Archaeol Anthropol Sci (2018) 10:1485–1502
DOI 10.1007/s12520-017-0465-x

ORIGINAL PAPER

The potential of stable Cu isotopes for the identification of Bronze Age ore mineral sources from Cyprus and Faynan: results from Uluburun and Khirbat Hamra Ifdan

Moritz Jansen[1] · **Andreas Hauptmann**[2] · **Sabine Klein**[2] · **Hans-Michael Seitz**[3]

Received: 6 November 2016 / Accepted: 12 January 2017 / Published online: 8 February 2017

Abstract Copper isotope ratios differ between hypogene sulfidic, supergene sulfidic and oxidized ore sources. Traditional lead isotope signatures of ancient metals are specific to deposits, while Cu isotope signatures are specific to the types of ore minerals used for metal production in ancient times. Two methodological case studies are presented: First, the mining district of Faynan (Jordan) was investigated. Here, mainly oxidized copper ores occur in the deposits. The production of copper from Fayan's ore sources is confirmed by the measurement of the Cu isotope signature of ingots from the Early Bronze Age metal workshop from Khirbat Hamra Ifdan. Based on our results illustrating differences in the Cu isotope composition between the ore mineralizations from Timna (Israel) and Faynan, it is now possible to determine these prehistoric mining districts from which copper artifacts originated by combining trace elements and Pb isotopes with Cu isotopes. The second case study presents data on Late Bronze Age copper production in Cyprus. Oxhide ingots from the shipwreck of Uluburun (Turkey) were tested for their lead isotope signatures and assigned to Cypriot deposits in the recent decades. The oxhide ingots from Uluburun show a Cu isotope signature which we also found for oxidized copper ores from Cyprus, while younger oxhide ingots as well as metallurgical slag from the Cypriot settlements Kition and Enkomi show a different signature which might be due to the use of sulfidic ore sources from a greater depth of deposits. We assert that there could be a chronological shift from oxidized to sulfidic ore sources for the copper production in Cyprus, requiring different technologies. Therefore, Cu isotopes can be used as a proxy to reconstruct mining and induced smelting activities in ancient times.

Keywords Eastern Mediterranean Bronze Age · Cu isotopes · Copper ingots · Oxhide ingots · Provenance studies · MC-ICP-MS

Introduction

In archaeometallurgy, lead isotope analysis is tremendously important in terms of provenance studies. The utilization of alternative isotope systems of elements, suchs as osmium, tin, or copper, has become increasingly important in the last 20 years due to the development of high-resolution multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). These "non-traditional" isotope systems now can be investigated with high precision.

Copper has two stable isotopes: ^{63}Cu with an abundance of 69.2 % and ^{65}Cu with abundance of 30.8 % show a significant natural variability in copper deposits (Albarède 2004). Next to them, there are several short-life radioactive isotopes. The most stable one is ^{67}Cu which unfortunately has a half-life of less than 3 days. Therefore, the radioactive isotopes are not useful for archaeometric research.

For archaeometallurgy, the stable Cu isotopes provide a promising approach for the identification of ore types used in ancient times, since copper and copper-based artifacts from

✉ Moritz Jansen
moritzj@upenn.edu

[1] Center for the Analysis of Archaeological Materials, University of Pennsylvania Museum of Archaeology and Anthropology, 3260 South Street, Philadelphia, PA 19104, USA

[2] Forschungsstelle Archäologie und Materialwissenschaften, Deutsches Bergbau-Museum, Herner Straße 45, 44791 Bochum, Germany

[3] Institut für Geowissenschaften, Goethe-Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

primary (hypogene) sulfidic, secondary (supergene) sulfidic, or oxidized ores can be differentiated through their Cu isotope signature (Klein et al. 2010).

Cu isotopes and archaeometallurgy

First attempts to use isotopes of copper in archaeometallurgy were conducted in the mid-1990s (Gale et al. 1999; Woodhead et al. 1999). Through the analysis of material from copper smelting and fire refining experiments, a fractionation of Cu isotopes was not detected for metallurgical operations. In addition, Bronze Age oxhide ingots showed significant differences in their Cu isotope composition. Gale et al. (1999) saw a huge potential for provenance studies in combination with Pb isotopes.

The first systematic investigations were carried out on Roman coins, ingots, and bronzes which were compared to deposits from the Iberian Peninsula and Siegerland and Lahn-Dill (Germany) (Klein et al. 2002, 2004, 2007, 2009; Durali-Müller 2005). These studies discerned deposits with overlapping Pb isotope signatures by using Cu isotopes, and the analysis of coins allowed the detection of shifts in using those deposits through time.

Markl et al. (2006) stated that there is no benefit in using Cu isotopes for provenance studies of single artifacts, since the variation within a deposit is larger than between different deposits. Asael et al. (2007, 2009, 2012) investigated ore minerals, which crystallized under different redox conditions and different ore forming stages for their Cu isotope signature. They directly compared the primary material with supergene sulfides and secondary oxidized minerals from the same deposit (Timna) and found that the Cu isotope signatures of oxidized copper minerals are regularly shifted to more positive values in relation to the sulfide minerals. Klein et al. (2010) postulated the ability to distinguish between sulfidic and oxidized ore sources of artifacts: In this study, the analyzed primary sulfides mainly had a composition between δ^{65}Cu = −0.4 and +0.3 ‰, oxidized ores (hydrocarbonates) usually had a heavier composition of δ^{65}Cu > +0.3 ‰ (enriched in the heavier isotope ^{65}Cu) and supergene sulfides were lighter in their composition with δ^{65}Cu < −0.4 ‰ (enriched in the lighter isotope ^{63}Cu). Archaeological artifacts can tangentially be assigned by this classification.

In Fig. 1, the Cu isotope fractionation is demonstrated for a sulfidic ore body exposed at the surface and subsequently weathered. The sketch refers to the isotope composition of copper ores only. In contrast to surface-near oxidized copper ores, iron oxides and hydroxides like goethite and hematite as well as jarosite show negative δ^{65}Cu values (Mathur et al. 2009a), not shown in Fig. 1. The use of iron ores from the gossan, as flux in the ancient smelting activities, should not affect the Cu isotope signatures since the copper content of these sources is negligible.

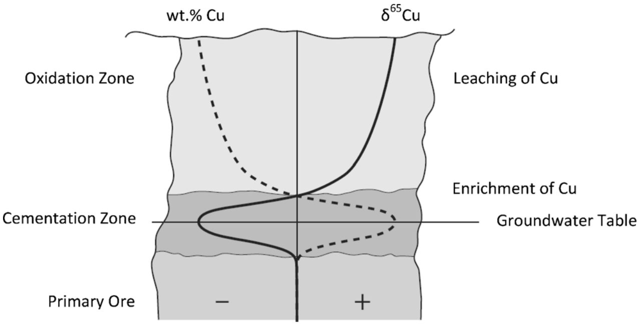


Fig. 1 Sketch of the distribution of stable Cu isotopes of copper ores in a near-surface area of a sulfidic vein deposit. In the upper oxidation zone, ores like malachite have a heavy isotopic composition which further down changes in the cementation zone with supergene sulfidic ores like chalcocite and covellite. The primary sulfidic ores like chalcopyrite were formed at high temperature and show a narrow homogenous isotopic composition. Alternatively, the hyperbole can also "swing" from one extreme to the other in the isotopic composition depending on the genesis and formation of the cementation zone

Figure 1 reflects the following principles:

1. The sulfidic ore body initially was formed under high temperature. The hypogene ore has a homogenous composition of δ^{65}Cu ± 0 ‰.
2. During the formation of secondary zoning of the deposit due to weathering, low temperature processes cause isotope fractionation. Copper is dissolved, depleted, and transported with seepage water towards the groundwater table. On its way, ^{65}Cu is preferentially precipitated in oxidized copper minerals above the groundwater table. As a result of this, these sources of the oxidation zone become heavier in their Cu isotope composition. The copper ores show positive δ^{65}Cu values.
3. The dissolved copper from the oxidation zone is now enriched in ^{63}Cu and migrates towards the groundwater table to the cementation zone where it is precipitated under reducing conditions forming supergene sulfides. These minerals are isotopically lighter and show negative δ^{65}Cu values.
4. The transition from the oxidation to the cementation zone should be characterized by δ^{65}Cu values around 0 ‰, since the depletion and enrichment processes compensate one another and oxidized and supergene sulfides occur together. The Cu isotope signature would be the same as that from the primary ore body.
5. The described δ^{65}Cu curve is inversely proportional to the copper content of the zones. The oxidation zone near the surface is less rich than the primary ore zone, while the cementation zone is enriched in copper.

Aside from the aforementioned papers, little other work has been published discussing Cu isotopes. Bendall (2003) analyzed Celtic coins made of deliberate gold–silver–copper alloys for their Cu isotope composition. Artioli et al. (2008)

investigated Italian deposits with Cu isotopes to contribute to future provenance studies. Mathur et al. (2009b) demonstrated that US cents from the nineteenth and twentieth century shifted from imported Cornwall ores and Michigan ores to the use of highly variable porphyry copper deposits around 1880. Silver-based coins dating from the fourth century BC until the eighteenth century AD were analyzed by Desaulty et al. (2011), and it was demonstrated that European silver can be distinguished from Mexican and Andean sources by a combination of Pb, Ag, and Cu isotopes. Balliana et al. (2013) investigated Roman bronzes from Northern Spain for Sn and Cu isotopes. A few analyses were undertaken on copper artifacts from the Old Copper Culture and compared to the native copper occurrences in Michigan (Mathur et al. 2014). In terms of wider usage of Cu isotopes in archaeometry, turquoise (Hull et al. 2008) and glass (Lobo et al. 2014) were also analyzed for their Cu isotopes to test the applicability for provenancing these materials.

To sum up, the Pb isotope signature is specific for the identification to deposits, while the Cu isotope signature is specific to the identification of ore mineral sources within the deposit. In the ideal case, the combination of Pb and Cu isotopes from an artifact would not only provide information about the provenance but also about the type of ore used in ancient times. Thus, conclusions can be made about the depth of the mining activities in ancient times, even if all traces were destroyed by later mining activities. The shift from colorful oxidized ores near the surface to sulfidic ores at a greater depth of the same deposit would have required substantial developments in winning methods, e.g., hauling, mine draining, and timbering to support deeper adits. In addition, the extraction of copper from sulfidic ores, especially chalcopyrite, in comparison to oxidized ores requires advancements in the techniques of smelting. Preceding roasting of the ores can be postulated. Thus, the use of sulfidic ores is linked with changes in the techniques of exploitation and smelting, resulting in the fact that the identification of ore types used in prehistoric times is of substantial interest.

Aims and material

In this study, the potential of Cu isotopes is evaluated by the direct comparison of ancient copper with its ore sources. Therefore, prehistoric ingots were analyzed and compared to their deposits, assigned by lead isotope signatures. Ingots of unalloyed copper as an intermediate product for the exchange and trade of raw materials were used to minimize the possibility of mixed copper from different mining regions. The latter could occur by the reuse and melting down of copper from different sources to produce the final artifacts which would blur the initial Cu isotope signature of the mineral sources. Usually, ingots in prehistoric times were made from freshly produced copper as indicated by the absence of tin.

