raw copper (difficult to assess for data compiled by Pfeiffer 2013: arsenic and lead levels are not consistently reported together). Although there is increased lead content (on average) in copper alloys with lower $^{206\text{-}207\text{-}208}Pb/^{204}Pb$ ratios (towards Wadi Tarr LI ratios), this is not systematic. This should not be expected either: lead contents in added arsenic minerals may have varied and, more importantly, these alloy compositions do not necessarily exemplify "fresh alloys": many may well represent (repeatedly) recycled and mixed copper.

It should further be noted that technological traditions may have varied significantly throughout the Nile Valley: within Egypt and particularly between Egypt and Nubia. Indeed, the Egyptians undertook military attempts at expansion in Nubia, but Egyptian rule was not established until the New Kingdom period (Tallet et al. 2019). While contact thus certainly existed (including more peaceful trade encounters, either directly or as part of the Red Sea trade with Punt: Bard and Fattovich 2018; Tallet 2013, 2017), the Nubians may have relied on different provisioning and production systems for copper (including "local" ores, e.g. drawing on southern Eastern Desert deposits and perhaps ores in Darfur: Afia and Widatalla 1961; Herbert 1984; Master et al. 2016). These sources have not yet been characterised geochemically and may equally have entered Egyptian copper circulation. Shaw (1998) notes, for example, that some "twelfth-dynasty Egyptian fortresses in the Second Cataract region of Nubia … probably served as bases for the procurement and processing of metals". The interpretation of the Kerma daggers presented here will be revisited by Rademakers et al. (in preparation) as part of a forthcoming study of nearly 50 Kerma copper alloy artefacts.

As a final note, the recurrence of tin is commented on here. Contrary to antimony and silver, it is geologically unlikely to be accessory to arsenic minerals and thus, it is unlikely to have been introduced during arsenic alloying. While it is mostly present at levels unlikely to constitute an intentionally added alloy component, these contents significantly exceed those encountered in Sinai ores[23] or raw copper,[24] as well as in most Protodynastic and Old Kingdom copper[25]. Intriguingly, in the two artefacts (mirrors E.01969 and E.03996) where it is present at ca. 1% (suggesting active alloying), it is accompanied by more abundant arsenic in a ternary alloy. This may mark early Egyptian experimentation with tin as an alloy component. A source of tin could have been added to existing arsenical copper, or to raw copper together with arsenic (mineral or speiss). Alternatively, arsenic or arsenical copper may have been mixed with a recycled tin bronze.

From smelting workshops to a Middle Kingdom metal stock?

Copper mining during the Middle Kingdom took place in the form of large-scale, state-organised expeditions, targeting several deposits in Sinai. This has been previously documented by inscriptions in Sinai (Bloxam 2006; Petrie 1906; Tallet 2012, 2015, 2016-2017, 2018; Tallet and Mahfouz 2012; Tallet et al. 2011) and is confirmed here by the geochemical analysis of workshop remains. Primary production took place in centralised workshops close to the mines, but for certain periods smelting operations were moved across the Red Sea to Ayn Soukhna, where Sinai ore was brought by boat. While small-scale production (by local population groups) may have taken place outside of the state-controlled mining expeditions, their enormous scale suggests that the bulk of raw Sinai copper was produced and imported to the Nile Valley by the state. Raw copper may equally have been imported into Egypt from abroad at this time. Currently available data indicates that this played only a marginal role with respect to Egypt's "domestic" production, but the available sample of copper circulating during the Middle Kingdom is very small. Candidates to investigate are, among others, copper from Anatolia, the Arabah Valley, Arabian Peninsula, Cyprus and Greece.

Alloying appears to have been an integral part of the Middle Kingdom production chain of copper artefacts. The clearest examples are seen in the deliberate choice for higher alloy components in mirror disks, most likely to obtain the best reflective properties (as already noted by Eaton and McKerrell 1976). Less striking examples are found in the widespread lower arsenic

[22] Hauptmann (2007) similarly dismisses Wadi Tarr as a source for arsenical copper objects in the Southern Levant. While this may very well be true, this argument is equally based on the premise that arsenical copper was produced directly from Wadi Tarr ores, rather than by alloying with (other) copper (resulting in mixed LI ratios).

