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Iron in copper metallurgy at the dawn of the Iron Age: Insights on iron invention from a mining and smelting site in the Caucasus

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A B S T R A C T

Despite enormous interest in the origins of the iron, the world's quintessential industrial metal, the technological foundations of the invention and innovation of extractive iron metallurgy remain unclear. While fundamental aspects of geology and thermodynamics favor a model for the invention of iron by copper smelters, empirical archaeological evidence to support this model is lacking. Reanalysis of the smelting workshop at Kvemo Bolnisi, originally published as an iron smelting site in the 1960s and dated to the late 2nd millennium BC, offers insights by which copper smelters recognized and experimented with iron oxides. Chemical and microscopic analysis of slags and minerals samples via optical microscopy and SEM-EDS conclusively shows that metalworkers at the site were smelting copper rather than iron. However, our analyses, coupled with a reassessment of the excavation report, show that iron oxides were deliberately stockpiled and added to the furnace as a separate component of the charge to flux the silica-rich host rock. These discoveries make Kvemo Bolnisi arguably the earliest unequivocal example of the deliberate use iron oxide fluxes in copper metallurgy. The knowledge and behaviors reflected in the Kvemo Bolnisi copper smelting technology have important implications for theories about the invention of iron metallurgy by copper smelters.

1. Introduction

The technology and organization of metal economies—especially bronze and iron, play a major role in debates about the nature of the Bronze Age-Iron Age transition in the Eastern Mediterranean and the ancient Near East (Erb-Satullo, 2019). In recent decades, scholarship has moved away from seeing the iron weaponry as a causative factor in the Bronze Age collapse to seeing the spread of iron technology as a consequence of changing trade networks and the socio-political reorganization that emerged in the wake of the 12th century BC crisis. Nevertheless, many aspects of the technology and organization of metal production during this period remain unclear. This lack of evidence has obscured the technical choices and cognitive shifts underpinning iron invention as well as the economic conditions of early iron adoption. As result, proposed mechanics of innovation remain in the realm of untested hypothesis.

One major key issue that requires further investigation is the relationship between the bronze and iron industries, and whether iron metallurgy is best conceived as an independent industry emerging in competition to that of bronze, or whether it was a technology developed by bronzeworkers and emerging as an addition to an existing repertoire of metalworkers. There are several different dimensions or aspects of this "relationship" between bronze and iron. The hypothesis that iron smelting was first invented by copper smelters would be described as a possible technological aspect of this relationship, one pertaining to the smelting stage. This hypothesis remains attractive (contra Liss et al., 2020), but there is little direct evidence to support it (Erb-Satullo, 2019:566, 575; Merkel and Barrett, 2000). Other aspects include technical cross-fertilization in the metal-shaping stage (e.g. parallel forms and/or bimetallism), or co-location of secondary working activities, both of which *do* have support in the archaeometallurgical record (Erb-Satullo et al., 2020b).

A primary appeal of the hypothesis that iron was invented by copper metallurgists is that iron and copper co-occur geologically. Iron oxide-rich weathering features (gossans) often form above copper deposits, and many important copper minerals (e.g. chalcopyrite) also contain iron. In many cases, therefore, copper miners and smelters unavoidably encountered iron-bearing minerals and added them to the furnace. Iron-rich copper smelting slags containing fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) are ubiquitous. Even wüstite (FeO) and metallic iron phases appear on occasion, especially in the Late Bronze Age and Iron Age (Erb-Satullo et al., 2014:157; Hauptmann, 2020:407).

This geological association—which forms the foundation for the attractiveness of the "iron-invention-from-copper-smelting" hypothesis—also presents a major interpretive problem for the study of early iron invention. If iron-bearing minerals are ubiquitous, even unavoidable, in the process of copper ore mining and smelting, how can archaeologists document an invention process by which copper workers

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began to recognize iron oxides as a material capable of being smelted to produce a new metal? The mere *presence* of iron in copper smelting wastes is insufficient, as it is ubiquitous essentially from the very earliest stages of copper smelting. Even the presence of *metallic* iron in copper smelting slags is circumstantial: it shows that redox conditions and temperatures were high enough to reduce iron, but it is not sufficient to prove that metalworkers realized this and experimented with iron bearing minerals in their own right. Direct evidence for the invention of iron by copper smelters (e.g. unambiguous evidence for the smelting of useable iron at a copper smelting site) has not yet been identified.

An alternative approach focuses on intentionality—specifically on cases where we can identify that ancient metalworker recognized and intentionally used iron-bearing minerals in a metallurgical process. One such example is the use of iron oxides as a flux in copper smelting processes. The addition of iron oxides to a furnace or crucible charge lowers the melting temperature of a silica-rich materials present in the host rock (gangue) of the ore deposit, producing a fluid slag that separates more easily from the metal, improving yield. Identifying the beginning of intentional and directed use of iron oxides as fluxes in copper is not a trivial process. Because of the geological co-occurrence or iron oxides and copper ores, ores can be naturally "self-fluxing" if they contain suitable mixtures of minerals that melts at a lower temperature. In other words, the mined ore and associated host rock can produce a fluid slag without special intervention and without requiring nuanced understanding of iron oxides (or other fluxes) as a separate material.

Reviewing scholarship on fluxes in copper metallurgy, Hauptmann points out that early work tended to assume intentional fluxing without adequate consideration of the possibility that fluxing agents may have entered the furnace charge unintentionally along with the ore itself (2007:249–251; 2020:245). He suggests that deliberate fluxing of copper ores was probably an Iron Age phenomenon. Prior to this, metalworkers probably observed and appreciated the improved properties of self-fluxing ores and may have deliberately selected them. In terms of technical knowledge serving as precursors to the invention of iron smelting, however, these choices are cognitively different from the process of collecting, adding, and balancing iron oxides (or other fluxing minerals such as manganese) as a component of the furnace charge *separate* from the ore. Most importantly for the invention of iron, the latter represents an awareness of iron-bearing materials as a separate material and implies an element of active experimentation with proportions to achieve the desired effect. Evidence for experimentation with iron-bearing rocks and minerals at high temperatures offers fertile ground for invention, analogous to what is seen in early stages of the invention of copper metallurgy in the Balkans (Radivojević, 2015).

This discussion of intentionality, technical choices, and experimentation naturally requires detailed investigation of Late Bronze and Early Iron Age smelting sites, ideally both for iron and copper. Yet, iron smelting sites are extremely rare, as are Late Bronze and Early Iron Age (LBA-EIA) copper smelting sites outside of a few well-studied regions like the southern Levant, Cyprus, and the eastern Black Sea area (Erb-Satullo et al., 2017; Knapp and Kassianidou, 2008; Levy et al., 2012; Veldhuijzen and Rehren, 2007). Secondary workshops, where bronze and/or iron were shaped through casting and/or forging into objects, are better documented now (Erb-Satullo et al., 2020b; Lehner, 2017; Veldhuijzen, 2009; Workman et al., 2020; Yahalom-Mack et al., 2014), as they tend to be found within settlement sites. Concerningly, re-consideration of older literature has sometimes revealed cases of mis-dating (Ben-Yosef et al., 2010) or mis-identification of production residues (Erb-Satullo et al., 2014; Pigott, 2003). Careful scrutiny of production remains is clearly necessary to produce a solid foundation for broader assessments of metal economies and technological innovation.

With rich ore deposits, abundant remains of mining and metal production, and huge numbers of metal objects, the South Caucasus is an ideal place to establish this foundation. Since at least the 1950s, local scholars in the South Caucasus have systematically investigated traces of LBA-EIA metal production (Gzelishvili, 1964). Until recently, however, the region has played a very limited role in wider discussions about bronze and iron metallurgy in the period between 1500-500 BC. Research carried out over the last 15 years has shown the advantages of reassessing and extending earlier work. Most notably, an extensive Late Bronze and Early Iron Age smelting landscape in western Georgia (ancient Colchis, on the Black Sea littoral, see Fig. 1) was shown conclusively to relate to copper smelting, not iron smelting as had originally been proposed (Erb-Satullo et al., 2014; Khakhutaishvili, 2009 [1987]). A comprehensive program of radiocarbon dating, landscape survey, and laboratory analysis of production debris helped to reconstruct the technology and organization of a bronze economy immediately preceding and contemporary with the earliest appearance of iron in the region (Erb-Satullo, 2022; Erb-Satullo et al. 2017, 2018).

Beyond Colchis, no other areas of the South Caucasus (and indeed few other places in the entire Near East) have as rich a record of Late 2nd/early 1st millennium BC smelting sites. It is still unclear whether this is due to patterns of archaeological research, modern land-use, or a genuine difference in the scale of ancient production. At the very least, it seems likely that these rich copper smelting industries extend some distance along the southern Black Sea coast, into modern-day Turkey, but these smelting landscapes are largely unexplored (Lutz et al., 1994).

In this context, the few cases of possible Late Bronze and Early Iron Age smelting activity outside Colchis take on particular importance. One such site, Kvemo Bolnisi (Fig. 1), was first explored in the 1950s, and identified as an iron smelting site, in part due to a large pile of hematite (Fe_2O_3) minerals found in the workshop (Gzelishvili, 1964:34). However, mention of copper ore deposits nearby the smelting workshop, as well as the wider context of misidentification of LBA-EIA copper smelting debris, suggested that this identification merits reassessment. Samples of slag as well as potential ore and flux minerals were analyzed via optical microscopy and SEM-EDS. The analysis aimed to confirm the type of metal produced at the site and the stage of production (smelting, refining, casting), and to compare the technology of production with contemporary metallurgical sites elsewhere in the Caucasus, with particular attention to the role of hematite in the metallurgical process.