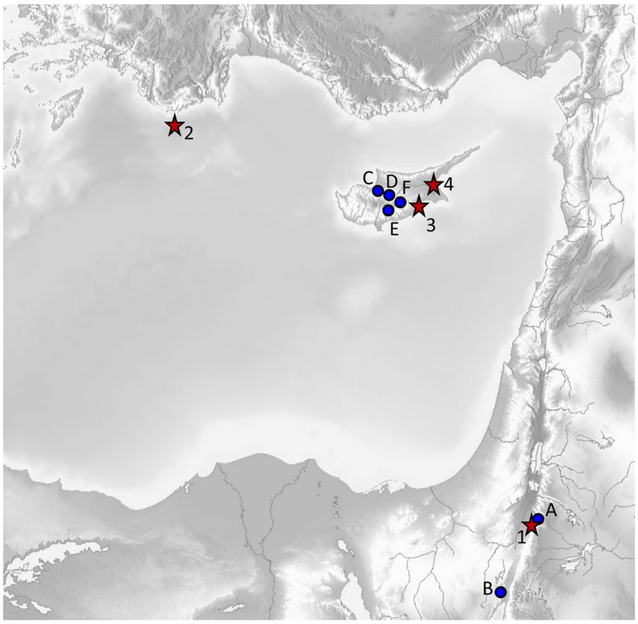


Fig. 2 Location of copper deposits (*blue circles*) and archaeological sites (*red stars*) reported in this study. Two case studies were investigated: First, Early Bronze Age ingots from Khirbat Hamra Ifdan (*1*) were compared to ores from the Faynan mining district (*A*) and from the Timna and Wadi Amram district (*B*; not analyzed in this study). Detailed maps of the Faynan region and the site Khirbat Hamra Ifdan are published by Levy et al. (2002) and Hauptmann (2007). Second, Late Bronze Age copper oxhide ingots from the shipwreck of Uluburun (*2*) were compared to slag from the LBA metal workshops of Kition (*3*) and Enkomi (*4*) and ores from the deposits of Skouriotissa (*C*), Mitsero-Kokkinoyia (*D*), Kalavassos (*E*), and Sha (*F*). A detailed map of all copper deposits from Cyprus is published by Stos-Gale et al. (1997)

Two case studies are presented in this paper (Fig. 2):

First, the oxidized ores of a sediment hosted deposit are investigated: Ore samples from the prehistoric mining district of Faynan (Jordan) were analyzed for their Cu isotope signature. The ore deposits were formed through complex geological multi stage processes beginning in the Precambrium (Hauptmann 2007). The ore samples were compared to nine copper ingots from the site of Khirbat Hamra Ifdan (2700–2200 BC), which is the largest Early Bronze Age (EBA) metal workshop in the Levant (Levy et al. 2002). The isotope composition of the oxidized ores, which were mainly exploited in prehistoric times, should be reflected in locally produced copper artifacts. One type of ingot found at Khirbat Hamra Ifdan is the “crescent-shaped” bar ingot. Over 100 of these ingots were found on various sites in the Levant. Previous studies demonstrated by a combined geochemical and lead isotope characterization that the ingots were produced from Faynan ores (most recently Hauptmann et al. 2015). Massive copper production occurred in the EBA district of Faynan. Since the EBA, copper was smelted near the mines, as indicated by nearby slag heaps (Hauptmann 2007). The metal workshops of Khirbat Hamra Ifdan are dated to the same period and obtained their raw materials from those smelting sites

(Hauptmann et al. 2015). Information about the ores and ingots is compiled in Table 1.

Second, various ores of sulfide deposits from Cyprus were analyzed, whose outcrops were subject to the isotope fractionation due to weathering processes outlined above. For the production of prehistoric copper from such deposits, different types of ore minerals are at disposal: primary sulfides, supergene sulfides, and oxidized ore minerals. The use of volcanogenic massive sulfide (VMS) copper deposits from Cyprus is considered a paragon for the prehistoric exploitation of sulfidic ores in archaeometallurgy. During the Late Bronze Age, large-scale copper production of oxhide ingots was conducted in Cyprus, proven by Pb isotope analyses: after three decades of research, Stos-Gale and Gale (2009) stated that all copper oxhide ingots produced after 1400 BC were produced from Cypriot ore. They were traded overseas through the entire Mediterranenan and beyond, which was substantiated by the loads of shipwrecks such as Uluburun and Gelidonya on the shore of Southern Anatolia. Uluburun dates to the end of the fourteenth century BC, and excavations revealed 354 complete oxhide ingots as well as fragments and planoconvex ingots, the largest accumulation of oxhide ingots from a single site (Pulak 2000). In contrast, only minor archaeological evidence is present for copper production for the Late Bronze Age in Cyprus. Ancient mining traces were mostly destroyed by the modern opencast activities occurring near the 30 ore bodies in Cyprus (for an overview of copper occurrences in Cyprus, see Stos-Gale et al. 1997). Just a single Late Bronze Age (LBA) smelting site in Politiko Phorades has been found (Knapp et al. 2001). However, LBA metallurgical remains were excavated at metal workshops in Enkomi, Kition, Hala Sultan Tekke, and Agios Dhimitrios (e.g., Zwicker 1985; Karageorghis and Kassianidou 1999).

Twenty oxhide ingots from the Uluburun shipwreck were matched against primary and supergene ores from the Cypriot deposits in this study. Ancillary, published Cu isotope data of oxhide ingots from other sites in Cyprus, Crete, and Sardinia were also compared. In addition, a few slag samples from metal workshops of the Cypriot Late Bronze Age settlements Kition and Enkomi were analyzed. It is of special interest which ore mineral types were used in the LBA in Cyprus. Information about the ores and ingots is compiled in Table 2.

Methods

Sample preparation

The preparation of the samples was conducted in the Research Center for Archaeology and Material Sciences at the German Mining Museum (Deutsches Bergbau-Museum). The samples from the prehistoric ingots were taken by drilling using 2-mm steel drill bits (DIN 338, type VA). The patina was drilled and discarded before fresh metal was taken from the uncorroded core. This is a necessary step since copper isotopic fractionation caused by the corrosion could alter the intitial signature of the ancient metal (Mathur et al. 2014). The ore samples were pounded and separated from gangue and host rock, and the concentrate was powdered in agate mills.

Maréchal et al. (1999) and Maréchal and Albarède (2002) have shown that ion exchange chromatography can cause fractionation of Cu isotopes. Because matrix effects for Cu isotope measurements have not been observed for copper ores (Graham et al. 2004; Markl et al. 2006), as well as for matrices with substantial Fe, S, Pb, Zn, and Sn contents (Zhu et al. 2000; Larson et al. 2003; Durali-Müller 2005; Balliana et al. 2013), ores and prehistoric copper alloys were measured directly without chromatographic purification in this study.

The chemical preparation of samples was carried out in a clean laboratory. Deionized water (Milli-Q) and ultraclean acids (double distilled) were used for cleaning vessels and instruments, sample dissolution, and final dilutions. Of metal, 50–100 mg was dissolved overnight in closed Teflon beakers (Savillex) on a hotplate using a 3 g mixture of 7 M HNO_3 and 6 M HCl (1:1) and 250 mg of ore and slag samples using 5 g HF/HNO_3 (5:1). 10 μl (solution from metals) and 50 μl (solution from ores) respectively were taken and evaporated with 1 ml of 7 M HNO_3 as basis for the Cu isotope measurements. Chemical blanks were processed with each set of samples ($n = 4$).

Measurements

The determination of the Cu isotope composition was conducted at the Institute for Geosciences of the Goethe-University Frankfurt using a MC-ICP-MS (Thermo Fisher Scientific, Neptune). The method was established and described by Bendall (2003), Durali-Müller (2005), Markl et al. (2006), and Klein et al. (2009, 2010). The measurement settings are compiled in Table 3.

The dissolved and evaporated samples were taken up in 2 % HNO_3 and diluted to a Cu content of about 300 ppb. A copper standard solution (NIST SRM 976; Shields et al. 1964) was used as a primary standard (300 ppb). For the purpose of mass bias correction, sample and standard solutions were spiked with 1 ppm of the Ni standard reference material (NIST SRM 986 certified with a $^{62}Ni/^{60}Ni$ ratio of 0.1386; Gramlich et al. 1989). The standard–sample–standard bracketing method was applied in order to compensate instrumental drift during the analytical campaign. Solutions were run through a glass spray chamber fitted with an ESI microconcentric nebulizer with an uptake rate of 50 μl/min. With standard H-cones, an intensity of about 4 V (10^{11} Ω resistor) for ^{63}Cu at a 300-ppb concentration level was achieved. A measurerment consisted of 20 cycles (4 blocks of 5 cycles). Cu isotope compositions are expressed in per mill deviation ($\delta^{65}Cu$ notation) from NIST SRM 976 standard reference material:

Table 1 Compilation of the samples from Jordan

Sample ID	Site	Description	δ^{65}Cu	2σ
JD-3/1b	Wadi Khalid, footwall cb3	"Matrix mineralization" in conglomerate	−0.05	0.04
JD-3/3a	Wadi Khalid, top wall cb2	Cu-Mn ore	−0.16	0.03
JD-3/5	Wadi Khalid, top wall cb2	Cu-bearing dolomite	−0.27	0.04
JD-3/15	Wadi Khalid, top wall cb2	Chrysocolla in Cu-Mn-bearing siltstone	−0.16	0.05
JD-3/22	Wadi Khalid, top wall cb2	Cu silicates, vein mineralization in sandstone	+0.02	0.04
JD-II/3	Wadi Khalid, top wall cb2	Malachite in P-Mn-bearing schist	−0.20	0.06
JD-I/22	Wadi Dana, top wall cb2	Mn ore with Cu silicates in schist	−0.20	0.03
JD-I/26	Wadi Dana, top wall cb2	Mn-Cu-bearing shale	−0.08	0.04
JD-13/9	Wadi Dana, top wall cb2	Cu-bearing shale containing Mn ore	−0.34	0.04
JD-13/14a	Wadi Dana, top wall cb2	Cu-Mn ore in siltstone	−0.03	0.04
JD-13/14b	Wadi Dana, top wall cb2	Cu ore from Cu-Mn-bearing siltstone	−0.20	0.04
JD-III/12b	Wadi Dana, top wall cb2	Siltstone containing Cu ore	+0.07	0.04
JD-III/18	Wadi Dana, footwall cb3	"Matrix mineralization" in conglomerate	0.00	0.06
JD-12/1	Wadi Ratiye, cb4	"Tile ore" (Cu-Fe ore) in sandstone	−0.83	0.04
JD-WA/1	Wadi Abiad, cb4	Cu mineralization in veins, sandstone	+0.07	0.03
JD-24/1a	Wadi Abu Kusheiba, cb3/cb4	Cu concretion in sandstone	−0.21	0.04
JD-41/1	Umm ez-Zuhur, cb2	Cu ore	−0.28	0.04
JD-41/3	Umm ez-Zuhur, cb2	Cu-bearing Mn ore	−0.30	0.03
JD-41/4	Umm ez-Zuhur, cb2	Cu-bearing Mn ore in schist	−0.24	0.04

Sample ID	Archive no.	Description	δ^{65}Cu	2σ
KHI 57	No. 18479	Bar ingot, 13 cm, 88 g (from area C)	−0.14	0.04
KHI 62	No. 20069	Longish ingot, 6.5 cm, 11 g (from area C)	−0.05	0.05
KHI 74	No. 20505	Bar ingot, 19.5 cm (from area Y)	−0.05	0.04
KHI 75	No. 20505	Bar ingot, 19.1 cm (from area Y)	+0.05	0.04
KHI 87	No. 18385	Large ingot, fragment, 4.5 cm, 78 g (from Area C)	−0.07	0.06
KHI 88	No. 40044	Ingot, fragment, 6.5 cm, 123 g (from area Y)	−0.02	0.05
KHI 93	No. 56684	Bar ingot, 21 cm, 221 g (from area H)	−0.07	0.07
JD-45/24a	No. 16005-1	Bar ingot, fragment (from area H)	−0.09	0.05
JD-45/24b	No. 16005-2	Bar ingot, fragment (from area H)	−0.15	0.05

Ores from Faynan (upper part) and Early Bronze Age ingots from Khirbat Hamra Ifdan (lower part) with descriptions and their Cu isotope composition measured in this study. A geochemical characterization of the ores is published by Hauptmann (2007). The ores belong to three different geological units: Dolomite Limestone Shale (cb2), Variegated Sand- and Claystones (cb3), Massive Brown Sandstone (cb4). Samples of the ingots originate from previous studies by Levy et al. (2002) and Hauptmann et al. (2015). δ^{65} Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ). Repeated measurements of NIST SRM 976 result in a ratio of ^{63}Cu/^{65}Cu = 2.2432 ± 0.0004 (n = 31) in agreement with the certified value of ^{63}Cu/^{65}Cu = 2.2440 ± 0.0021

$$\delta^{65}\mathrm{Cu}\ [‰] = \left[\left({}^{65}\mathrm{Cu}/{}^{63}\mathrm{Cu}_{\mathrm{sample}}\right)/\left({}^{65}\mathrm{Cu}/{}^{63}\mathrm{Cu}_{\mathrm{NIST\ 976\ standard}}\right)-1\right] \times 10^{3}$$

Internal precision is typically as low as 0.02 ‰ (2SE). The chemical blank tests did not show significant intensities (<0.005 V) on the observed masses. Repeated measurements (n = 31) of NIST SRM 976 result in a ratio of ^{63}Cu/^{65}Cu = 2.2432 ± 0.0004(2σ) which is in agreement with the reference value (certified with a ^{63}Cu/^{65}Cu ratio of 2.2440 ± 0.0021 by Shields et al. 1964).