[23] Only Nabi Salah ore sample 48 has an elevated (2600 µg/g) tin level (Beit Arieh 2003), but no LI ratios are available.

[24] Tin contents in some Sinai copper finds summarised by Pfeiffer (2013) are comparable, but their dating is unclear and not all elements (e.g., arsenic) are consistently reported on, making it difficult to differentiate possible alloys.

[25] At least those characterised by Rademakers et al. (2018b)—tin contents exceeding 500 µg/g occur in a few artefacts presented by Kmošek et al. (2018), but are not further discussed there.

contents—low compared to contemporary arsenical copper in other cultures, but conspicuously high compared to the otherwise similar raw copper produced from Sinai ores. This mirrors the observations made for the Protodynastic and Old Kingdom periods by Rademakers et al. (2018b), suggesting a strong degree of continuity in terms of metallurgical technology within Egypt. A comparison of elemental data (Fig. 7) corroborates the continued use of similar (Sinai) ores. Steadily increasing cobalt, iron and zinc concentrations may reflect both changing furnace conditions and the exploitation of different ores over time, although these are difficult to interpret without the analysis of smelting remains. The average increases in silver, arsenic, lead and tin concentrations may reflect changing alloying practices.

Overall, an important diachronic change can be noted, however, with respect to the alloys' LI ratios. Indeed, the range of LI ratios witnessed in these artefacts is far more narrow than that witnessed in Protodynastic and Old Kingdom copper (Fig. 5)—however it is noted that relatively fewer Middle Kingdom artefacts have been analysed so far. Contrary to these earlier periods, no radiogenic LI ratios have been encountered so far in Middle Kingdom copper, nor any "old lead" characterising some of the Old Kingdom metals. This most likely indicates a shift in ore deposits being exploited. Rademakers et al. (2018b) noted a shift between Protodynastic and Old Kingdom periods already, and LI data suggests that some of these mining zones were maintained during the Middle Kingdom while others were abandoned—in line with available field evidence (Tallet 2016-2017; Verly and Rademakers forthcoming).

Beyond mining, recycled metal was another important source of copper for secondary production. This is well indicated by the finds of scrap metal in workshops and the state's metal administration (e.g. the conversion of worn tools into a single "unit" for re-casting by coppersmith Nakhti, described in the Middle Kingdom Papyrus Reisner II: Simpson 1965). Relatively low arsenic (and tin) concentrations in several Egyptian artefacts may be a reflection of such (repeated) recycling over (possibly long periods of) time—in contrast with newly alloyed high-arsenic copper (besides alloy composition, the secondary working of artefacts further determined their properties). Recycling could therefore have played an important role in changing the LI ratios of Middle Kingdom metal stock on average, particularly if (fragments of) different objects were remolten and mixed together.

This means three factors need to be taken into account when comparing the LI ratios of copper alloys to those of raw copper[26]: (1) raw copper (prills) smelted from different ores was mixed together to produce objects (Hauptmann 2007; Rademakers et al. 2020; Verly and Rademakers forthcoming) thereby averaging their lead contributions; (2) there may be a lead contribution from the alloy component (arsenic and/or tin); (3) there may be a shift when scrap/artefact fragments are mixed during recycling. For this reason, it makes sense to look at copper alloy compositions less on an individual artefact level, but rather as representatives of a metal stock, circulating within Egypt at a certain point in time. This stock would be replenished by fresh metal from mining expeditions (exploiting various mines over time), representing large "injections" at distinct moments in time. Some of that metal may have gone into large-scale projects (and objects), while part of it may have been distributed across a larger number of smaller artefacts. The deposition of artefacts in funerary contexts over time represents our main window into the composition of such a stock. As some of these objects may have been in circulation for a long time, while others were freshly made (Rademakers et al. 2018b), and different social strata may have had access to different parts of the metal stock (Rehren and Pusch 2012), our window is probably small and rather opaque.