2. Kvemo Bolnisi in its Late Bronze and early Iron Age context

The site of Kvemo Bolnisi in southern Georgia has long been cited as an iron smelting site (Inanishvili, 2007:7). Excavated in 1958–1959, it was one of the first smelting workshops ever formally excavated in Georgia, and indeed in the Caucasus as a whole (Gzelishvili, 1964:31–38). Gzelishvili's excavation report dates occupation of the site to the античный "Antique" (i.e. Classical Era), and the предантичный "pre-Antique," periods, with the latter given an absolute dates range of the 13th-7th century BC, based on ceramic comparisons. Maps and descriptions suggest that the site was larger in its earlier phase, with structures on the summit, a settlement on the slopes, and a cemetery in the saddle along alongside a modern trackway (Fig. 2). By contrast, Classical-era structures are limited to the summit, while the area of the LBA-EIA settlement was used as a cemetery in the Classical Era.

Gzelishvili's report provides details about the workshop's spatial layout, contents, and chronology. It consists of a furnace set against a wall built against the hillslope, a pile of "several hundred kilograms" of hematite (the iron oxide Fe_2O_3) preserved on the floor (Fig. 3), and a slag heap (Gzelishvili, 1964:33). Gzelishvili dates the workshop to early phase of the site in the late 2nd millennium BC based the presence of sherds in the slag heap with strong parallels to other sites of this period. One of the sherds he mentions is a fragment of a heavily ornamented, very distinctive type of goblet which current chronologies still assign to the late 2nd millennium BC (Akhvlediani, 2001:Fig. 1; Gzelishvili, 1964:33, Pl.5, nos. 8 and 10). Intriguingly, this type of goblet appears in a grave from not far from Kvemo Bolnisi (Beshtasheni Grave 13, dated to the 14th-12th centuries BC) which also contains one of the earliest iron objects known from the Caucasus (Akhvlediani, 2001). A late 2nd millennium date for this ceramic is also provisionally supported by finds

Fig. 1. Map of the South Caucasus showing the location of Kvemo Bolnisi and Colchis, a region with the well-documented LBA-EIA copper smelting landscapes discussed in the text.

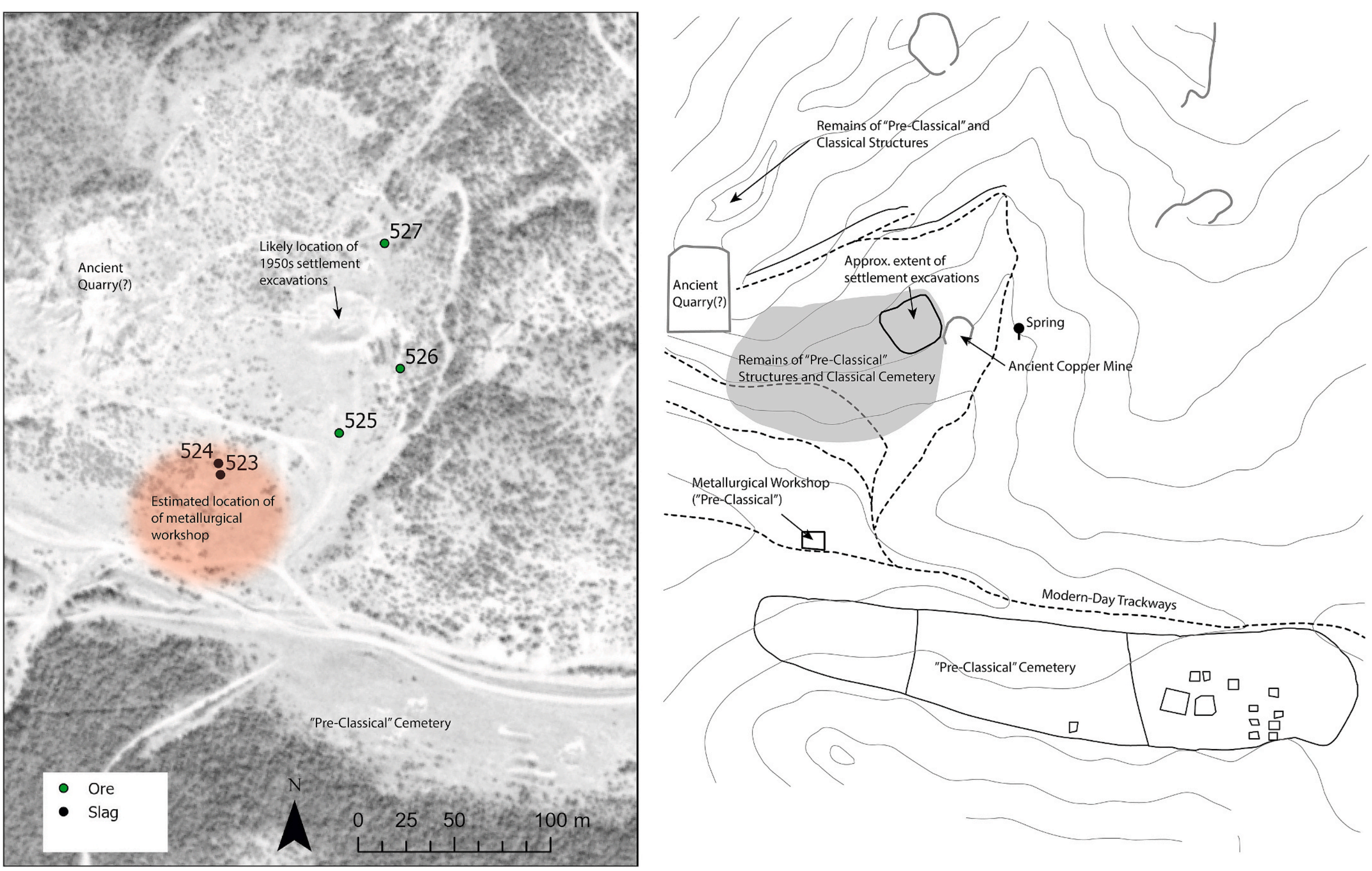

Fig. 2. Maps of the Kvemo Bolnisi showing a 1975 Hexagon Image (Mission 1210-3, frame 57) (left), and a map redrawn from that of Gzelishvili (1964:32) (right). The scale bar in the original Gzelishvili map is clearly incorrect, so it is omitted. GPS points correspond to the locations of collected copper-bearing minerals and slag (see supplementary dataset S2). The hematite sample was collected near waypoint 523.

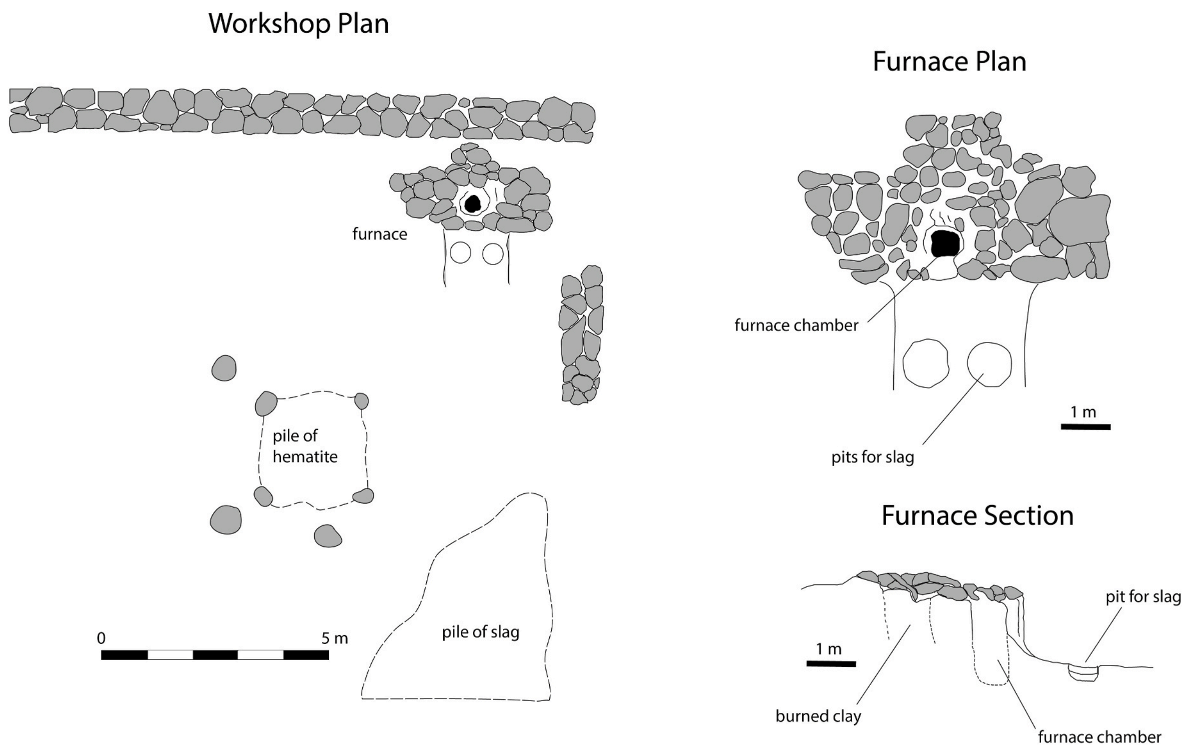

Fig. 3. Plan of metal workshop at Kvemo Bolnisi. Redrawn after Gzelishvili (1964:34).

from Project ARKK excavations at nearby Dmanisis Gora, co-directed by the lead author (NES) and Dimitri Jachvliani. Based on the available evidence, a late 2nd millennium BC date for the Kvemo Bolnisi metallurgical workshop appears plausible.

The furnace itself appears to have been built in such a way to enable tapping, as two pits for slags were noted near the open side of the furnace. Intriguingly, the excavation report describes the finds of a small amount of malachite in the workshop, but the report states that the excavators were "unable to establish the meaning" of its presence (Gzelishvili, 1964:33). Given the finds of copper ore, it remains unclear why the identification as an iron smelting workshop was favored. As the 1964 publication does not include chemical or microscopic analyses of the slags, the basis for this interpretation seems to be the substantial quantity of hematite in the workshop.