Results

Faynan and Khirbat Hamra Ifdan

The Cu isotope composition of the ore samples from Faynan significantly varies by δ^{65}Cu = −0.83 to +0.07 ‰ with an average of −0.18 ‰. Besides a single outlier (δ^{65}Cu = −0.83 ‰), the ores form a cluster with a continuous increase from δ^{65}Cu = −0.34 to +0.07 ‰.

Table 2 Compilation of the samples from Cyprus and Turkey

Sample ID	Site	Description	δ^{65}Cu	2σ
Cy-2010/3_1	Kokkinoyia	Primary sulfide ore (pyrite/chalcopyrite)	−0.37	0.11
Cy-2010/5_1	Skouriotissa	Supergene sulfide ore	−0.46	0.05
Cy-2010/5_2	Skouriotissa	Oxidized ore (brochantite)	+0.17	0.04
Cy-2010/5_4	Skouriotissa	Primary sulfide ore (pyrite/chalcopyrite)	−0.30	0.08
Cy-2010/5_5a	Skouriotissa	Oxidized ore (brochantite)	+0.03	0.06
Cy-2010/5_6a	Skouriotissa	Supergene sulfides in sediment	−1.80	0.17
Cy-2010/5_6b	Skouriotissa	Primary sulfide ore (pyrite/chalcopyrite)	−0.39	0.11
Cy-2010/5_6d	Skouriotissa	Supergene sulfide ore (digenite)	−1.42	0.06
Cy-296k[a]	Sha	Oxidized ore (brochantite)	+1.05	0.07
Cy-590i[a]	Kalavassos	Oxidized ore (brochantite)	+0.16	0.07
KW 2177	Uluburun	Oxhide ingot	+0.36	0.04
KW 2412	Uluburun	Oxhide ingot	+0.25	0.03
KW 2719	Uluburun	Oxhide ingot	+0.04	0.03
KW 2847	Uluburun	Oxhide ingot, two handled	+0.24	0.03
KW 2885	Uluburun	Oxhide ingot	+0.39	0.06
KW 2904	Uluburun	Oxhide ingot	−0.13	0.05
KW 2919	Uluburun	Oxhide ingot	0.00	0.04
KW 3040	Uluburun	Oxhide ingot	+0.36	0.06
KW 3096	Uluburun	Oxhide ingot	+0.23	0.05
KW 3427	Uluburun	Oxhide ingot	+0.35	0.05
KW 3472	Uluburun	Oxhide ingot	+0.25	0.02
KW 3599	Uluburun	Oxhide ingot	+0.34	0.04
KW 3692	Uluburun	Oxhide ingot	+0.37	0.03
KW 3773	Uluburun	Oxhide ingot, two handled	+0.39	0.05
KW 3775	Uluburun	Oxhide ingot	+0.36	0.05
KW 3838	Uluburun	Oxhide ingot	+0.25	0.04
KW 3918	Uluburun	Oxhide ingot	+0.45	0.04
KW 3984	Uluburun	Oxhide ingot	+0.40	0.05
KW 4228	Uluburun	Oxhide ingot	+0.01	0.05
KW 4241	Uluburun	Oxhide ingot	0.00	0.05
Cy-1/1a	Kition	Large block (same as 1b), area II, room 14, floor II	−0.36	0.05
Cy-1/1b	Kition	Large block (same as 1a), area II, room 14, floor II	−0.33	0.04
Cy-1/3	Kition	Planoconvex slag, area II, sq. Δ5, room 12, floor III	−0.69	0.04
Cy-1/6	Kition	Irregular shaped slag, area II, room 15, floor II	−0.21	0.06
Cy-2/2a	Enkomi	Plate slag, area III, T-Δ, 58–60, between floor I and II	−0.17	0.05

Ores from Cyprus (upper part, including identified ore mineral phases detected with X-ray diffraction), ingots from Uluburun (middle part), and slag from LBA settlements from Cyprus with descriptions and their Cu isotope composition measured in this study. Ore samples were taken at the mines during a fieldwork in 2010 and from the Zwicker survey collection. The samples of the oxhide ingots originate from the study by Hauptmann et al. (2002). Kition: floor III is dated to the end of the thirteenth century BC (Zwicker 1985) and covered by the later floor II; Enkomi: floor I and II are dated to the end of occupied period thriteenth–twelfth century BC (see Dikaios 1969–71). Archaeometallurgical studies on the slag samples are published by Hauptmann (2011) . δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ). Repeated measurements of NIST SRM 976 result in a ratio of ^{63}Cu/^{65}Cu = 2.2432 ± 0.0004 (n = 31) in agreement with the certified value of ^{63}Cu/^{65}Cu = 2.2440 ± 0.0021

[a] Ore samples taken from the survey collection by Zwicker stored in Nicosia

Neither ores from different geological units of Faynan nor ores from different sites within the Faynan region demonstrate significant differences in their copper isotopic composition (Fig. 3a). The ingots from Khirbat Hamra

Table 3 Measurement settings of the multi-collector ICP mass spectrometry (MC-ICP-MS)

Instrument	Thermo Fisher Scientific, Neptune
Resolution mode	Low resolution ($\Delta m/m = 400$)
Cone material and type	Aluminum; H-cones
Faraday cup configuration	^{60}Ni (L1), ^{62}Ni (L3), ^{63}Cu (C), ^{65}Cu (H3)
Correction of mass bias	^{62}Ni/^{60}Ni ratio; exponential law
Glass spray chamber	50 μl/min ESI microcentric nebulizer
RF power	1370 W
Sample gas	1.03 l/min
Aux gas	1.17 l/min

Ifdan show a range of δ^{65}Cu = −0.15 to +0.05 ‰. They form a cluster with non-significant variation (Fig. 3b).

Uluburun, Enkomi, Kition, and Cyprus

The ores investigated in our study represent the ore mineral sources available from all known deposits in Cyprus during ancient times: primary sulfidic ore consisting mainly of pyrite with more or less chalcopyrite, rich supergene sulfidic ore with copper minerals like chalcocite, covellite, and digenite, and oxidized ores which are available as copper sulfates in Cyprus (brochantite and chalcanthite). The group of ten ores varies between δ^{65}Cu = −1.80 and +1.05 ‰. Significant differences are detected between sulfidic and oxidized ores. The primary sulfides have a low variation of δ^{65}Cu = −0.39 to −0.30 ‰. The supergene sulfides, whose texture easily can be differentiate from primary sulfides, have a lighter isotopic composition of δ^{65}Cu = −1.80 to −0.46 ‰, while the oxidized ore (copper sulfates) possesses a heavier composition of δ^{65}Cu = +0.03 to +1.05 ‰ (Fig. 4a).

The characterization of the Cu isotope signatures of the oxhide ingots demonstrates a variation between δ^{65}Cu = −0.13 and +0.45 ‰. Two clusters and an oulier are identifiable: the outlier shows the lowest value of δ^{65}Cu = −0.13 ‰, the first cluster demonstrates a composition between δ^{65}Cu = 0.00 and +0.04 ‰ of four identical values, and the second cluster shows δ^{65}Cu = +0.23 to +0.45 ‰ with respectively five and ten identical values forming two subgroups which are not significant considering the analytical uncertainty (Fig. 4b).

The δ^{65}Cu values of LBA slag samples from Kition and Enkomi show values between δ^{65}Cu = −0.69 and −0.17 ‰ (Fig. 4c). Two samples from the top and the bottom of the same slag block from Kition demonstrate a homogenous compostion in larger chunks of metallurgical slag (δ^{65}Cu = −0.36 and −0.33 ‰).

Discussion

Khirbat Hamra Ifdan and Faynan

The Cu isotope composition of the ingots from Khirbat Hamra Ifdan is well within the variation of the ores from Faynan (Fig. 5), linking the copper to these ore mineral sources. As Gale et al. (1999) demonstrated, Cu isotope fractionation does not occur through metallurgical processes, and smelted copper should reflect its sources' Cu isotope signature. For the metal from Khirbat Hamra Ifdan, the local provenance from Faynan was discussed by Levy et al. (2002) and Hauptmann et al. (2015). Two of the analyzed ingots belong to the crescent-shaped ingots, which were widely distributed in the Southern Levant. Hauptmann et al. (2015) suggested a single origin of these ingots due to a homogenous chemical and Pb isotope composition, which is identical with ores from Faynan. The collection of small copper lumps and prills from crushed slag, derived from various smelting sites, were commonly remelted and recycled, causing a high level of homogeneity in the chemical and Pb isotope composition. This is supported through our study by the homogenous Cu isotope composition of the ingots since they form a single cluster. Lighter and heavier compositions in the Cu isotope signature from different ore minerals and raw metals as well as extreme anomalies would be balanced by the mixing of ores and metals, explaining the little variation of the ingots' Cu isotope signature.

In the Early Bronze Age Faynan, typically ores from the Dolomite Limestone Shale DLS unit (cb2) and minimal ores from the variegated sand and claystone unit (cb3) were exploited, which are both characterized by oxidized ores (Hauptmann 2007). Only in Wadi Ratiye significant amounts of copper sulfides mixed with oxidized copper minerals and iron hydroxides occur as "tile ore" in the massive brown sandstone (MBS) unit (cb4). The use of this geological source is not evident before the Roman period. A sample (JD-12/1) from such sulfide-rich ore was included in the present study. This reflects an outlier in our dataset showing a very light Cu isotope composition (δ^{65}Cu = −0.83 ‰) which is not consistent with the signature of the ingots from Khirbat Hamra Ifdan. It can be expected that copper that is smelted from this ore would also be significantly different in Cu isotope composition.

Only a few samples from the geological units cb3 and cb4 of Faynan were analyzed. The archaeological evidence with massive Early Bronze Age mining traces pinpoints the early copper originating from Faynan to the cb2 (Hauptmann 2007). The samples from cb3 and cb4 demonstrate comparable Cu isotopic composition as ores from cb2. Therefore, from a geochemical point of view, the copper from Khirbat Hamra Ifdan could have derived from ore minerals of all geological units.