Nonetheless, it makes sense to adopt this model when considering copper alloy compositions, in particular for taking a diachronic approach to assess Egyptian metal stock. This could, for example, explain the tin contents in the alloys presented here. The appearance of tin as an alloy component in Egypt, often still together with arsenic, is not only attested in the assemblage presented here, but equally at Kahun (Gilmore 1986) and Tell el-Dab'a[27] (Philip 2006). Its timing nonetheless remains poorly constrained to the First Intermediate Period to Middle Kingdom[28] (Cowell 1987; McKerrell 1993). This vagueness mostly relates to dating uncertainties

[26] Raw copper itself may further reflect different ores mixed in a single smelting batch.

[27] Many of the analysed artefacts from Tell el-Dab'a date to the (transition to the) Second Intermediate Period, which is characterised by a fast succession of kings, often described in ancient texts as a period of chaos. The organisation of metal production by the state may have changed significantly at that time. Furthermore, the 12th Dynasty material at Tell el-Dab'a shows strong connections with Syro-Palestine, including metalwork of Syro-Palestinian styles, and there is significant settlement by west Asian population during the 13th Dynasty (Philip 2006, p. 27), suggesting possibly different metal provisioning systems at this Delta site. Overall, Philip (2006, p. 228) notes a relative paucity of metals from the Middle Kingdom strata: possibly, "the issue and recycling of metal tools was more closely controlled during the Middle Kingdom", although other factors probably play into the observed pattern as well. Arsenic appears in similar concentrations (0.1–3%) in artefacts dated to later strata, in some cases accompanied by tin in variable levels (trace to percentage level), in other cases as a pure arsenical copper alloy. This validates the gradual replacement of arsenic by tin in bronze, as suggested by the data presented here. Philip (2006, p. 211) views arsenic as an ore contaminant, not actively sought (or even recognised) by the Tell el-Dab'a metalworkers (except for chisel 6110). It is, however, difficult to discuss the levels of arsenic here without LI ratio data, as the arsenic concentrations of the relevant source materials should be assessed (as for the low tin concentrations). Philip (2006, p. 215) notes that "the presence of tin, at well below optimum levels, in some of the artefacts from Tell el-Dab'a certainly points towards a degree of recycling".

[28] Exceptions exist, such as two tin bronzes from the 2nd Dynasty Tomb of Khasekhemwy (Cowell 1987—these can be considered "ternary bronzes", with ca. 0.5–1% arsenic content) and a Predynastic to Old Kingdom tin bronze from Buto (Pernicka and Schleiter 1997). Without lead isotope analysis, it is not possible to verify if these represent imports or rather early examples of tin alloying in Egypt.

for many objects analysed in the past. Regardless, tin's general adoption in Egypt seems strikingly late compared to the Levant, where alloying appears to take off in earnest already in the second half of the 3rd millennium BCE (Eaton and McKerrell 1976; Hauptmann 2007)—while arsenical copper remains relatively more important in Egypt. This is overall indicative of a distinct technological trajectory in the Nile Valley, compatible with the important domestic metallurgical production discussed above. The appearance of low tin contents (nonetheless exceeding those in raw Sinai copper) during the Middle Kingdom may reflect the influx of tin bronzes (from abroad?) and their dilution over time when integrated into circulating metal stock[29]. Indeed, these are still all arsenical copper alloys in the "Egyptian tradition" (low to medium arsenic alloys, cfr. Rademakers et al. 2018b). The exceptions are two mirrors with up to 1% tin, but these have high levels of arsenic too: an already "light-coloured" copper (tin bronze) could thus have been selected to produce a silvery reflecting mirror by the further addition of arsenic. Of course, it is equally possible that the Egyptians themselves started to experiment with tin bronze production. Cementation using placer cassiterite might be indicated by traces of gold associated with high tin concentrations (Rademakers et al. 2017), but is difficult to detect without a much larger dataset and the analysis of crucible remains.