Chemical analyses of alleged "pre-Antique" iron slags from "Bolnisi" reported in Ivanishvili (2007:12–14) are possibly from the Kvemo Bolnisi LBA-EIA site, but do not report copper content and provide no microscope images, so it is not possible to confirm their identification as iron slags. Analyses of an iron bloom from Bolnisi with heterogeneous carburization is also described by Ivanishvili, though the date is not specified and its association with Kvemo Bolnisi LBA-EIA site is even less certain than the slag analyses, as Gzelishvili makes no mention of a bloom in his report.

In sum, careful reading of Gzelishvili's descriptions and available analytical data indicate a considerable degree of uncertainty about the identification of the metal produced at the Kvemo Bolnisi workshop. Yet, as one of the few known LBA-EIA metallurgical sites in the Caucasus outside Colchis, and given presence of both iron and copper ores in the immediate vicinity (Erb-Satullo, 2018; Nazarov, 1966), it remains a significant site. In light of other instances of mis-identification (Erb-Satullo et al., 2014), a reassessment was clearly merited.

The site was relocated on survey by Project ARKK through comparison of hand-drawn Soviet-era maps with Google Earth imagery. Slag samples were recovered from the same area of the site where the smelting workshop was located (Fig. 2), though no structural traces of the furnace or workshop itself remained. Ceramics found on the surface of the site are broadly consistent with the dating of the site in earlier publications. These broadly fell into the category of grey wares with some color variations from black to buff. Decorations and other features observed included pattern burnishing, comb stamping, strap-handles, carinated bowls, all of which are consistent with Late Bronze and Iron Age pottery. The ceramics found at the site during the re-location of the site therefore give no reason to revise the original chronological designations to any significant degree.

3. Materials and methods

Slag and mineral samples were collected from the surface of the site in locations close to the metallurgical workshop and the copper mine reported in the original Gzelishvili publication (Fig. 2). The limitations of hand-drawn maps and the current condition of the site made it impossible to pinpoint the exact locations of features mapped in the late 1950s, but we are confident that the sample findspots correspond roughly to the locations described in the earlier excavations.

All slag samples and a fragment of black sparkly mineral (suspected on point of collection to be hematite) were found around waypoints 523 and 524. All copper-bearing mineral and rocks were collected from waypoint 526, which corresponds very closely with the ancient copper mine described by Gzelishvili, except OR01, which derives from waypoint 527, and OR16, which derives from waypoint 525.

Macroscopically, the slag samples were black with spots of orange, the latter likely due to the corrosion of iron-bearing phases (Fig. 4). In fracture, it was often possible to see whitish inclusions (suspected and later determined to be largely unreacted quartz gangue). Copper-green corrosion was rare. Some slags showed evidence of flow in the form of crinkly surface textures, but they differ from the morphology of traditional tap slags with obvious signs of pooling, or fused masses of rivulets (cf. Erb-Satullo et al., 2020a:Fig. 4). Notably lacking among the samples collected is the clear macroscopic distinction in slag types seen at contemporary metallurgical sites in Colchis.

Samples were mounted in resin, ground and polished using standard procedures. Reflected light polarising optical microscopy was conducted

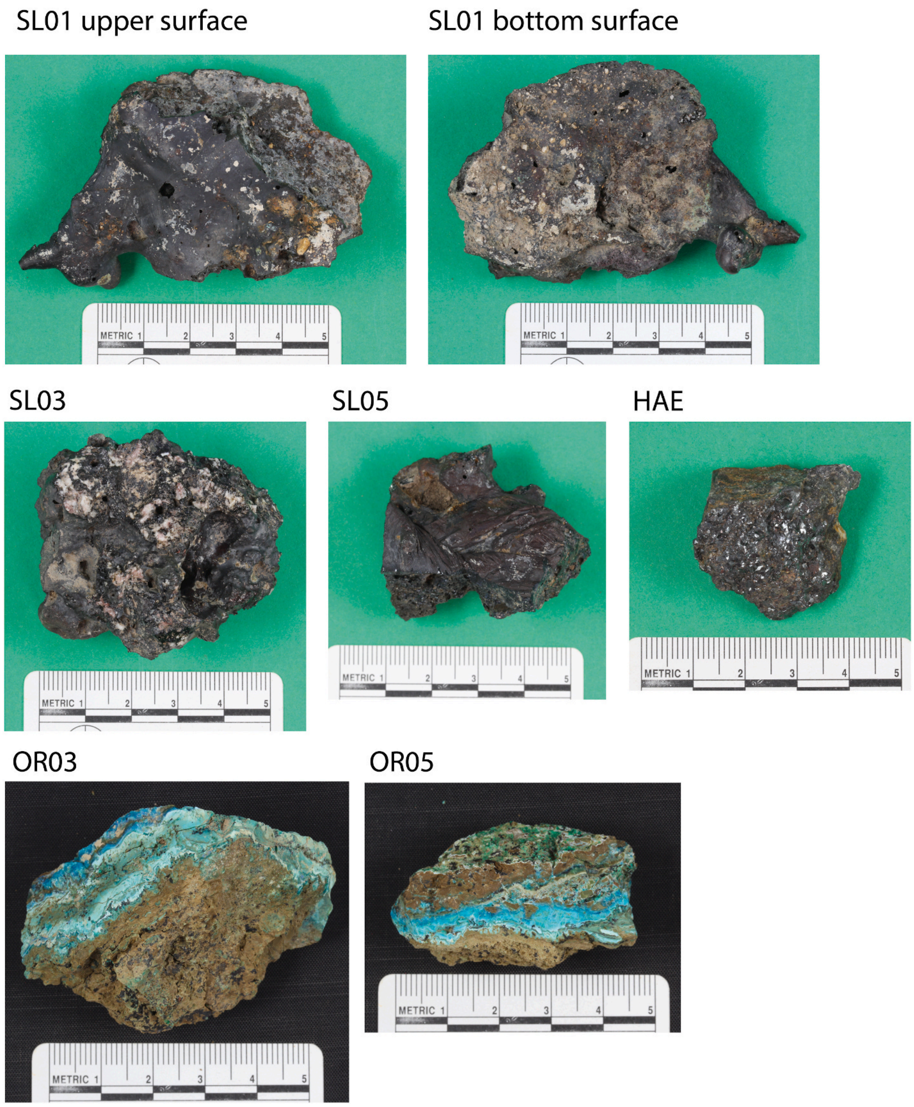

Fig. 4. Images of selected slag and mineral samples.

with a Zeiss Axiolab 5 polarising microscope fitted with a Axiocam 208c camera. Scanning electron microscopy was carried out with a Tescan Vega 3 Electron Microscope with an Oxford Instruments Xplore 15 EDS detector. In order assess the bulk chemical composition of the melted slag, a minimum of 4 area analyses were undertaken avoiding unreacted and partially reacted inclusions, gas bubbles, and obviously corroded zones. Area analyses were averaged together to account for heterogeneity in slag melts and furnace conditions typical of pre-modern metallurgy. Spot analyses of individual phases, including analysis of atomic ratios where appropriate, was used to confirm identifications from the optical microscopy, and to distinguish between optically similar phases. Some ambiguities in phase identifications remain—for instance the boundaries between fine-grained, amorphous chrysocholla and cupriferous clays, and between copper chloride hydroxide polymorphs like atacamite and paratacamite.

Instrument accuracy and precision was monitored by repeat analysis of fayalite (MAC ref. no. 1-026-3-0025) and fused basalt glass (USGS BHVO-2G) reference standards (supplementary dataset S1). Accuracy and precision were very good: almost always better than 5 % relative error and mostly better than 3 % for elements present above 0.3 wt%. Data are reported in the main paper as normalized values, but non normalized values are included in the supplementary information. The beam measurement routine in Oxford Instruments AZtec software was run to monitor beam current indirectly and ensure reliable non-normalized results. In general, analytical totals were close to 100 % for most slag analyses, but lower for the ore/gangue/flux analyses due to sample porosity, the presence of light elements (e.g. hydrogen) not easily detectable via SEM-EDS, and/or the presence of elements in compounds that differ from standard oxide reporting conventions.

As slags and ore samples are often heterogeneous, an estimate of average bulk composition for the melt was obtained by averaging a minimum of 4 separate area analyses. Care was taken to ensure that each area analysis was much larger than the microstructural variation within it. In cases of possible ore and flux samples with multiple distinct zones (e.g. a copper-mineral rich vein within a silicate host rock), these areas were analyzed separately as “ore”, “flux”, and “gangue” areas. Individual area analyses and the calculations of averages are provided in supplementary dataset S1. In addition, more than 1400 optical photomicrographs, SEM images, and EDS spectra have been published in a companion dataset on the Project ARKK Dataverse, hosted on the Harvard Dataverse repository (Erb-Satullo and Klymchuk, 2025).

4. Analytical results

4.1. Possible ore and flux samples

Optical microscopy and SEM analysis demonstrated that the black sparkly rock fragment collected from near the slags was definitely hematite, disseminated within a matrix consisting mostly of quartz and clay minerals. The hematite forms thin tabular crystals, which gives it a highly noticeable and distinctive sparkly macroscopic appearance, something that would likely have made it readily identifiable to ancient metalworkers (Fig. 5). SEM-EDS area analyses detected no copper, either in the hematite or in silicate matrix. In terms of chemical composition (Table 1), the dominance of quartz means that the "gangue" matrix is mostly silica (>90 wt% SiO_2), with smaller quantities of Mg, Al, and Fe. The areas dominated by hematite are almost entirely iron oxide (>75 wt % FeO), with the balance mostly silica, due to the presence of quartz and low levels of clay minerals infilling between the tabular hematite crystals.