Provenance studies based on lead isotope ratios are problematic for the nearby ancient mining districts Timna and Faynan (Fig. 2), since they are formed in a similar genesis from the

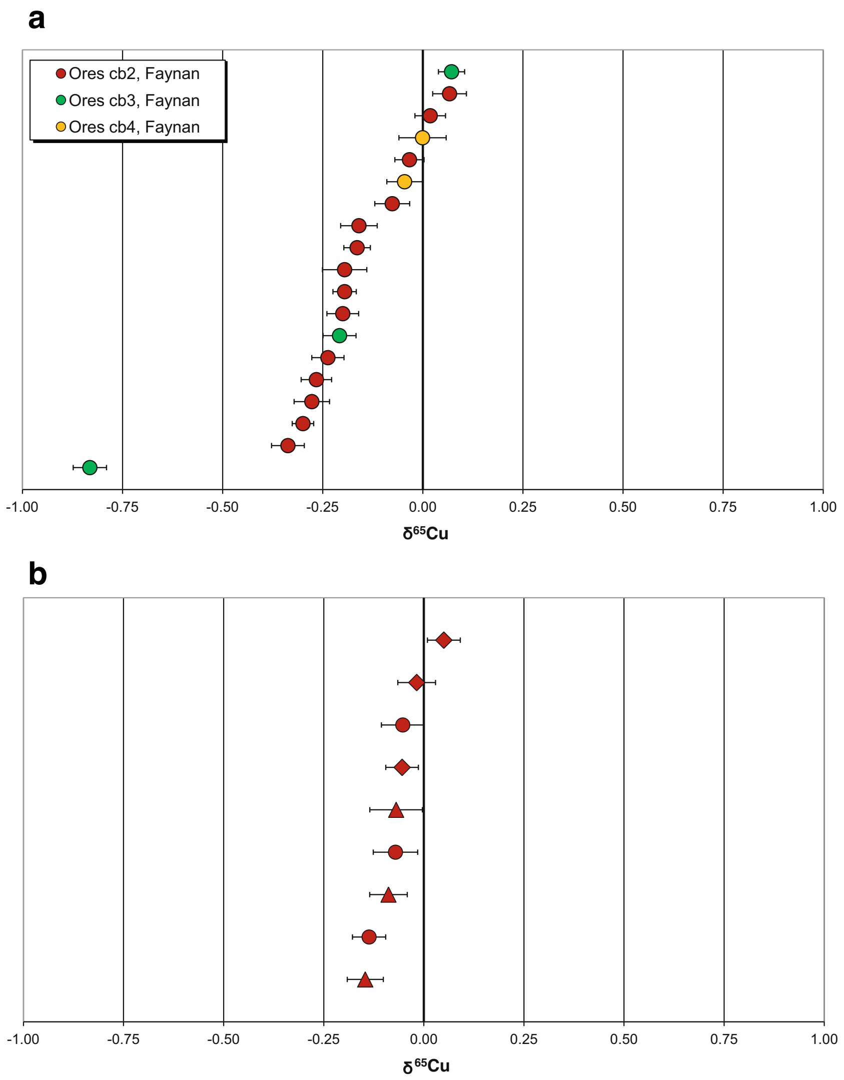
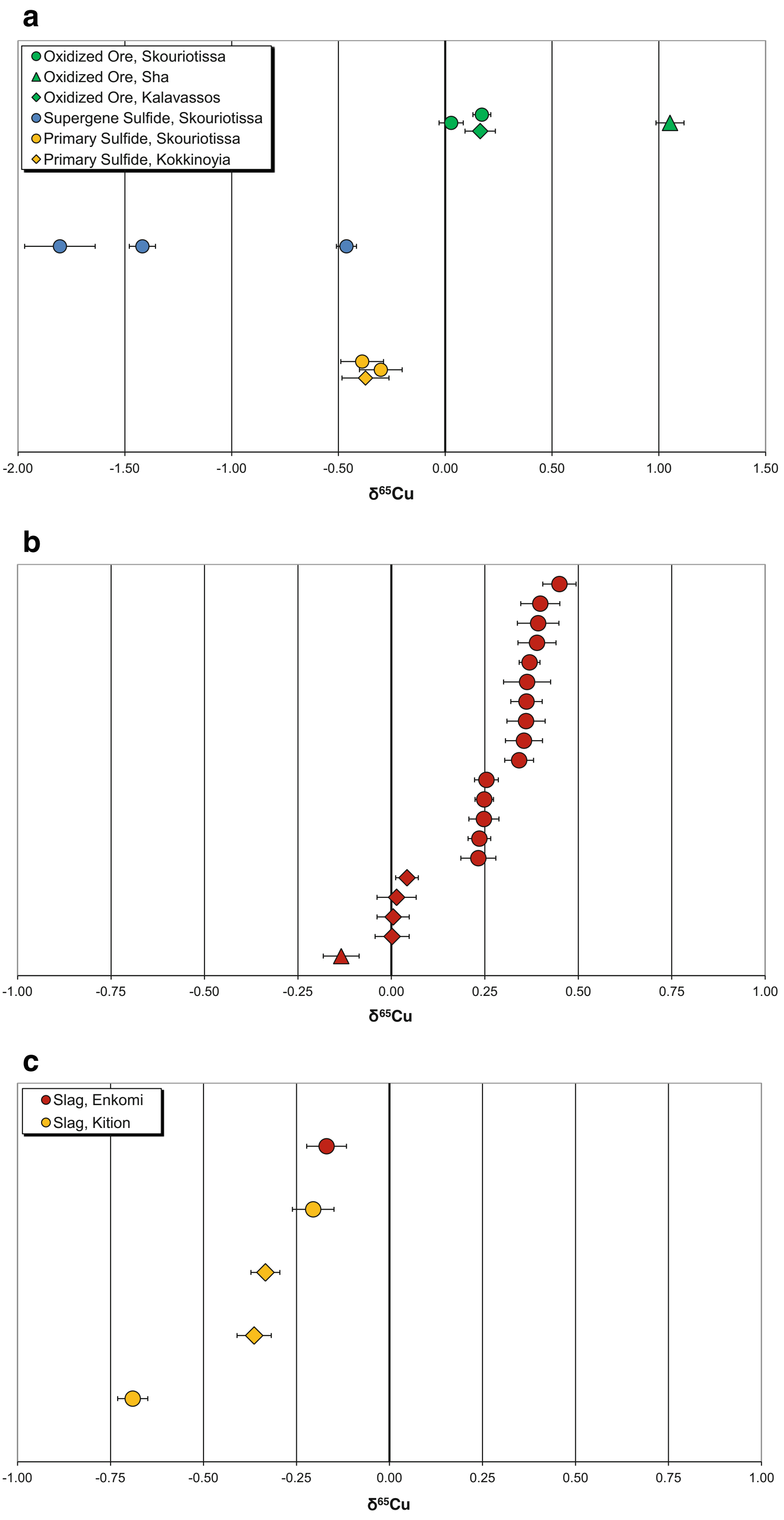


Fig. 3 **a** Univariate diagram of the Cu isotope compositions of 19 ore samples from Faynan (Jordan). The ores belong to three different geological units: dolomite limestone shale (cb2), variegated sand and claystones (cb3), and massive brown sandstone (cb4). The ores form a homogenous cluster. **b** Univariate diagram of the Cu isotope compositions of nine ingots from the metal workshop of Khirbat Hamra Ifdan in Faynan (Jordan) showing a homogenous composition. They were excavated in three areas, indicated by different symbols (*circles*: area C; *triangles*: area H; *diamonds*: area Y). The samples are presented in an ascending order of the copper isotope composition and separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ)

Precambrium onwards and are geologically identical (Hauptmann 2007). The ores from both deposits are slightly enriched in uranium, causing variable Pb isotope ratios. However, archaeological excavations indicate that different geological units were used in the early stages of mining operations in both regions. In Faynan, the DLS (cb2) was extensively exploited since the Early Bronze Age (Hauptmann 2007), and its equivalent in Timna, the Timna formation, was only exploited in a small scale at a single outcrop on the eastern border of the Timna valley (Rothenberg and Shaw 1990; for doubts on site 250a see Anver 2002). By contrast, the MBS (cb4) in Faynan was exploited at small scale in the Early Bronze Age (Hauptmann 2007), while the huge outcrop of its equivalent in Timna, the Amir formation, was extensively mined at least since Late Bronze Age with some older evidence for the Chalcolithic period (Conrad and Rothenberg 1980, Drenka 2003).

In general, Cu isotope signatures are not useful as tracers for provenance studies since the differences between ore minerals within a single deposit are larger than the variation between deposits (Markl et al. 2006). However, the variation detected in the ore mineral sources from Faynan DLS (cb2) is quite small (δ^{65}Cu = −0.34 to +0.07 ‰), compared to the variation detected by Markl et al. (2006) in hydrothermal veins (this study showed that deposits in the Black Forest in Southern Germany show a variation of δ^{65}Cu = −2.9 to +2.4 ‰, which is increased by the factor of 13 compared



to ores from Faynan). The small variation in Faynan ores is a specific characteristic that can be used to identify copper smelted from these sources.

Therefore, a comparision to other deposits in the Levant is of interest to evaluate the potential for provenance studies in this particular case. Asael et al. (2007, 2009, 2012) analyzed

◀◀ **Fig. 4** **a** Univariate diagram of the Cu isotope compositions from ten different ores originating from Cyprus. The ore types (primary sulfidic ore, supergene sulfidic ore, and oxidized ores) show significant differences. Ores of the same type but from different sites show similar values. The types of ore as well as samples of these types are separated from each other on the vertical axis. **b** Univariate diagram of the Cu isotope compositions of 20 oxhide ingots of the shipwreck from Uluburun (Turkey). The ingots form two clusters (indicated by *diamonds* and *circles*) with partly identical compositions. The second cluster with higher δ^{65}Cu values forms two subgroups, but considering the analytical uncertainty, the difference is not significant. The samples are presented in an ascending order of the isotope composition and separated from each other on the vertical axis. **c** Univariate diagram of the Cu isotope compositions of five samples of slag from the metal workshops of the LBA settlements of Kition and Enkomi (Cyprus). Two samples from the same large block show identical values (*yellow diamonds*). The samples are presented in an ascending order of the isotope composition and separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ)

ore samples from Timna for their Cu isotope ratios. However, in these studies, sulfidic and oxidized copper phases in each sample were split using a micro drill and separately analyzed, whereas our study presents analyses for chunks of ores from Faynan without microscopic separation. Depending on the portion of oxidized and sulifidic ore in Timna ores, the bulk value should vary in between the extreme ratios given by Asael et al., resulting in an intermediate composition of prehistoric copper.

It does not make sense to compare ancient copper to the ores of the Precambrian basement from Timna, which is not exposed and could not have been reached in ancient times. For comparison to the Cu isotope signatures, our study concentrates on the specific sources that were accessable to the ancient miners (following data provided by Asael et al. 2007, 2009 and 2012; this dataset is comparable to the current study since a similar protocol, including the sample standard bracketing technique, was used).

The limited outcrop of the Timna formation was a minor source for the Early Bronze Age copper exploitation (Rothenberg and Shaw 1990). It shows an average of δ^{65}Cu = +0.10 ‰ (*n* = 19; δ^{65}Cu = −0.47 to +0.40 ‰) by analyzing copper silicates from the sandstone and shist from the Timna formation. Although the average is different from the ores of Faynan (δ^{65}Cu = −0.14 ‰), the Cu isotope composition of ore minerals from Faynan and the metals from Khirbat Hamra Ifdan is included in the spread of the composition of those ore minerals from Timna. Different ore minerals from the concretions in dolomite from the Timna formation show Cu isotope ratios which are signifantly lighter: sulfide phases of the concretions show an average of δ^{65}Cu = −2.04 ‰ (*n* = 28; δ^{65}Cu = −3.18 to −1.24 ‰), and oxidized ore phases show an average of δ^{65}Cu = −0.85 ‰ (*n* = 19; δ^{65}Cu = −1.63 to −0.09 ‰). Copper smelted from these sources would not have the composition of the ingots from Khirbat Hamra Ifdan.