The main strength in considering Egyptian copper alloys as windows into a changing stock lies in the opportunity to model changes over time. As illustrated in Fig. 5, stock LI ratios seem to narrow significantly with respect to preceding periods. Looking towards the New Kingdom, Rademakers et al. (2017) have proposed the existence of a "metal stock" with a rather narrow isotopic range ("domestic copper"), encountered both at Pi-Ramesse and Amarna[30], supplemented by fresh metal arriving from various sources (Sinai and Eastern Desert, but equally Cyprus, Timna, Faynan and possibly Oman). As such, the analysed Middle Kingdom copper represents an earlier stock: its range is narrower than that for early periods, while still broader than that of the New Kingdom. Such a gravitation towards narrower LI ranges over time is exactly what one would expect for economies relying on recycling as a widespread practice (Pernicka 2014). Of course, this does not exclude the influx of fresh metals, which continue to pull the metal stock composition towards more extreme LI ratios. However, when a narrowing range of mines is exploited over time, this effect may be diminished. Importantly, the presented sample here is very small, and the visibility of fresh metal arriving into this system may be limited. It seems likely that "foreign" metal arrived into Nile Valley as well, but the scale is difficult to assess for now. Nonetheless, the importance of import and international trade seems to increase mainly during the New Kingdom (although recycling equally plays a central role: Rademakers et al. 2017), when Egypt became involved in wider Late Bronze Age exchange across the eastern Mediterranean (Van De Mieroop 2007). This hypothesis stands to be tested by more extensive artefact analysis in the future: the proposed diachronic perspective is specifically aimed at such evaluations.

The foregoing discussion highlights the relevance of production sites as points of reference for provenance analysis (cfr. Rademakers et al. 2017 and references therein). Rather than considering absolute (geological) provenance, it may be more helpful to outline the expected composition of raw copper coming out from primary workshops (e.g. Sinai, Ayn Soukhna) and secondary workshops (e.g. Pi-Ramesse, Amarna) as reference groups for provenancing artefacts. Such a perspective automatically integrates mixing, alloying and recycling, and a specific time window. Targeted analysis of such production sites is thus essential in further elaborating provenance studies, as well as understanding the development of Egyptian copper technology.

Conclusion

This paper significantly increases our knowledge on the elemental, mineralogical and lead isotope composition of copper production remains from Sinai and copper alloy artefacts from Middle Kingdom Egypt and Classic Kerma. Results indicate that Egyptian copper technology followed a trajectory largely independent from nearby production and trade in the Levant, and was embedded in a mostly state-controlled production system strongly focused on "domestic production" of copper from Sinai ores. This production system appears to have followed a two-step process, whereby raw, rather pure copper was smelted first. In a secondary metallurgical stage, arsenical copper alloys were produced, making up the most important copper alloy for the Middle Kingdom and preceding periods in Egypt. The precise alloying process remains to be elucidated, however. Tin equally appears in the assemblage as an alloy component and is gradually adopted alongside arsenical copper. Constraining the exact timing of tin bronze adoption in early Egypt requires more widespread analysis of well-dated artefacts and production remains.

Given the particular nature of Egyptian metallurgical technologies, it is suggested here to treat remains of each

[29] Low tin concentrations are often interpreted as a sign of recycling (e.g., Maddin et al. 2003; Pernicka 2014). Gilmore (1986) equally interprets low tin contents in Middle Kingdom Kahun alloys as a possible result of mixing scrap bronze alloys.

[30] The changing stock may equally be reflected in other materials. The idea to trace copper sources in Egyptian Blue was presented by Jaksch et al. (1983) for the New Kingdom, and by Schiegl et al. (1990) for the Old Kingdom up to the Roman period. They suggest that the chronological distribution of arsenic, tin and lead in copper-based pigments may allow for a more accurate dating of changes in Egyptian bronze technology. Rademakers et al. (2017) highlight this relation between New Kingdom pigments and circulating copper alloys in terms of LI ratios.

production step as distinct categories in discussions of provenance. Copper alloys, representing the final step of the production chain, offer a unique diachronic perspective on changing metal stock, circulating and being recycled within ancient Egypt. While the presented assemblage is relatively small, it indicates a changing pattern of provisioning with respect to the preceding periods, while still differing from that of the more internationally oriented New Kingdom era.

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