Copper-bearing mineral samples consist of a range of copper carbonate hydroxides and silicates disseminated within a low-iron, high silica gangue consisting mostly of quartz and orthoclase feldspar (Fig. 6, supplementary dataset S2). Given varieties in crystal habit, coloration, and the presence of many polymorphs of similar chemical composition, and the presence of very fine, often microcrystalline intergrowths due to weathering and recrystallization, some mineral identifications retain ambiguity, as noted below. Green malachite and blue azurite are a major presence, as are greenish to greenish brown chrysocolla, a hydrated copper alumino-silicate. SEM-EDS spot analyses of the copper-aluminosilicates revealed varying ratios of copper to aluminum in these samples. Low-copper variants are effectively part of the gangue and are probably cupriferous clays. Rarer are copper chlorides (probably atacamite or paratacamite), which were identified in a few samples. Manganese-bearing minerals were also a common accessory mineral, frequently forming botryoidal structures that are likely lamellar intergrowths of a manganese oxide (e.g. pyrolusite) and chrysocolla. Baryte ($BaSO_4$) was identified in small amounts. By contrast iron-bearing

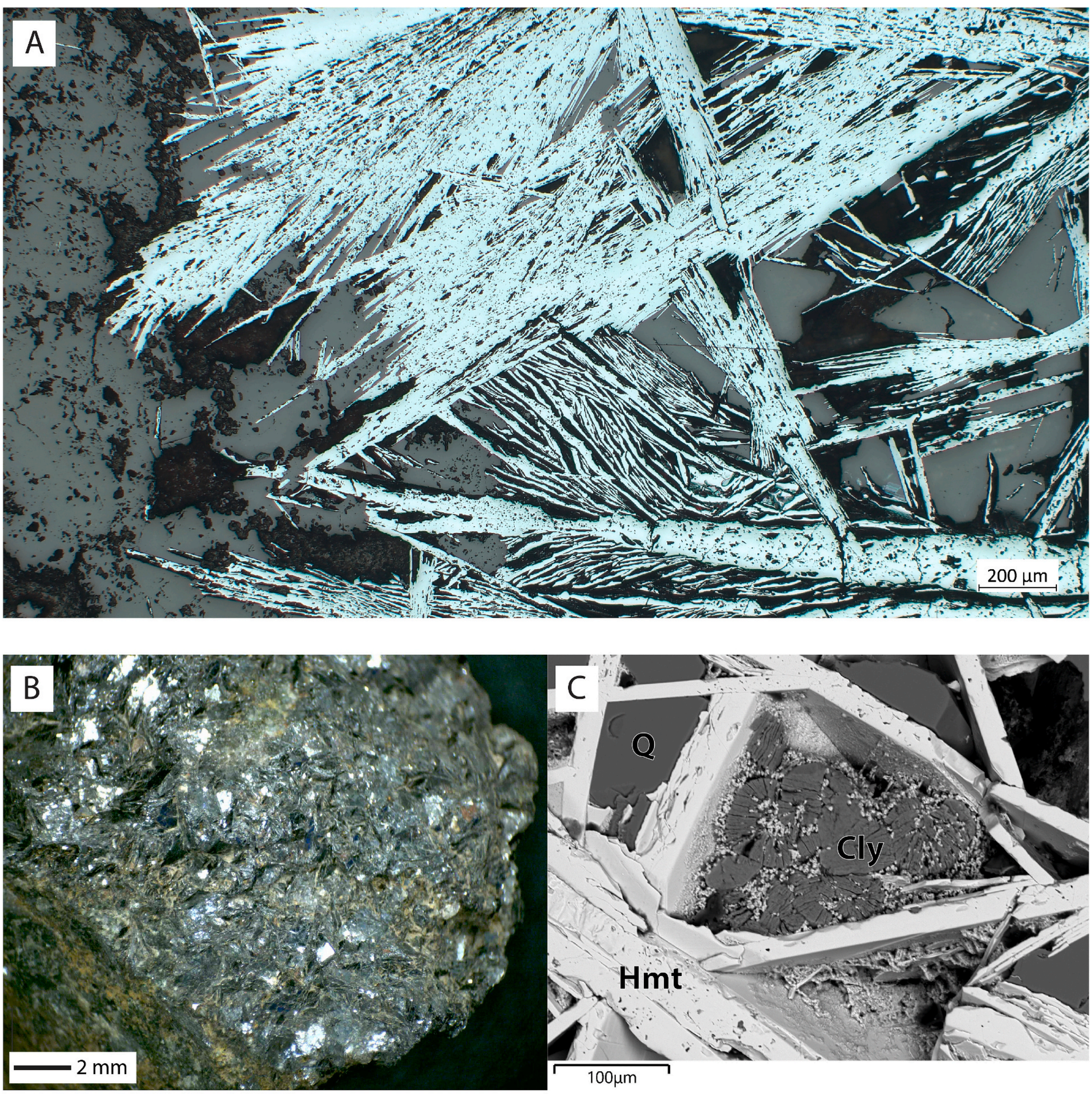

Fig. 5. Optical photomicrograph in plane-polarized light (A), low power optical microscope image (B) and SEM backscatter image (C) of the hematite sample (HAE) found near the workshop. Platy hematite crystals (Hmt) are contained with a matrix consisting of quartz (Q), felspar, and clay minerals (Cly).

Table 1
Bulk compositional analyses of potential ore and flux samples. Values are normalized and are the average of separate analyses of at least four different areas the sample. Detection limit was determined conservatively to be 0.15 %. See supplementary dataset S1 for complete raw data. With respect to area analyzed these heterogeneous samples, "ore" refers to the analysis of copper-mineral rich areas that could be used as copper ore, "gangue" refers to the host rock (where present) and/or parts of the mineralization that are very low in copper. The iron oxide rich parts of the hematite sample (HAE) are referred to as "flux" rather than ore.

Sample	Part of Sample Analyzed	Na2O	MgO	Al2O3	SiO2	P2O5	SO2	Cl	K2O	CaO	TiO2	MnO	FeO	CuO	BaO
OR01	ore	bdl	0.6	9.4	35.4	0.7	0.3	bdl	1.8	0.3	0.2	bdl	24.2	27.2	bdl
OR02	ore	bdl	1.2	15.4	44.3	bdl	0.3	bdl	1.3	1.4	bdl	0.4	1.5	34.3	bdl
OR03	ore	bdl	0.9	15.1	37.9	bdl	0.5	bdl	0.7	1.3	bdl	0.3	0.8	42.5	bdl
OR04	ore	bdl	0.7	23.8	45.2	0.2	0.5	bdl	0.4	2.3	bdl	1.1	0.3	25.5	bdl
OR05	ore	bdl	0.8	23.3	40.8	0.2	0.9	bdl	0.5	2.0	bdl	bdl	0.3	31.2	bdl
OR06	ore	bdl	0.5	7.8	15.3	bdl	0.2	0.8	0.2	0.6	bdl	2.9	0.3	71.4	bdl
OR07	ore	bdl	0.7	23.9	38.2	0.2	0.9	bdl	0.4	1.9	bdl	bdl	0.3	33.4	bdl
OR08	ore	bdl	1.3	19.1	48.9	bdl	0.3	bdl	1.5	2.3	bdl	0.3	1.2	25.1	bdl
OR09	ore	bdl	0.8	24.1	42.6	0.2	0.5	bdl	0.6	2.8	bdl	0.8	0.2	27.5	bdl
OR10	ore	bdl	1.3	10.7	43.5	bdl	bdl	bdl	1.2	1.3	bdl	0.6	1.4	40.0	bdl
OR11	ore	bdl	0.7	20.2	42.6	bdl	bdl	bdl	1.2	0.9	bdl	1.0	2.0	31.4	bdl
OR12	ore	bdl	0.5	26.1	34.1	0.2	0.6	2.6	0.3	1.5	bdl	bdl	bdl	34.1	bdl
OR13	ore	bdl	1.7	12.4	48.6	bdl	bdl	bdl	1.9	1.2	0.2	0.9	3.2	29.9	bdl
OR14	ore	bdl	0.7	22.8	42.8	0.2	0.5	bdl	0.5	2.3	bdl	1.3	0.5	28.4	bdl
HAE	flux	bdl	0.2	0.7	23.4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	75.7	bdl	bdl
OR02	gangue	bdl	0.2	15.1	68.5	bdl	0.7	bdl	5.8	0.4	bdl	bdl	4.2	3.8	1.2
OR04	gangue	bdl	0.7	21.3	62.7	0.2	bdl	bdl	1.6	1.2	0.4	bdl	5.8	6.0	bdl
OR06	gangue	bdl	0.2	12.7	71.7	bdl	bdl	bdl	7.1	0.2	0.2	bdl	4.4	3.6	bdl
OR08	gangue	bdl	1.5	29.4	51.5	bdl	0.5	bdl	2.8	2.4	bdl	0.2	2.0	8.9	0.8
OR09	gangue	bdl	1.8	29.8	51.3	bdl	bdl	bdl	3.9	1.6	bdl	bdl	2.5	9.1	bdl
OR15	gangue	bdl	0.2	15.1	68.0	bdl	bdl	bdl	5.6	0.4	0.4	bdl	3.1	7.1	bdl
OR16	gangue	0.4	0.8	17.9	67.5	0.2	0.3	bdl	2.7	0.9	0.4	bdl	4.0	4.8	bdl
HAE	gangue	bdl	2.0	1.9	93.1	bdl	bdl	bdl	bdl	0.2	bdl	bdl	2.8	bdl	bdl