The Amir formation is not only largely exposed in Timna but also in the nearby Wadi Amram. Both were extensively mined at least since the Late Bronze Age with some evidence for the Chalcolitic period (Conrad and Rothenberg 1980; Drenka 2003; Rothenberg 1996–97; Willies 1991). Cu isotopes from sulfidic ore phases from the Amir formation in Timna show an average of δ^{65}Cu = −2.51 ‰ (*n* = 19; δ^{65}Cu = −3.81 to −0.66 ‰), and oxidized phases in the same ores result in an average of δ^{65}Cu = −0.65 ‰ (*n* = 18; δ^{65}Cu = −1.27 to +0.41 ‰). Copper ores from the Amir formation in Timna therefore show a different Cu isotope signature than it was found for the ingots of Khirbat Hamra Ifdan (Fig. 6). In the nearby Wadi Amram, the sulfidic phases show

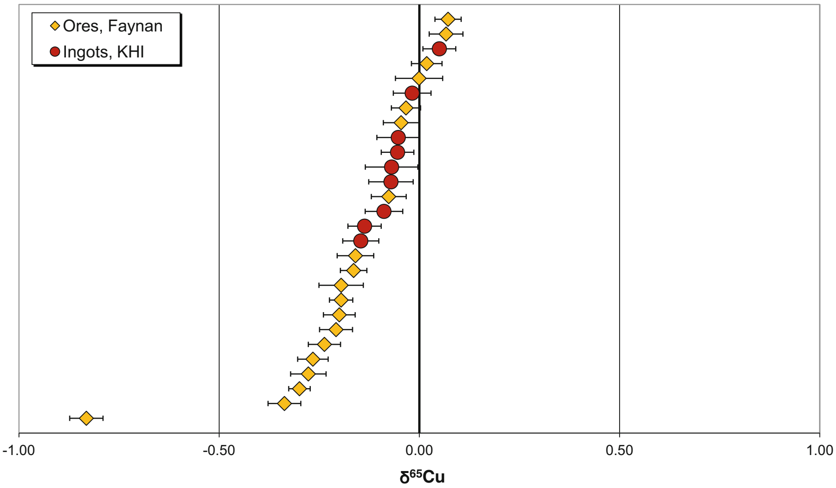


Fig. 5 Univariate diagram of the Cu isotope compositions of ore samples of different geological units from Faynan (Jordan) compared to copper ingots from Khirbat Hamra Ifdan (KHI). The ingots match to the variation of the ores. The samples are presented in an ascending order of the isotope composition and separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ)

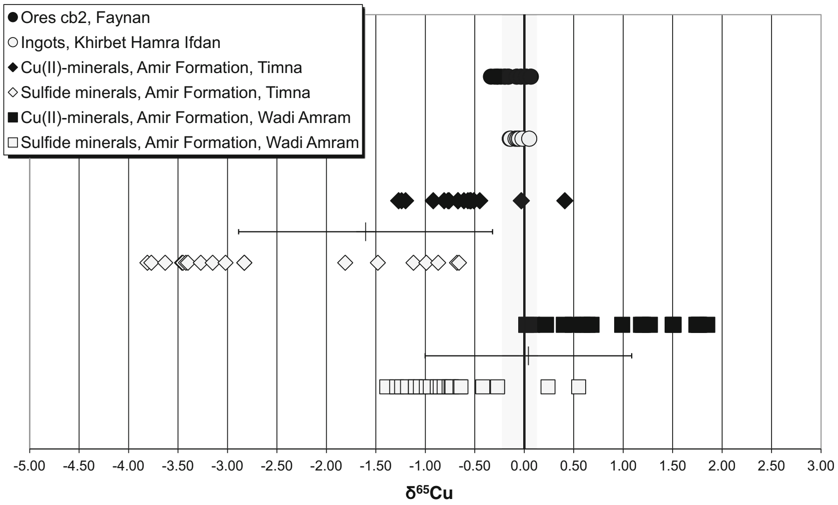


Fig. 6 Univariate diagram of the Cu isotope compositions of copper ingots from Khirbat Hamra Ifdan in comparison to ore sources from the Wadi Arabah. Ores from the Amir formations of Timna and Wadi Amram were analyzed by Asael et al. (2007, 2009, 2012). The *bars* indicate the average of all micro samples of the different geological units as well as their standard deviation. The ingots are identical in their Cu isotopic signature with ores from the dolomite limestone shale (cb2) and the Amir formation in Wadi Amram, while ores from the Amir formation in Timna are significantly lighter in their Cu isotope composition and can be excluded as an ore source. The different ore deposits and ingots are separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty (2σ) is smaller than the symbols

an average of δ^{65}Cu = −0.80 ‰ (n = 21; δ^{65}Cu = −1.39 to +0.55 ‰) and oxidized phases in the same ores have an average of δ^{65}Cu = +0.94 ‰ (n = 19; δ^{65}Cu = +0.02 to +1.85 ‰). In contrast to Timna, a mixture of oxidized and suflidic ore phases from the Amir formation in Wadi Amran could produce a similar composition as the ingots from Khirbat Hamra Ifdan.

In conclusion, the Cu isotope variations between ores from Timna, Wadi Amram, and Faynan support provenance studies of ancient copper: Cu isotope signatures contribute to the characterization of copper smelted from different mineral sources in the Wadi Arabah which previously have been difficult to distinguish by Pb isotopes and trace elements alone. This is of particular interest, e.g., for the late second and the first millennia BC since extensive copper production took place at that time in both mining districts Timna and Faynan or, e.g., for the differentiation of ore sources which were used on smelting sites in the Southern Wadi Arabah, originating either from Wadi Amram or from Timna.

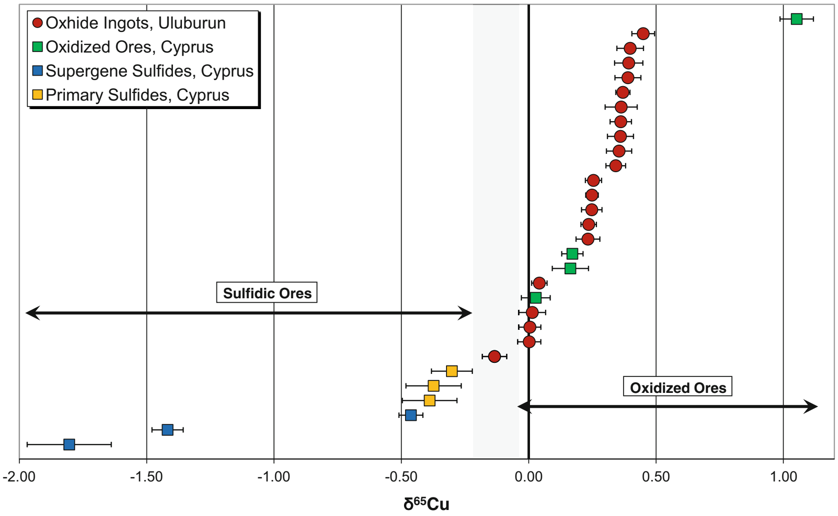


Fig. 7 Univariate diagram of the Cu isotope compositions of 20 oxhide ingots from the LBA shipwreck of Uluburun (Turkey) in comparison to ten ore samples from Cyprus. The *gray zone* represents a field in which neither the sulfide nor the oxidized ores can be confidently assigned. The oxhide ingots are consistent with the oxidized ore (copper sulfates). The samples are presented in an ascending order of the isotope composition and separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty is given as standard deviation (2σ)

Uluburun, Enkomi, Kition, and Cyprus

The primary sulfidic ore from the VMS deposits in Cyprus possesses a homogenous Cu isotope composition, while oxidized ores are isotopically heavier and supergene sulfides are isotopically lighter. These match the general principle of the Cu isotope system of sulfidic vein deposits (see again Fig. 1). The comparison of the Cu isotope signature of the Uluburun oxhide ingots with ores from Cyprus demonstrates that these correlate with oxidized ores, while primary and supergene sulfidic ores from Cyprus are significantly different in Cu isotope composition (Fig. 7, the ingot with the low δ^{65}Cu value is close to both oxidized and sulfidic ores and this will be discussed later). An oxidized mineral source like the copper sulfates is therefore reasonable for the production of the Uluburun oxhide ingots, and sulfidic ore mineral sources like chalcopyrite, covellite, and chalcocite can be excluded. Already Bruce et al. (1937), but also Muhly et al. (1980), have discussed the Late Bronze Age use of copper sulfate ore from Cyprus, even though from a modern perspective these ores are not abundant (Constantinou 1982). For the Troulli deposit, rich occurrences of copper sulfate were described by Zwicker (1985). In the Bronze Age, all of the more ore less untouched copper deposits in Cyprus could bear such rich sources of oxidized ore, including the deposits of the Solea region (e.g., Apliki, Mavrovouni, Skouriotissa) which were identified as the origin for the copper of Late Bronze Age oxhide ingots dating after 1400 BC, including the Uluburun ingots, based on Pb isotope studies (Stos-Gale et al. 1997; Gale 2011).

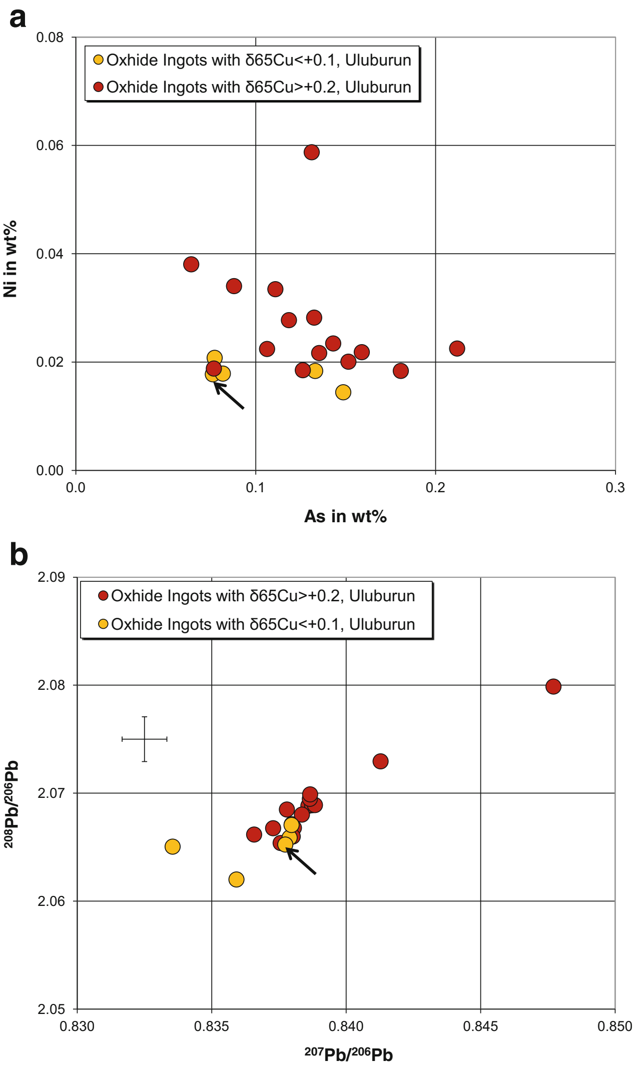


Fig. 8 Binary diagrams of **a** As and Ni contents (data from Hauptmann et al. 2002) and **b** lead isotope ratios (data from OXALID) of the Cu isotope clusters of oxhide ingots from Uluburun showing non-significant differences. The outlier with the negative δ^{65}Cu value is marked with an arrow

Two clusters (one with two subgroups) in the Cu isotope composition of the oxhide ingots were detected. The differences could be explained by the use of different mineral sources, while ingots with the same Cu isotope ratios could derive from the same mineral sources within a deposit. Those different groups should also be reflected in the chemical and Pb isotope composition. The oxhide ingots from Uluburun are characterized by low trace element concentrations (Hauptmann et al. 2002). The Cu isotope ratios do not correlate with the contents of As and Ni (Fig. 8a), which are the only significant trace elements detected for the Uluburun ingots that can be used for provenance studies based on chemical composition. The outlier with the low δ^{65}Cu value (δ^{65}Cu = −0.13 ‰) clusters together with two other ingots with δ^{65}Cu < 0.1 ‰ values (δ^{65}Cu = 0.00 and +0.04 ‰), and one with δ^{65}Cu > 0.2 ‰ (δ^{65}Cu = +0.39 ‰), demonstrating that the various Cu isotope ratios are not associated with differences of those trace elements. Only very low concentrations of sulfur (mean of 0.13 wt% sulfur) and variations of this element between the ingots were detected by Hauptmann et al. (2002), which could also indicate an oxidized ore source rather than sulfidic ore for all of the ingots (the ingot with the low δ^{65}Cu value contents 0.05 wt% of sulfur).