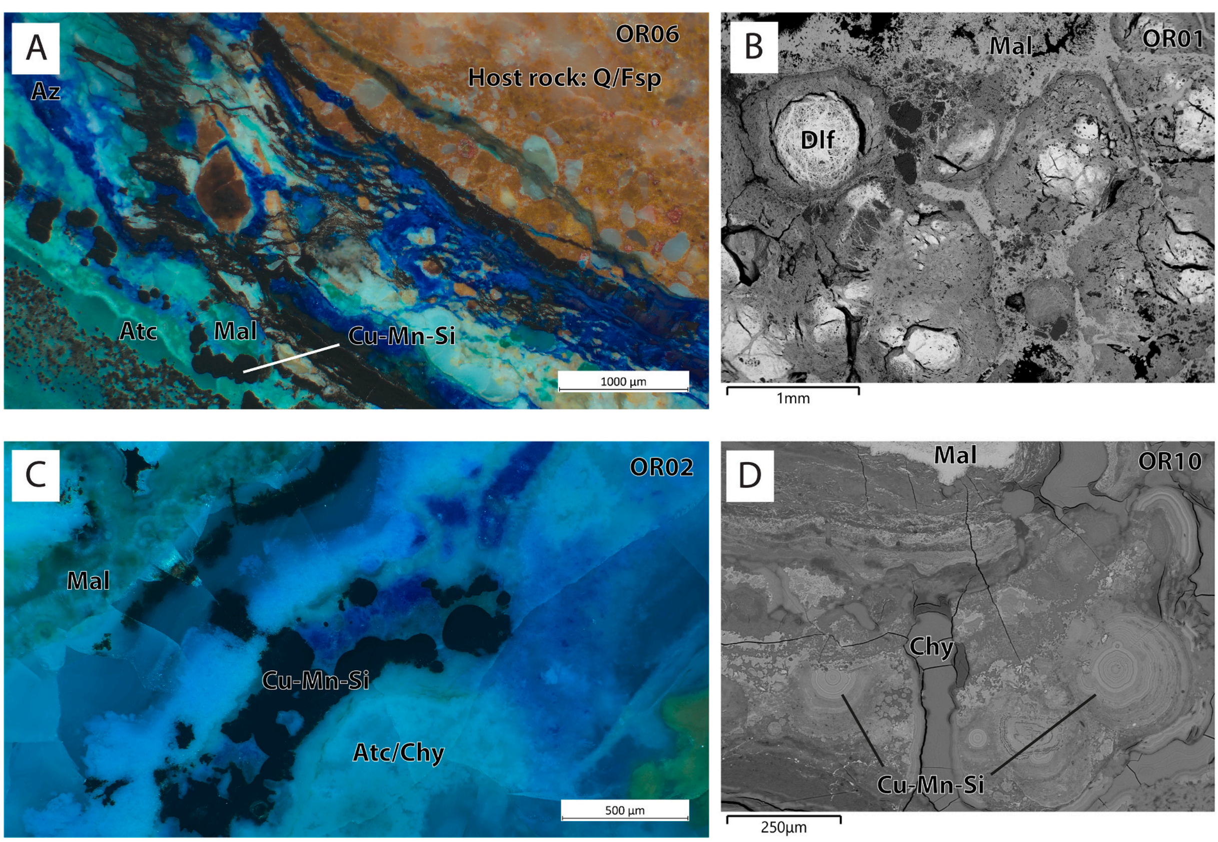

Fig. 6. Polarizing optical microscope (A and C; XPL) and SEM (B and D) images of copper mineral samples. Minerals are often finely intergrown micro/crypto crystalline textures difficult to resolve via optical and SEM-EDS analysis. Suspected intergrowths are indicated by "/". Key: Az-azurite; Atc-copper chloride hydroxide, probably atacamite; Mal-malachite; Chy-chrysocolla; Dlf-delafossite; Cu-Mn-Si-lamellar intergrowths of copper, manganese, aluminum and silica in a botryoidal structure, probably chrysocolla with manganese oxide.

minerals are either absent or only a very minor component of these samples, enough to produce an orange staining on the silicate gangue but generally <8 wt% FeO in area analyses of the gangue matrix and even less in the copper-rich areas (Table 1). The one exception is the OR01, an unusual, spatially isolated sample collected from WP527 (Fig. 2). This collection location is farther from the smelting workshop than most other mineral samples, which come from an area near the alleged ancient copper mine identified in the Soviet-era fieldwork. This sample contained 24.2 wt% FeO, and consisted spherical and rounded masses of iron- and copper-iron oxides (mostly likely delafossite) (Fig. 6B). Evidence from partially-reacted ore trapped within the slags, however, suggests that the ancient smelting process used copper ores with much less iron (see section 4.2). No copper sulfide or iron sulfide phases were identified in these samples, indicating a well-developed oxidized zone in this deposit.

In term of bulk chemistry of these geological samples (Table 1), the macro-heterogeneity of most samples, with veins of copper-rich minerals running through the host rock, merited separate area analyses of areas rich in copper minerals ("ore") and those corresponding to the host rock ("gangue"). As ore and gangue were sometimes finely intergrown, and copper-bearing aluminosilicates with widely varying copper content were often major components of these samples, the division was not always sharp. Generally, however, copper-content of "gangue" areas were mostly 3–10 wt% CuO, 50–70 % SiO_2, and 10–30 wt% Al_2O_3, while "ore" areas were typically 25–45 wt% CuO and 30–50 wt% SiO_2, and 7–26 wt% Al_2O_3.

4.2. Slag mineralogy and microstructure

Optical and scanning electron microscopy identified numerous silicate, oxide, sulfide, and metallic phases within the slag samples, as well as partially melted and/or incompletely homogenized inclusions that formed part of the original furnace charge (Supplementary Dataset S2). Identification of these phases provides crucial information about the type of metal produced, the stage of production, the composition of the furnace charge (including the types of ores used) and other aspects about the metallurgical processes (e.g. redox conditions in the furnace).

Freshly-formed silicate neophases consist primarily of fayalite (sometimes with low levels of magnesium) and a glassy phase, while many samples contained a barium-potassium feldspar (part of the orthoclase-celsian solid solution series). The glassy phase is often dominant, while the fayalite crystals often take the form of fine-grained laths. Iron oxides are present in a number of samples, but generally they are a minor component. Both of these features are indicative of an iron content on the low end of what of the range for typical copper smelting slags.

The presence of copper metal phases in every sample analyzed makes the slags' association with copper metallurgy clear. In many samples metal prills were numerous, with sizes ranges from <10 to ~1400 μm. Copper and copper-iron sulfides of various types were also identified, including chalcopyrite/bornite, covellite, and chalcocite/digenite, though the more copper-enriched, low-iron forms predominated. Iron sulfides lacking significant copper content (e.g. pyrrhotite) were noted in a small number of instances, but are generally rare in the assemblage.

With respect to indicators of reducing conditions, magnetite is more common than wüstite, but as noted above, free iron oxides are a relatively minor component of slag mineralogy, except where they appear as part partially reacted inclusions. Iron metal phases were identified and confirmed by SEM-EDS in five samples, with two more samples containing probable iron phases identified by optical microscopy alone. Iron metal appears as discrete phases within copper metal prills, and as small particles or aggregates (Fig. 7). Occasional particles of metallic iron are not unusual in Late Bronze Age and Early Iron Age slags in the Near East, when furnaces were capable of operating at sufficiently reducing conditions (Erb-Satullo et al., 2014:157; Hauptmann, 2007:207). Morphology and micro-contextual associations of metallic phases are essential for interpreting their potential relevance to iron smelting. In most Late Bronze Age copper smelting slags, iron phases are small, isolated or intergrown to such an extent with copper that it would have been impossible to notice them and extract them from the copper metal in a way that would render them workable. The metallic iron in the Kvemo Bolnisi slags largely aligns with this pattern, though SL06 is somewhat notable in that it has an area with a cluster of reduced iron particles without much associated copper metal (Fig. 7B).

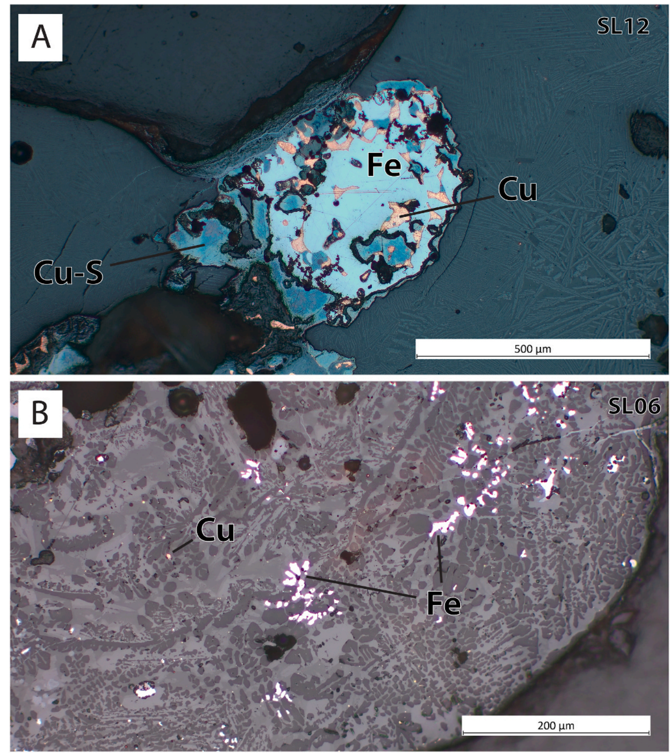

Fig. 7. Optical microscopy images of metallic iron phases in slags.

A number of the slag contain partially reacted chunks of ore (Fig. 8). These consist of unreacted and partially reacted quartz grains with clusters of copper prills disseminated along what, in the original ore, were likely veins of copper-rich minerals that have now been reduced to metal. Iron oxides, if present in the ore, appear to be a relatively minor phase, as the gangue in these partially reacted inclusions is more silica-rich than the slag itself. These observations suggest that Kvemo Bolnisi copper smelters used silica-rich, iron-poor ores. The lack of sulfide phases in these ore-gangue clusters further suggests that the ores are primarily oxidic in origin, and that sulfide phases in the slag are essentially detrital. In all these respects, the chunks of partially reacted gangue in the slags mirror the mineralogy of the copper-bearing minerals and the host rock in most of the geological samples *except* OR01, the sample dominated by delafossite, a copper-iron oxide. Apparently, OR01 was not a type of mineralization smelted by the ancient metalworkers at the site, possibly because it is a minor component of the ore deposit. (Only one such sample was collected).

The source of the iron in the slags, implied by the pile of hematite mentioned in original excavation reports and the hematite fragment analyzed by the present study, is conclusively determined by an inclusion of partially reacted hematite and quartz identified within the copper smelting slag SL02 (Fig. 9). The microstructure of the chunk grades from un-reduced hematite to magnetite and/or wüstite towards the interface with the slag. No copper-bearing phases are present within this partially reacted chunk, but the slag it is embedded in contains numerous small copper prills. Similar microstructures, consisting of iron oxides and silica in partially reacted rock fragments without abundant associated copper metal phases, were noted in SL03-2. In both samples, the partially reacted iron oxides preserve the relict platy habit of the hematite crystals that match the mineral sample HAE (compare Figs. 5 and 9A). Taken together with the other evidence, this suggests very strongly that the hematite-quartz rock fragments did not derive from the ore, but from a flux component intentionally mixed in with the ore charge.

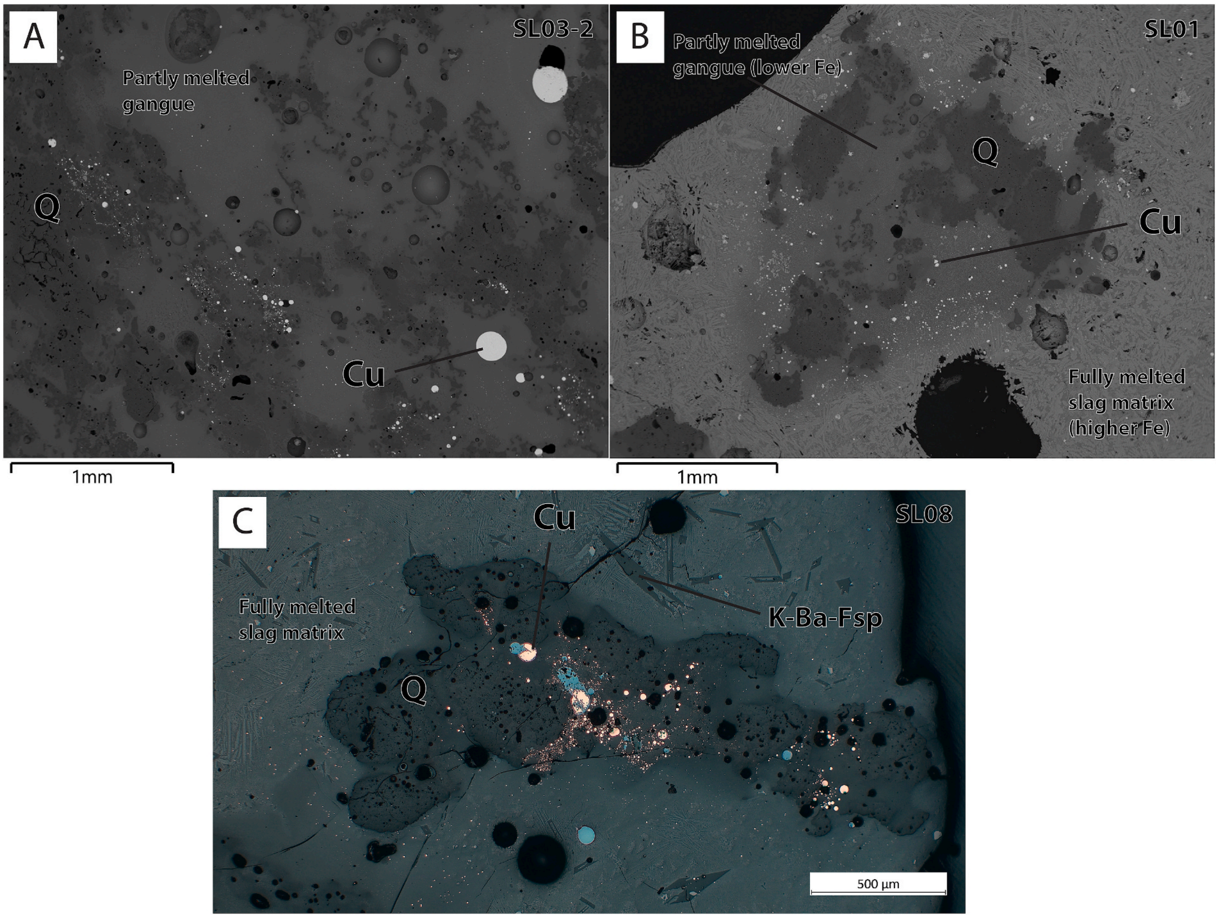

Fig. 8. SEM (A, B) and optical microscope (C) images of partially reacted copper ore. The association between silica-enriched, partially melted gangue and copper metal prills, and the absence of directly associated iron oxides, is clear indication of the use of a silica-rich, iron-poor ore. Abbreviations: Cu – copper metal, K-Ba-Fsp – potassium-barium feldspar, Q – quartz.

Despite their geographic proximity and similar date, it is worth noting here the major differences between the Kvemo Bolnisi slags and those of Colchis (western Georgia) (Erb-Satullo et al. 2014, 2015). Specifically, Colchian slags generally contain much higher frequencies of sulfides and free iron oxides. Fayalite phases are more developed on average in Colchian slags, forming larger crystals and taking up a higher volume fraction. Conversely, Kvemo Bolnisi slags on the whole have a more developed glassy phase. By contrast, at Kvemo Bolnisi, barium-containing feldspars were encountered in a larger fraction of samples. Finally, copper metal prills were far more common in the Kvemo Bolnisi assemblage than they are in the Colchian slags, in which they are rare. The implications of these differences for comparative interpretations of technological processes will be discussed further below.

4.3. *Slag chemistry*

SEM-EDS analyses of slags targeted areas of the sample that were fully molten, avoiding partially reacted inclusions, as well as gas bubbles, cracks, and corroded/weathered areas. The chemistry of the slag samples was for the most part, quite consistent (Table 2). Slag samples contained between 9 and 11 % Al_2O_3, 38–50 % SiO_2, and 32–41 % FeO, with smaller amounts of CaO (2–5 %) and K_2O (1.4–2 %). Copper content was mostly between 0.5 and 1.7 wt% CuO. Barium, sulfur, and magnesium content, however, divide the analyzed samples into two groups (Fig. 10). The larger group is distinguished by high barium content (4–6 wt% BaO) as well as low levels of sulfur (0.3–0.6 wt% SO_2) and magnesium (0.5–0.7 wt% MgO). The second group consisting of SL02, SL03-1, SL03-2, and SL07, contains far less barium (maximum 0.3 wt%), slightly higher magnesium content between 1 and 1.6 % MgO, and almost no detectable sulfur (average < 0.15 wt%). With respect to other elements, however, these two groups are largely similar. In combination with the microstructural evidence from the slags, and the analysis of the ore samples, it seems likely that the chemical differences in the two slag groups relate to the composition of the ore and/or gangue; the barium content is too high for clay furnace lining or fuel ash to have been the main contributor. Baryte ($BaSO_4$) was identified in several copper mineral samples, though the barium content was lower than the higher barium slag group. While the chemistry of the slags is not an exact quantitative match with the geological copper mineral samples investigated, they are close enough to suggest—considering spatial variation in the mineralogy of an ore body—that the Kvemo Bolnisi copper smelting process primarily used a silica-rich oxidic ore from this deposit.

Silicon and aluminum in the slag may derive in part from clay furnace lining, but given the gangue composition and the presence of copper-aluminosilicates in the ore body it is likely that the ore/gangue charge were contributed as well. As with microstructure and mineralogy, slag chemistry also indicated clearly that iron content (~30–40 wt% FeO), which is much higher than the possible copper ore samples, did not derive from the ores.

In order to visualize contributions of various additives to the furnace charge, slag compositions were plotted alongside the compositions of copper-rich mineral areas (i.e. potential ore), host rock (possible gangue), hematite, and hematite host rock (i.e. hematite gangue) were plotted on a ternary SiO_2-Al_2O_3-FeO(+MnO) phase diagram (Fig. 11). To facilitate plotting, copper and other elements were removed and