The Uluburun copper was comprehensively analyzed for its lead isotope compositon by Gale and Stos-Gale. The dataset is accessible through the online database OXALID (Stos-Gale and Gale 2009). There is no significant correlation between Cu and Pb isotope ratios of the ingots (Fig. 8b), even though two ingots of δ^{65}Cu < 0.1 ‰ (δ^{65}Cu = 0.00 and +0.01 ‰) show the lowest Pb isotope ratios while two ingots of δ^{65}Cu > 0.2 ‰ (δ^{65}Cu = +0.24 and +0.35 ‰; both subgroups of the second cluster are represented) demonstrate the highest Pb isotope ratios. Again, the outlier clusters together with ingots of various Cu and Pb isotope compositions. Maybe a more comprehensive Cu isotope characterization of the oxhide ingots from Uluburun could provide a more differentiated conclusion, but for this study, neither trace elements nor Pb isotope ratios of individual ingots are

Table 4 δ^{65}Cu [‰] values with standard deviation (2σ) calculated from published data by Gale et al. (1999) using MC-ICP-MS and Woodhead et al. (1999) using TIMS

Sample ID	Site	Date	^{63}Cu/^{65}Cu	SD	δ^{65}Cu	2σ
MAT1	Mathiati, Cyprus	13th–12th century BC (LC IIC-IIIA)[b]	2.24570	0.00011	−0.64	0.10
E13	Enkomi, Cyprus	13th–12th century BC (LC IIC-IIIA)[b]	2.24852	0.00011	−1.89	0.10
SK1	Skouriotissa, Cyprus	13th–12th century BC (LC IIC-IIIA)[b]	2.24475	0.00006	−0.21	0.06
LAN1	Lanusei, Sardinia	13th–11th century BC (RBA-FBA2)[c]	2.24449	0.00001	−0.10	0.01
THB	Agia Triada, Crete	1500–1450 (LM IB)[d]	2.24536	0.00005	−0.49	0.04
THE	Agia Triada, Crete	1500–1450 (LM IB)[d]	2.25370	0.00008	−4.18	0.07
THG	Agia Triada, Crete	1500–1450 (LM IB)[d]	2.24885	0.00006	−2.04	0.05
THI	Agia Triada, Crete	1500–1450 (LM IB)[d]	2.24735	0.00002	−1.37	0.02
SRM 976	NBS/NIST Standard		2.24427	0.00017		
N/A[a]	Komos, Crete	1350–1250 (LM III A2-B)[e]	2.24461	0.00011	+0.04	0.10
N/A[a]	Capoterra, Sardinia	13th–11th century BC (RBA-FBA2)[c]	2.24583	0.00026	−0.50	0.23
SRM 976[a]	NBS/NIST Standard		2.244705	0.00039		

[a] Measured by Woodhead et al. (1999)

[b] Dating by Kassianidou (2009)

[c] Dating by Lo Schiavo (2009)

[d] Dating by Stos-Gale (2011)

[e] Dating by Woodhead et al. (1999)

related to their Cu isotope composition and therefore no categorical answer can be made to explain the Cu isotope clusters of the Uluburun ingots.

The data by Gale et al. (1999) and Woodhead et al. (1999) on oxhide ingots from Crete, Sardinia, and Cyprus was recalculated to ensure comparability to our dataset (Table 4). The ingots from Agia Triada (Crete) date to the sixteenth/fifteenth century BC (Fig. 9). They do not correlate with Cypriot ore in their Pb isotope composition (Stos-Gale 2011); these separate by lead isotopes into two clusters resulting from different ore forming events, which can be recalculated by the Cumming-Richards Model III having model ages of approximately 375 Ma and around 640 Ma years (Gale and Stos-Gale 1986). Both isotope clusters of Agia Triada ingots cannot be traced back to any determined copper deposit in the Mediterranean and Near East. Timna and

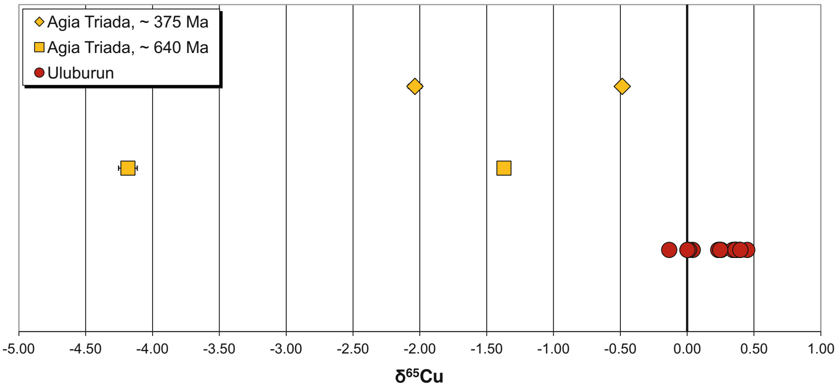


Fig. 9 Univariate diagram of the Cu isotope compositions of four sixteenth/fifteenth century BC oxhide ingots from Agia Triada (Crete). The four ingots from two deposits with different Pb isotope model ages (other than Cyprus, see Stos-Gale 2011) are significantly lighter in their Cu isotope composition than ingots from Uluburun. The groups of ingots are separated from each other on the vertical axis. δ^{65}Cu [‰] was measured with MC-ICP-MS, and analytical uncertainty (2σ) is smaller than symbols

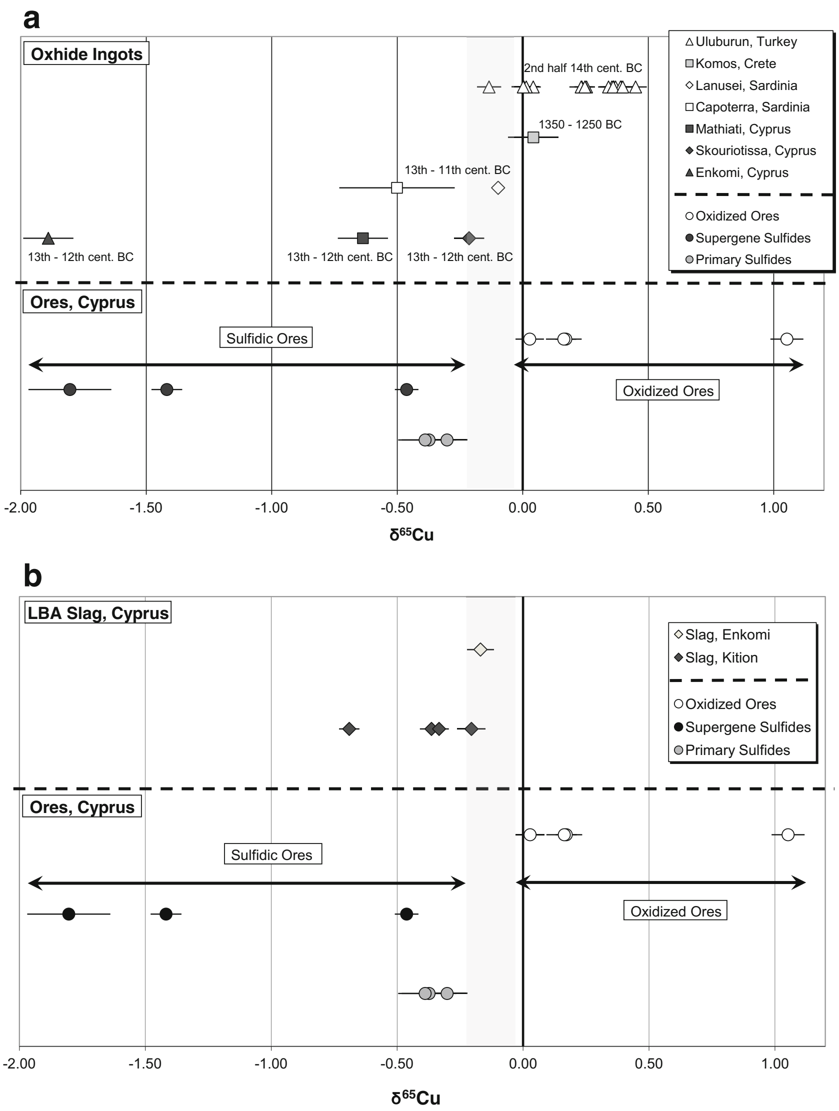


Fig. 10 Univariate diagram of the copper isotopic composition of **a** six oxhide ingots from Cyprus, Sardinia, and Crete (Gale et al. 1999; Woodhead et al. 1999) and 20 oxhide ingots of the Late Bronze Age shipwreck of Uluburun/Turkey (*upper part of the diagram*) which were probably produced in Cyprus. **b** Six samples of metallurgical slag from Kition and Enkomi (Cyprus). Oxhide ingots and slag are compared to ten ore samples from Cyprus (*lower part of both diagrams*). The areas of sulfidic and oxidized ores are marked. The *gray zone* represents a field of the graph that, so far, neither the sulfidic nor the oxidized ores can be confidently assigned. The change from oxidized to sulfidic ores in the thirteenth century BC is recognizable. The different ore types as well as ingots and slag coming from different sites are separated from each other on the vertical axis. Analytical uncertainty is given as standard deviation (2σ)

Faynan are quite similar but not fully consistent to the model age cluster of 375 Ma in their lead isotope ratios (Stos-Gale 2011). If the ingots from this latter cluster were made of copper ores from a deposit in the Wadi Arabah, one would expect consistent Cu isotope signature either to ores from Faynan or to ores from Timna (see "Khirbat Hamra Ifdan and Faynan" section). Therefore, we can exclude the Faynan ores since the oxhide ingots from Agia Triada have a lighter Cu isotope composition which only matches to Timna ores (see Fig. 6). These ingots also do not match to the Cu and Pb isotope composition of the oxhide ingots from Uluburun. The negative δ^{65}Cu values of less than −0.5 ‰ for all of the Agia Triada ingots might indicate the use of supergene sulfidic ore sources which typically have such lower ^{65}Cu/^{63}Cu ratios (Klein et al. 2010) or oxidized ores derived from those.

The other six oxhide ingots analyzed by Gale et al. (1999) and Woodhead et al. (1999) are later in date and have concurrent Pb isotope data with Cypriot ores from Apliki, Skouriotissa and Mavrovouni (Stos-Gale et al. 1997; Gale 1999). While the ingots from Kommos, Lanusei, and Skouriotissa are overlapping in Cu isotope signature with the outlier and lighter cluster of ingots from Uluburun, the ingots from Enkomi, Mathiati, and Capoterra do not overlap with the ingots from Uluburun at all (Fig. 10a).

If the oxhide ingots from Uluburun were smelted from ores of Cyprus, only the oxidized ores from there are conisistent with their Cu isotope signature. This is also true for the oxhide ingot from Kommos (Crete). The ingot from Lanusei (Sardinia) is similar to the negative outlier from Uluburun falling in an area between oxidized and sulfidic ores, while the ingot from Capoterra (Sardinia) matches to primary and supergene sulfides from Cyprus. The Cypriot ingots from Enkomi and Mathiati are consistent with supergene sulfides, and the ingot from Skouriotissa overlaps with primary sulfides. By correlating the dates of the ingots, a shift from oxidized to sulfidic ores is noticeable on the basis of the Cu isotopes in the thirteenth century BC. It can be hypothesized that first oxidized ores at the outcrop of Cypriot copper deposits were exploited and then a rich cementation zone with sulfidic ores could have been reached by the ancient miners.

Future research should characterize the Cu isotope signature of native copper in Cyprus. In 1939, 1 ton of native copper was exploited in Mavrovouni (Tylecote 1982). Against this background, Ikehata et al. (2011) demonstrated supergene native copper in VMS deposits possess a Cu isotope signature of heavier composition than its primary sulfides, it could be assumed that—if native copper from Cyprus played a role as a mineral source for copper metal—this might result in comparable isotope composition like the oxidized ores (copper sulfates) characterized in this study. What counts against the exploitation of native copper here is that in the oxhide ingots of Uluburun large amounts of slag inclusions were detected (Hauptmann et al. 2002). This iron silicate slag is expected as a smelting product of copper ores but not for melting native copper.

The metallographic examination of oxhide ingots is in the line with our hypothesis. As for the Uluburun ingots, Hauptmann et al. (2002) characterized them as pure copper with minor amounts of copper sulfide inclusions but large amounts of copper oxide inclusions (from casting) and slag inclusions (from smelting). They stated that chalcopyrite was used for the primary production of the copper, whose sulfur was mostly separated out through roasting and whose iron was extracted by oxidation and subsequent slagging, causing the Fe-free copper sulfide inclusions in the metals as relics of the roasted sulfidic ore. The identified slag inclusions clearly demonstrate that the copper was not "refined" by multiple re-melting procedures after smelting. However, in this study, we state for the production of the Uluburun ingots, based on the Cu isotope signatures, that oxidized ores like copper sulfates were used. They could be responsible for the minor sulfide inclusions due to the reduction of sulfate to sulfur forming minor copper sulfide inclusions.