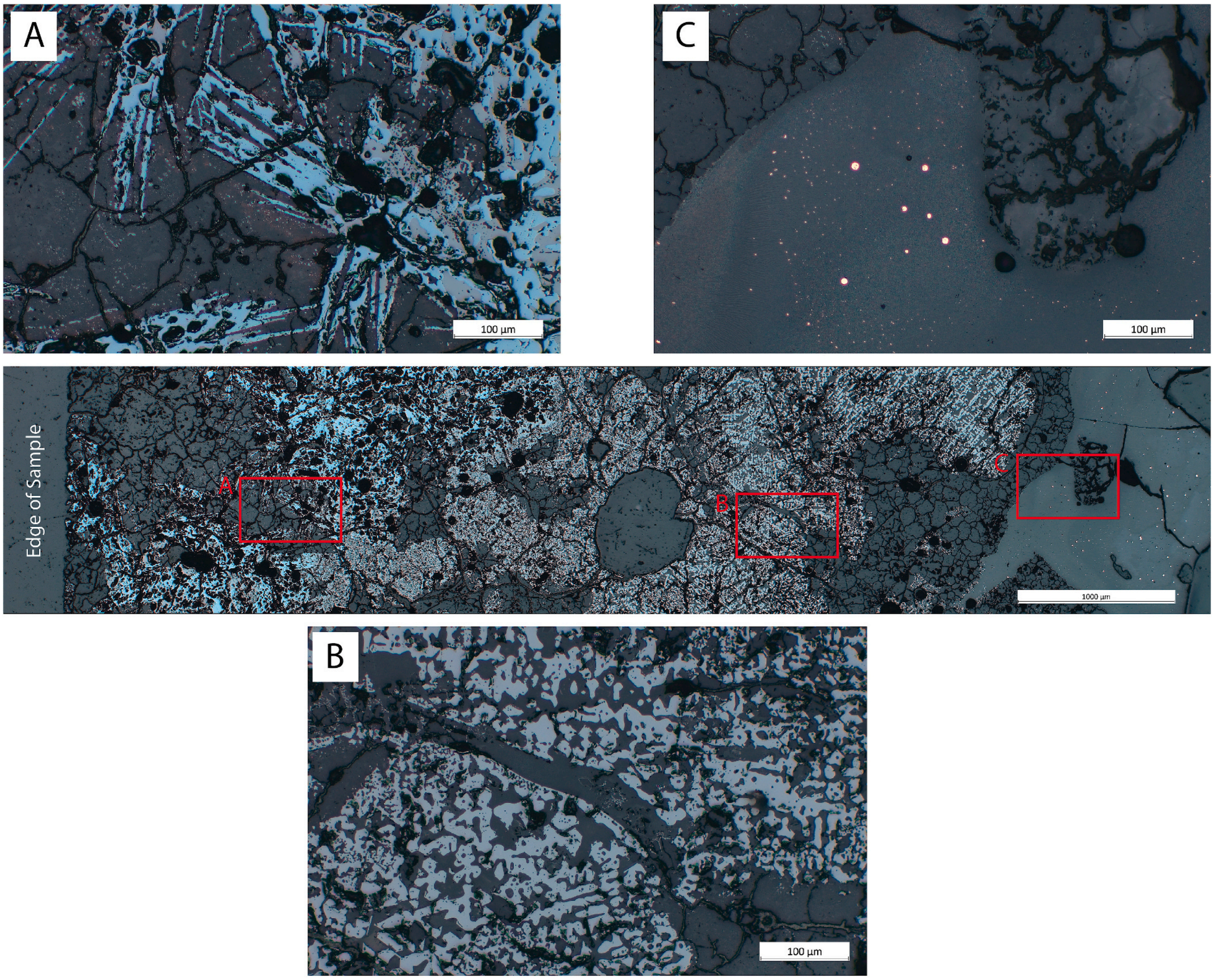

Fig. 9. Optical photomicrograph of a partially reacted inclusion of hematite in a quartz matrix within a piece of copper smelting slag (SL02). Less reacted areas (A) preserve hematite with the platy crystal habit seen in Fig. 5. Melting and reduction is clearly apparent moving from left to right (right side of A, and B), before reaching the interface with the slag (C), which contains numerous small copper metal prills (bright spots with reddish tint). Note the lack of any copper prills in the partially reacted inclusion itself.

Table 2
Bulk compositional analyses of slags. Values are normalized and are the average of separate analyses of at least four different areas the sample. Detection limit was assessed conservatively to be 0.15 %. See supplementary dataset S1 for complete raw data.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2	K_2O	CaO	TiO_2	MnO	FeO	CuO	BaO
SL01	0.4	0.7	9.1	39.1	0.4	0.3	1.8	4.9	0.4	0.3	35.6	1.1	6.0
SL02	0.2	1.0	9.9	46.9	0.3	bdl	1.9	3.6	0.5	0.4	34.1	1.0	0.2
SL03-1	bdl	1.1	10.3	49.3	0.2	bdl	2.0	2.2	0.4	0.7	32.0	1.7	bdl
SL03-2	bdl	1.1	7.7	45.8	0.2	bdl	1.4	2.5	0.3	0.4	39.3	1.2	bdl
SL04	0.2	0.5	10.6	42.4	0.3	0.3	1.9	3.0	0.5	0.4	33.7	0.7	5.4
SL05	0.2	0.7	9.5	44.0	0.3	0.5	1.8	2.7	0.5	0.4	32.8	0.6	6.1
SL06	0.2	0.6	10	41.8	0.3	0.4	1.8	2.9	0.5	0.4	35.2	0.8	5.1
SL07	0.2	1.6	9.5	40.2	0.2	bdl	1.7	3.5	0.4	0.5	40.7	1.2	0.3
SL08	0.2	0.6	9.1	38.7	0.3	0.3	1.7	3.2	0.5	0.4	38.1	1.3	5.7
SL09	0.2	0.6	9.0	41.8	0.3	0.6	1.7	2.6	0.5	0.4	35.5	0.6	6.2
SL10	0.2	0.7	9.4	41.2	0.3	0.4	1.7	2.9	0.5	0.4	36.3	0.8	5.2
SL11	0.2	0.7	9.4	43.1	0.3	0.5	1.8	2.5	0.5	0.5	34.2	0.7	5.8
SL12	0.2	0.6	10.3	42.6	0.3	0.4	1.9	3.1	0.5	0.5	34.1	0.6	4.9
SL13	0.2	0.7	9.1	43.4	0.3	0.5	1.7	2.7	0.6	0.4	33.7	0.5	6.0
SL14	0.3	0.6	10.8	43.4	0.3	0.4	1.9	3.1	0.5	0.4	32.8	0.6	4.9

values were renormalized to 100 % (**see** Supplementary Data S1 and S3). Slag samples form intermediate compositions close to a linear trend line between the hematite sample and the copper ore and host rock samples. It is worth noting that, while the atypical sample OR01 does plot near the slags and could theoretically qualify as a self-fluxing ore, its use in ancient smelting processes is strongly contraindicated by clear evidence—from the partially-reacted ore-gangue inclusions in the slag themselves—for the use of iron poor ores (Fig. 8) and the separate addition of iron oxides (Fig. 9). Perhaps this unusual type of mineralization is a minor component of the ore body—only one small sample of

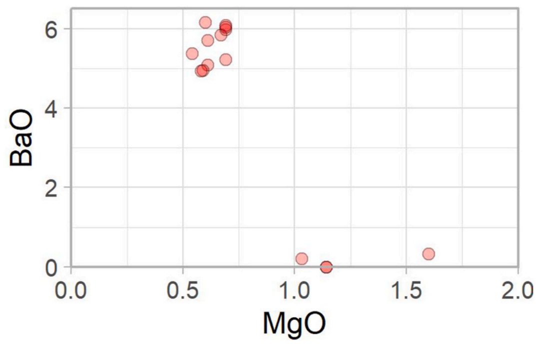

Fig. 10. Plot of BaO vs. MgO for slag samples.

this type was identified—or perhaps this part of the ore body was simply not mined in the Late Bronze and Early Iron Age.

The bulk chemical compositions of Kvemo Bolnisi slags are generally comparable with Late Bronze Age and Early Iron Age slags from Colchis, but several differences are worth noting. Zinc-bearing slags are frequently encountered in western Georgia, undoubtedly a product of the ores used (Erb-Satullo et al., 2017), while in Kvemo Bolnisi zinc was not detected in the bulk composition of the slag. By contrast, barium is present in Colchian copper smelting slags, but at levels generally under 3 wt% BaO, while a majority of Kvemo Bolnisi have >5 wt% BaO, most likely deriving from baryte accessory minerals in the ores. Similarly, the sulfur content of Kvemo Bolnisi slags reaches a maximum of 0.6 wt% SO_3, while most slags analyzed from western Georgia typically exceed this value. This difference that is readily visible mineralogically in the different frequencies of copper, iron, and copper-iron sulfides found in the two assemblages.

A selection of metal prills was analyzed in order to identify any alloying elements present in the copper produced from the smelting process (Table 3). The composition of small prills (many <100 μm) does not correspond precisely with that of the bulk composition of the metal product, but these analyses provide a qualitative assessment of the chemical composition of the metal produced. Some prills clearly contain multiple phases, so area analyses were used to average across different phases (e.g. prill 10 in SL07). Arsenic and antimony appear in a number of prills, up to 3.8 % As and 4.5 % Sb in prill 13 in SL09. Antimony was always found in As-bearing prills, but some arsenic-bearing prill did not contain antimony. Zinc content was detected, but in lower quantities (<0.4 wt%). There does not appear to be any correlations between the prills compositions, and the bulk slag chemistry groupings (those based on variations in Ba, Mg, and S). Kvemo Bolnisi prill compositions contrast with the copper prills analyzed in Colchian smelting slags, which do not contain appreciable quantities of As or Sb (Erb-Satullo et al., 2015:271).

5. Discussion

Analysis of the metallurgical slags shows unequivocally that they derive from a copper smelting process. This is amply documented by the presence of copper metal, copper sulfides, and chunks of partially reacted ore-and gangue. Iron metal phases were identified in between one half and one third of the slag samples, but their frequency and morphology is generally within the range typical of Late Bronze and Early Iron Age copper smelting slags. The discovery that yet another alleged iron smelting site in fact relates to copper smelting underscores the importance of caution when evaluating earlier claims of iron smelting, especially those without adequately documented chemical and mineralogical analyses of production debris. This remains an enduring challenge for the study of iron innovation in the Middle East and Central Eurasia.