As for ingots from Sardinia, Cyprus, and Crete, metallographic studies were conducted for Mathiati, Enkomi as well as Lanusei and Capoterra but not on ingots from Kommos and Skouriotissa. In the individual ingot from Lanusei, Lo Schiavo et al. (1990) did not identify inclusions of either copper sulfide or oxide but emphasize that it chemically lacks Co, Ag, and Pb as detected in other ingot fragments from Sardinia. If jointly considered with the Cu isotope signature, this is in parallel with the oxhide ingots from Uluburun and therefore points to an oxidized ore source. The ingot from Capoterra shows large quantities of copper sulfide inclusions containing Fe, Co, Ni, Pb, and Zn (Zwicker et al. 1980). The ingots of Mathiati have many copper sulfide and minor oxide inclusions, and two ingots from Enkomi have many copper sulfide inclusions with contents of As, Co, and Zn (Muhly et al. 1980). These inclusions trace back to a sulfidic ore source, as is consistent with the results of the Cu isotope measurements.

Besides the above-discussed elemental components, Maddin (1989) pointed out that the Uluburun oxhide ingots contain less arsenic (0.08 wt%, $n = 16$; compared to 0.15 wt%, $n = 114$ from Hauptmann et al. 2002) than later ingots from Gelidonya. The Kommos ingots, dating to the same period as Uluburun, show a mean of 0.13 wt% As (see Muhly et al. 1988), while later ingots from Cyprus show a mean of 0.45 wt% As (Muhly 1991). This is also confirmed by data from ingots of Enkomi, Mathiati, and Skouriotissa (Muhly et al. 1980, 1988; Gale and Stos-Gale 1984, 1986). The decreasing arsenic amount is just a tendency, since some of the ingots from Uluburun and also Lanusei show higher As values of up to 0.4 wt% (Lo Schiavo et al. 1990; Hauptmann et al. 2002), and later ingots from Capoterra and one example from Mathiati show lower As values of 0.1–0.2 wt% (Muhly et al. 1988; Lo Schiavo et al. 1990). Anyway, the As content potentially functions as an additional arguement for a replacement in the ore source from oxidized ores for earlier ingots and sulfidic ores for later ones. The assignment of higher As contents to sulfidic ore is based on the model of oxidized ores being very pure instead of sulfidic ores such as arsenic-rich copper sulfide minerals.

The Cu isotope composition of slag from the LBA settlements of Kition and Enkomi does not match the oxidized ores from Cyprus (Fig. 10b). They show a tendency towards sulfidic ores in their hypothetical ore source. The identification of copper sulfides in the slags (Hauptmann 2011) is in line with this hypothesis. The ore mineral source for the copper used in the metal workshops of Kition and Enkomi seems to be different to that one used for the Uluburun oxhide ingots. Only the outlier of the oxhide ingots with the low value of $\delta^{65}Cu = -0.13$ ‰ is consistent with the slag from Enkomi and with one from Kition. All slag samples are contemperous with the oxhide ingots found in Cyprus itself, and also the Cu isotope composition is consistent with those. These results indicate that similar ore mineral sources (mainly sulfidic ore) were used in the workshops at Kition and Enkomi and for the contemperous ingots.

To sum up, the combination of Pb and Cu isotopes helps to reconstruct the geological origin of the copper from Cyprus, both in deposits and ore mineral sources. For the oxhide ingots from Uluburun, we assume the use of an oxidized ore source, while slag from Kition and Enkomi and younger oxhide ingots were smelted from sulfidic ores. That means that both ore mineral sources were used in the Late Bronze Age Cyprus.

Conclusions

In this study, Bronze Age copper ingots and metallurgical slag were compared to ores from ancient mining districts by Cu isotopes. The ingots of the Early Bronze Age metal workshop of Khirbat Hamra Ifdan in the Faynan mining district demonstrate a homogenous Cu isotope composition which is identical to the signature of oxidized ores from nearby mineral sources. This is consistent with the local production of these ingots. In focus are differences in the Cu isotope composition of ore mineralizations from the prehistoric mining districts of Faynan, Timna, and Wadi Amram. Due to their similar geological genesis, these districts are almost impossible to distinguish on the basis of their chemical and lead isotope composition. However, our results indicate that varying geological units exploited at Timna and Faynan differ in their Cu isotope signature. Therefore, Cu isotope analysis is a useful method to differentiate between ancient copper deriving from the mining districts of the Wadi Arabah and could thus help to reconstruct changes in access to raw mineral sources over time in this region.

Late Bronze Age oxhide ingots were compared to sufidic and oxidized ores of the volcanogenic massive sulfide deposits on the island of Cyprus. The oxhide ingots of the shipwreck of Uluburun were identified as originating from Cyprus (most recently Stos-Gale and Gale 2009). They form clusters in their Cu isotope composition, which correlate with oxidized ores from Cyprus. The Cu isotope composition of stratified slag from the LBA settlements of Kition and Enkomi correlates with sulfidic ore. The Cu isotope analysis adds to the argument that for the copper ingots which were produced in Cyprus, initially oxidized ores were used. In the thirteenth century BC, a change to sulfidic ores is visible. The earlier ingots of the sixteenth/fifteenth century BC from Agia Triada (Crete) are not only different from the Uluburun ingots in the lead isotopic composition (most recently Stos-Gale 2011) but also in the copper isotopic composition.

With the determination of the Cu isotopic composition, it is possible to show that for the ingots of Uluburun, near-surface oxidized ores were used. Such ore mineral sources must have played, at least for a time, an important role in copper production in Cyprus. Today, from the perspective of the modern geologist, there are no profitable deposits of oxidized ores in Cyprus. But our understanding of economics should not be transferred to the prehistoric period. We hope that our study will give future research a push to rethink models of raw material use in Cyprus. Rich oxidized ore deposits could have been exhausted in antiquity, a fact which, given the incredible amount of four million tons of primarily Late Roman slag found in Cyprus, would not be surprising. A change to sulfidic ores in the diachronic comparison, which can maybe be detected in the thirteenth century BC, might be caused by the exhaustion of accessible sources of oxidized ore minerals. That means not only an advancement in mining technology (greater depths) but also would have required changes in the process of smelting. It has been stated that every oxhide ingot manufactured after 1250 BC derived from copper smelted from ores of a single rich deposit of Apliki in North-Western Cyprus (Stos-Gale et al. 1997). The exploitation of a rich cementation zone of sulfidic ores could have provided large amounts of copper for the entire Mediterranean and might have had socio-econmic consequences for the region of Apliki (Hauptmann 2009; Gale and Stos-Gale 2012).

In deposits which exclusively contain oxidized ores, like the sources from Faynan and Timna, Cu isotopes are an additional tracer for provenance studies if their variation is quite limited. In deposits with oxidized and sulfidic ores, like the weathered VMS deposits from Cyprus, they allow a reconstruction of the selective use of different copper sources, which in the ideal case could be chronologically resolved. For this purpose, a broad database with Cu isotope signatures of different ore deposits is necessary as already established for lead isotopes (e.g., the OXALID database by Gale and Stos-Gale). The acquisition of these data is just at its inception.

Acknowledgements This study was funded by the Leibniz-Kompetenzzentrum Archäometrie at the German Mining Museum (Deutsches Bergbau-Museum). In previous studies, Thomas E. Levy and Cemal Pulak provided the opportunity to take samples from Bronze Age ingots. We are grateful for the support of Vasiliki Kassianidou, George Hadjigeorghiou, Constantinos Xydas, and Lazaros Georgios during a stay in Cyprus for sampling ore specimens in the field and additional ones from the survey collection of Ulrich Zwicker. We thank Wolfgang Steger and Michael Bode who supported the sample preparation in the clean lab in Bochum. Sincere thanks are given to the anonymous reviewers for their valuable comments.

References

Albarède F (2004) The stable isotope geochemistry of copper and zinc. Rev Mineral Geochem 55:409–427. doi:10.2138/gsrmg.55.1.409

Anver U (2002) Studies in the material and spiritual culture of the Negev and Sinai populations, during the 6th-3rd millennia B.C. Dissertation, Hebrew University of Jerusalem

Artioli G, Baumgarten B, Marelli M, Giussani B, Recchia S, Nimis P, Giunti I, Angelini I, Omenetto P (2008) Chemical and isotopic tracers in Alpine copper deposits: geochemical links between mines and metal. Geo Alp 5:139–148

Asael D, Matthews A, Bar-Matthews M, Halicz L (2007) Copper isotope fractionation in sedimentary copper mineralization (Timna Valley, Israel). Chem Geol 243:238–254. doi:10.1016/j.chemgeo.2007.06.007

Asael D, Matthews A, Oszczepalski S, Bar-Matthews M, Halicz L (2009) Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits. Chem Geol 262:147–158. doi:10.1016/j.chemgeo.2009.01.015

Asael D, Matthews A, Bar-Matthews M, Harlavan Y, Segal I (2012) Tracking redox controls and sources of sedimentary mineralization using copper and lead isotopes. Chem Geol 310–311:23–35. doi:10.1016/j.chemgeo.2012.03.021

Balliana E, Aramendia M, Resano M, Barbante C, Vanhaecke F (2013) Copper and tin isotopic analysis of ancient bronzes for archaeological investigation: development and validation of a suitable analytical methodology. Anal Bioanal Chem 405:2973–2986. doi:10.1016/j.chemgeo.2009.01.015

Bendall C (2003) The application of trace element and isotopic analyses to the study of Celtic gold coins and their metal sources. Dissertation, University of Frankfurt

Bruce JL, Manglis CP, Creveling DM (1937) Antiquities in the mines of Cyprus. In: Gjerstad E, Lindros J, Sjöqvist E, Westholm A (eds) The Swedish Cyprus Expedition III, Stockholm, pp 639–671

Conrad HG, Rothenberg B (1980) Antikes Kupfer im Timna-Tal – 4000 Jahre Bergbau und Verhüttung in der Arabah (Israel). Der Anschnitt Beiheft 1, Bochum

Constantinou G (1982) Geological features and ancient exploitation of the cupriferous sulphide orebodies of Cyprus. In: Muhly JD, Maddin R, Karageorghis V (eds) Early metallurgy in Cyprus, 4000–500 B.C. Acta of the International Archaeological Symposium, Nicosia, pp 13–24

Desaulty AM, Telouk P, Albalat E, Albarède F (2011) Isotopic Ag-Cu-Pb record of silver circulation through 16th-18th century Spain. Proc Natl Acad Sci U S A 108:9002–9007. doi:10.1073/pnas.1018210108

Dikaios P (1969–71) Enkomi. Excavations 1948–1958. 4 volumes, Mainz

Drenka A (2003) New excavations in the chalcolithic mine T of Timna. Preliminary report of the excavations March-May 2001. Institute for Archaeo-Metallurgical Studies Newsletter 23:21–26

Durali-Müller S (2005) Roman lead and copper mining in Germany—their origin and development through time, deduced from lead and copper isotope provenance studies. Dissertation, University of Frankfurt

Gale NH (1999) Lead isotope characteristics of the ore deposits of Cyprus and Sardinia and its application to the discovery of the sources of copper for Late Bronze Age oxhide ingots. In: Young SMM, Pollard AM, Budd P, Ixer RA (eds) Metals in antiquity. British Archaeological Reports International Series 792, Oxford, pp 110–133

Gale NH (2011) Copper oxhide ingots and lead isotope provenancing. In: Betancourt PP, Ferrence SC (eds) Metallurgy: understanding how learning why. Studies in honor of James D. Muhly, Philadelphia, pp 213–220

Gale NH, Stos-Gale ZA (1984) Lead isotope and chemical analyses of silver, lead and copper artifacts from Pyla-Kokkinokremos. In: Karageorghis V, Demas M (eds) Pyla Kokkinokremos—a late 13th century BC fortified settlement in Cyprus. Report of the Department of Antiquities Cyprus 1984, Nicosia, pp 96–103

Gale NH, Stos-Gale ZA (1986) Oxhide copper ingots in Crete and Cyprus and the Bronze Age metals trade. The Annual of the British School at Athens 81:81–100

Gale NH, Stos-Gale ZA (2012) The role of the Apliki mine region in the post c. 1400 BC copper production and trade networks in Cyprus and in the wider Mediterranean. In: Kassianidou V, Papasavvas G (eds) Eastern Mediterranean metallurgy and metalwork in the second millennium BC. Oxbow Books, Llandysul, p 70–82

Gale NH, Woodhead AP, Stos-Gale ZA, Walder A, Bowen I (1999) Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry. Int J Mass Spectrom 184:1–9. doi:10.1016/S1387-3806(98)14294-X

Graham S, Pearson N, Jackson S, Griffin W, O'Reilly SY (2004) Tracing Cu and Fe from source to porphyry: in situ determination of Cu and Fe isotope ratios in sulfide from the Grasberg Cu-Au deposit. Chem Geol 207:147–169. doi:10.1016/j.chemgeo.2004.02.009

Gramlich JW, Machlan LA, Barnes IL, Paulsen PJ (1989) Absolute isotopic abundance ratios and atomic weight of a reference sample of nickel. J Res Natl Bur Stand 94:347–356. doi:10.6028/jres.094.034

Hauptmann A (2007) The archaeometallurgy of copper—evidence from Faynan, Jordan. Natural Science in Archaeology, Berlin/Heidelberg

Hauptmann A (2009) Lead isotope analysis and the origin of Sardinian metal objects. In: Lo Schiavo F, Muhly JD, Maddin R, Giumlia-Mair A (eds) Oxhide ingots in the Central Mediterranean. CNR - Istituto per gli Studi Micenei ed Egeo-Anatolici, Rome, p 499–514

Hauptmann A (2011) Slags from the Late Bronze Age metal workshops at Kition and Enkomi, Cyprus. In: Betancourt PP, Ferrence SC (eds) Metallurgy: understanding how learning why. Studies in honor of James D. Muhly, Philadelphia, pp 189–202

Hauptmann A, Maddin R, Prange M (2002) On the structure and composition of copper and tin ingots excavated from the shipwreck of Uluburun. B Am Sch Oriental Re 328:1–30. doi:10.2307/1357777

Hauptmann A, Schmitt-Strecker S, Levy TE, Begemann F (2015) On Early Bronze Age copper bar ingots from the Southern Levant. B Am Sch Oriental Re 373:1–24. doi:10.5615/bullamerschoorie.373.0001

Hull S, Fayek M, Mathien FJ, Shelley P, Durand KR (2008) A new approach to determining the geological provenance of turquoise artifacts using hydrogen and copper stable isotopes. J Archaeol Sci 35:1355–1369. doi:10.1016/j.jas.2007.10.001

Ikehata K, Notsu K, Hirata T (2011) Copper isotope characteristics of copper-rich minerals from Besshi-type Volganogenic massive sulfide deposits, Japan, determined using a femtosecond LA-MC-ICP-MS. Econ Geol 106:307–316. doi:10.2113/econgeo.106.2.307

Karageorghis V, Kassianidou V (1999) Metalworking and recycling in Late Bronze Age Cyprus—the evidence from Kition. Oxford J Archaeol 18:171–188. doi:10.1111/1468-0092.00078

Kassianidou V (2009) Oxhide ingots in Cyprus. In: Lo Schiavo F, Muhly JD, Maddin R, Giumlia-Mair A (eds) Oxhide ingots in the Central Mediterranean, Rome, pp 41–81

Klein S, Lahaye Y, Brey GP, von Kaenel HM (2002) Blei- und Kupferisotopenanalysen an Kupfermünzen der römischen Kaiserzeit. Berichte der Deutschen Mineralogischen Gesellschaft. Beiheft zum. Eur J Mineral 14:84

Klein S, Lahaye Y, Brey GP (2004) The early Roman imperial aes coinage II: tracing the copper sources by analysis of lead and copper isotopes—copper coins of Augustus and Tiberius. Archaeometry 46:469–480. doi:10.1111/j.1475-4754.2004.00168.x

Klein S, Rico C, Lahaye Y, von Kaenel HM, Domergue C, Brey GP (2007) Copper ingots from the western Mediterranean Sea: chemical characterisation and provenance studies through lead- and copper isotope analyses. J Roman Archaeol 20:203–221. doi:10.1017/S1047759400005377

Klein S, Domergue C, Lahaye Y, Brey GP, von Kaenel HM (2009) The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain). J Iber Geol 35:59–68

Klein S, Brey GP, Durali-Müller S, Lahaye Y (2010) Characterisation of the raw metal sources used for the production of copper and copper based objects with copper isotopes. Archaeol Anthropol Sci 2:45–56. doi:10.1007/s12520-010-0027-y

Knapp AB, Kassianidou V, Donnelly M (2001) Copper smelting in Late Bronze Age Cyprus—the excavations at Politiko Phorades. Near East Archaeol 64:204–210. doi:10.2307/3210830

Larson PB, Maher K, Ramos FC, Chang Z, Gaspar M, Meinert LD (2003) Copper isotope ratios in magmatic and hydrothermal ore-forming environments. Chem Geol 201:337–350. doi:10.1016/j.chemgeo.2003.08.006

Levy TE, Adams RB, Hauptmann A, Prange M, Schmitt-Strecker S, Najjar M (2002) Early Bronze Age metallurgy: a newly discovered copper manufactory in southern Jordan. Antiquity 76:425–437. doi:10.1017/S0003598X00090530

Lobo L, Degryse P, Shortland A, Eremin K, Vanhaecke F (2014) Copper and antimony isotopic analysis via multi-collector ICP-mass spectrometry for provenancing ancient glass. J Anal Atom Spectrom 29: 58–64. doi:10.1039/C3JA50303H

Lo Schivao F (2009) Oxhide ingots in Nuragic Sardinia. In: Lo Schiavo F, Muhly JD, Maddin R, Giumlia-Mair A (eds) Oxhide ingots in the Central Mediterranean. CNR - Istituto per gli Studi Micenei ed Egeo-Anatolici, Rome, p 225–410

Lo Schiavo F, Maddin R, Merkel JF, Muhly JD, Stech T (1990) Analisi Metallurgiche e Statistiche sui Lingotti di Rame della Sardegna/ Metallographic and Statistical Analyses of Copper Ingots from Sardinia, Ozieri

Maddin R (1989) The copper ingots from the Kas Shipwreck. In: Hauptmann A, Pernicka E, Wagner G (ed) Old Word archaeometallurgy—Archäometallurgie der Alten Welt. Proceedings of the International Symposium, Heidelberg 1987. Der Anschnitt Beiheft 7, Bochum, pp 99–105

Maréchal C, Albarède F (2002) Ion-exchange fractionation of copper and zinc isotopes. Geochim Cosmochim Acta 66:1499–1509. doi:10.1016/S0016-7037(01)00815-8

Maréchal CN, Telouk P, Albarede F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chem Geol 156:252–273. doi:10.1016/S0009-2541(98)00191-0

Markl G, Lahaye Y, Schwinn G (2006) Copper isotopes as monitors of redox processes in hydrothermal mineralization. Geochim Cosmochim Acta 70:4215–4228. doi:10.1016/j.gca.2006.06.1369

Mathur R, Titley S, Barra F, Brantley S, Wilson M, Phillips A, Munizaga F, Maksaev V, Vervoort J, Hart G (2009a) Exploration potential of Cu isotope fractionation in porphyry copper deposits. J Geochem Explor 102:1–6. doi:10.1016/j.gexplo.2008.09.004

Mathur R, Titley S, Hart G, Wilson M, Davignon M, Zlatos C (2009b) The history of the United States cent revealed through copper isotope fractionation. J Archaeol Sci 36:430–433. doi:10.1016/j.jas.2008.09.029

Mathur R, Wilson M, Parra ML (2014) Challenges of using copper isotope ratios to trace the origin of native copper artifacts: an example from the Keweenaw Peninsula. Ann Carnegie Museum 82:241–245. doi:10.2992/007.082.0304

Muhly JD (1991) The development of copper metallurgy in Late Bronze Age Cyprus. In: Gale NH (ed) Bronze Age trade in the Mediterranean. Studies in Mediterranean Archaeology 90, Jonsered, pp 180–197

Muhly JD, Maddin R, Wheeler TS (1980) The oxhide ingots from Enkomi and Mathiati and Late Bronze Age copper smelting in Cyprus. Report of the Department of Antiquities Cyprus 1980, Nicosia, pp 84–89

Muhly JD, Maddin R, Stech T (1988) Cyprus, Crete and Sardinia—copper oxhide ingots and the Bronze Age metals trade. Report of the Department of Antiquities Cyprus 1988, Nicosia, pp 281–298

Pulak C (2000) The copper and tin ingots from the Late Bronze Age shipwreck at Uluburun. In: Yalcin Ü (ed) Anatolian Metal I. Der Anschnitt Beiheft 13, Bochum, pp 137–157

Rothenberg B (1996–97) Researches in the Southern Arabah 1959–1990. Summary of thirty years of archaeo-metallurgical field work in the Timna Valley, the Wadi Amram and the Southern Arabah (Israel). Arx 2–3:5–42

Rothenberg B, Shaw CT (1990) The discovery of a copper mine and smelter from the end of the Early Bronze Age (EB IV) in the Timna valley. Institute for Archaeo-Metallurgical Studies Newsletter 15-16:1–8

Shields WR, Murphy TJ, Garner EL (1964) Absolute isotopic abundance ratio and the atomic weight of a reference sample of copper. J Res Natl Bur Stand 68A:589–592. doi:10.6028/jres.068A.056

Stos-Gale ZA (2011) "Biscuits with ears:" a search for the origin of the earliest oxhide ingots. In: Betancourt PP, Ferrence SC (eds) Metallurgy: understanding how learning why. Studies in honor of James D. Muhly, Philadelphia, pp 221–229

Stos-Gale ZA, Gale NH (2009) Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID). Archaeol Anthropol Sci 1:195–213. doi:10.1007/s12520-009-0011-6

Stos-Gale ZA, Maliotis G, Gale NH, Annetts N (1997) Lead isotope characteristics of the Cyprus copper ore deposits applied to provenance studies of copper oxhide ingots. Archaeometry 39:83–123. doi:10.1111/j.1475-4754.1997.tb00792.x

Tylecote RF (1982) The Late Bronze Age: copper and bronze metallurgy at Enkomi and Kition. In: Muhly JD, Maddin R, Karageorghis V (eds) Early metallurgy in Cyprus, 4000–500 B.C. Acta of the International Archaeological Symposium, Nicosia, pp 81–100

Willies L (1991) Ancient copper mining at Wadi Amram, Israel—an archaeological survey. Bulletin of the Peak District Mines Historical Society 11:109–138

Woodhead AP, Gale NH, Stos-Gale ZA (1999) An investigation into the fractionation of copper isotopes and its possible application to archaeometallurgy. In: Young SMM, Pollard AM, Budd P, Ixer RA (eds) Metals in antiquity. British Archaeological Reports International Series 792, Oxford, pp 134–139

Zhu XK, O'Nions RK, Guo Y, Belshaw NS, Rickard D (2000) Determination of natural Cu-isotope variation by plasma-source mass spectrometry: implications for use as geochemical tracers. Chem Geol 163:139–149. doi:10.1016/S0009-2541(99)00076-5

Zwicker U (1985) Investigations of samples from the metallurgical workshops at Kition. In: Karageorghis V, Demas M (eds) Excavations at Kition—V. The Pre-Phoenician levels I, Nicosia, pp 403–429

Zwicker U, Virdis P, Ceruti ML (1980) Investigations of copper ore, prehistoric copper slag and copper ingots from Sardinia. In: Craddock PT (ed) Scientific studies in early mining and extractive metallurgy, London, pp 135–163