5.1. Kvemo Bolnisi copper smelting technology in comparative context

Documentation of late 2nd and early 1st millennium BC copper smelting technologies and production sites in the Middle East is more uneven than one might expect given the extensive scholarship on the

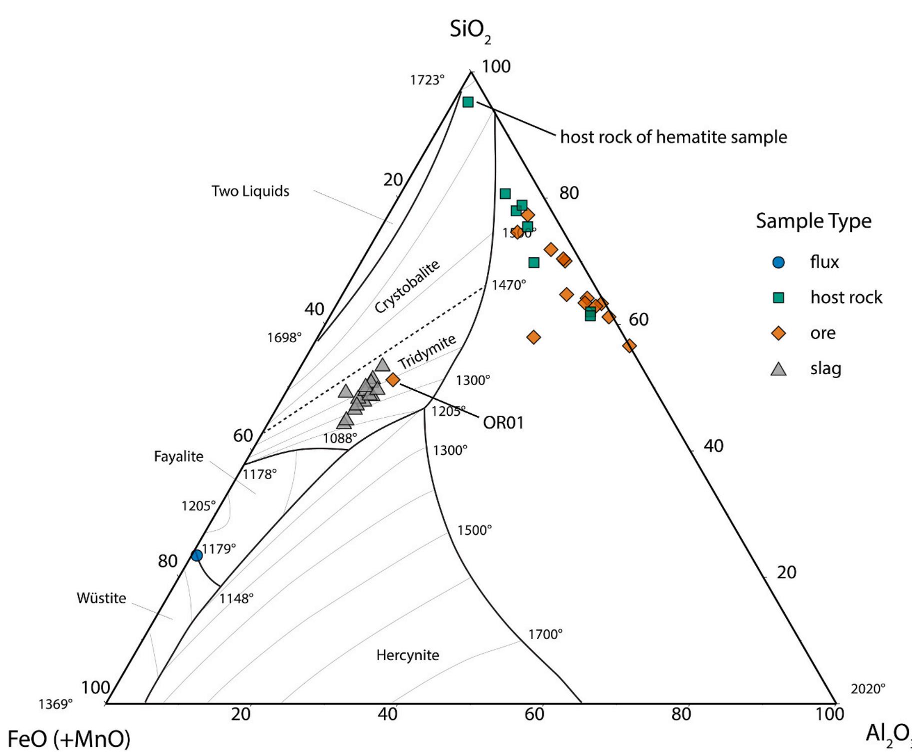

Fig. 11. Ternary SiO_2-Al_2O_3-FeO phrase diagram for slags and mineral samples. Plotted in R using ggtern (Hamilton and Ferry, 2018) and finished in Adobe Illustrator.

Table 3
Compositions of metallic prills within slags. Analysis type indicates whether the analysis was a spot or area analysis; area analyses often included more than 1 phase (usually sulfides and/or iron metal in addition to the copper-rich phase). Values are normalized. Detection limit was determined conservatively to be 0.15 %. Small O and Si peaks were detected, but were included in the deconvolution and so are not reported. (See supplementary dataset S1 for full data.)

Sample	Prill #	Analysis Type	P	S	Fe	Cu	Zn	As	Sn	Sb
SL02	1	spot	bdl	bdl	1.3	97.4	0.2	1.0	bdl	bdl
SL03-1	2	area	bdl	0.3	bdl	99.7	bdl	bdl	bdl	bdl
SL03-1	2	spot	bdl	bdl	bdl	100.0	bdl	bdl	bdl	bdl
SL03-1	3	area	0.2	bdl	3.0	96.9	bdl	bdl	bdl	bdl
SL03-1	3	spot	bdl	bdl	2.0	98.0	bdl	bdl	bdl	bdl
SL03-2	4	area	bdl	0.3	bdl	99.7	bdl	bdl	bdl	bdl
SL03-2	5	area	bdl	0.2	bdl	99.8	bdl	bdl	bdl	bdl
SL03-2	6	area	bdl	0.2	bdl	99.6	bdl	0.2	bdl	bdl
SL05	7	spot	bdl	bdl	1.3	98.4	bdl	0.4	bdl	bdl
SL05	7	area	bdl	0.2	1.6	97.9	bdl	0.4	bdl	bdl
SL05	8	spot	bdl	3.9	4.4	91.4	0.4	bdl	bdl	bdl
SL05	8	area	bdl	0.5	1.7	97.4	0.2	0.3	bdl	bdl
SL06	9	area	bdl	0.5	3.1	95.4	bdl	0.7	bdl	0.4
SL06	9	spot	bdl	bdl	1.9	97	bdl	0.7	bdl	0.4
SL07	10	spot	bdl	bdl	2.6	97.1	bdl	0.3	bdl	bdl
SL07	10	area	0.3	2.0	27.4	70.2	bdl	0.2	bdl	bdl
SL08	11	area	bdl	bdl	0.9	98.9	0.2	bdl	bdl	bdl
SL08	12	area	bdl	bdl	0.6	99.0	0.3	0.2	bdl	bdl
SL09	13	spot	bdl	bdl	1.3	90.4	bdl	3.8	bdl	4.5
SL09	14	spot	bdl	bdl	2.2	94.5	bdl	1.7	bdl	1.7
SL09	15	spot	bdl	bdl	1.5	92.4	0.2	2.7	bdl	3.2
SL10	16	area	bdl	0.2	0.9	98.3	bdl	0.3	bdl	0.3
SL10	17	area	bdl	bdl	0.2	99.8	bdl	bdl	bdl	bdl
SL11	18	area	bdl	bdl	1.7	98.1	bdl	0.2	bdl	bdl
SL12	19	area	1.0	2.6	76.3	20.2	bdl	bdl	bdl	bdl
SL14	20	area	bdl	bdl	0.3	95.2	0.2	3.3	bdl	1.0

Late Bronze Age copper trade. Still, comparisons between the Kvemo Bolnisi technologies and those elsewhere are instructive. The contrast between the Kvemo Bolnisi slags and those from the numerous Colchian copper smelting sites is surprisingly sharp, given their relative geographic proximity and contemporaneity. Chemistry and mineralogy of the Kvemo Bolnisi slags and ores indicate that the ores smelted were primarily oxidic ores (e.g. malachite, azurite, and chrysocolla) rather than the sulfide ores exploited in Colchis. The low levels of copper sulfides identified in the former are likely detrital. Other aspects of the smelting technology also differ, some—but perhaps not all—of which may be stem from the different requirements for extracting copper from oxide and sulfide ores. We found no evidence, for instance, of the two main macro-types of slag found at Colchian copper smelting sites: the spongy amorphous lumps and large dense slag cakes (Erb-Satullo et al., 2014:Fig. 4). These two types of slag were interpreted as evidence of multiple stages of smelting, probably connected with the production of an intermediate copper sulfide matte (Erb-Satullo et al., 2015). Unlike the Colchian furnaces, which are mostly deep pits, the furnace identified at Kvemo Bolnisi is against a structure wall, possibly to facilitate lateral access to the reaction chamber or to enable tapping of slag. While some evidence of slag flow was identified and plans of the excavated furnace identify two circular features identified as “pits for slag” in front of the furnace (Gzelishvili, 1964:34), the Kvemo Bolnisi slags do not have the characteristic ropey or pooling morphologies characteristic of other Near Eastern tap slags (e.g. Hauptmann, 2007:98, 129; Koucky and Steinberg, 1982; Sdralia et al., 2023).

Chemical analysis of metal prills in the slags indicates that the chemical composition of the resulting metal was different from that produced in Colchis. The recurring presence of arsenic and antimony in metal prills at Kvemo Bolnisi has no parallel in the Colchian smelting slags analyzed so far (Erb-Satullo et al., 2015:271). The chemistry of Colchian bronze artifacts suggests that arsenic and antimony were added as a separate step in secondary processing (Ho and Erb-Satullo, 2021), an alloying method that may also be documented in areas close to Kvemo Bolnisi (Erb-Satullo et al., 2020b:10). The Kvemo Bolnisi slags seem to indicate that in some cases, As and Sb content copper alloys may derive from materials added to the smelting furnace along with the copper ores. Nevertheless, we must remain cautious about inferring the resulting bulk metal composition from the composition of tiny prills in a heterogeneous melt.

Perhaps most strikingly, the spatial organisation of copper smelting activities is markedly different. In Kvemo Bolnisi, smelting took place in a workshop within or at the edge of a settlement, directly adjacent to the ore deposit. At Colchian smelting sites, there is little evidence of directly adjacent settlements or mining activities. Unlike Kvemo Bolnisi, Colchian smelting sites contain very few domestic, non-metallurgical ceramics, and it seems raw metal was shipped to lowland coastal settlements for secondary shaping into objects (Erb-Satullo, 2022). The co-location of mining, smelting, and settlement at Kvemo Bolnisi stands in marked contrast to this pattern.

The final point of comparison to other contemporary Caucasus copper smelting industries is one of scale. While the archaeological record is of course an imperfect reflection of ancient patterns, it is worth underlining that hundreds of copper smelting sites are known from Colchis (Erb-Satullo et al., 2017; Khakhutaishvili, 2009 [1987]:17; Sulava et al., 2020), and of those with radiocarbon dates, virtually all copper smelting sites date to the period between 1500 and 500 BC (Erb-Satullo et al., 2018). By contrast, Kvemo Bolnisi, despite being one of the first sites investigated, remains the only well-documented late 2nd to early 1st millennium BC copper smelting site known from eastern Georgia. Western Georgia and adjacent regions of northeastern Turkey (see Lutz et al., 1994) seem to have far more substantial numbers of known ancient metallurgical sites in comparison with Armenia, Eastern Georgia, and Azerbaijan, despite the major ore deposits present in the latter areas (Mederer et al., 2014). Patterns of archaeological research may influence this picture to some extent, but the difference in numbers of sites is so substantial that it is hard to imagine that it bears no relation to the relative outputs of ancient industries in these different zones.

5.2. *Use of iron oxide fluxes in copper smelting*

The discovery that Kvemo Bolnisi copper metallurgists were stockpiling iron oxides and adding them to the furnace to increase the fluidity of the slag deserves specific consideration. Critical reassessments of the earlier publications, combined with the analysis of the slag, copper mineral samples, and the hematite mineral sample, provide what is arguably the clearest and most convincing evidence for the deliberate use of iron oxides as fluxes in copper metallurgy prior to 500 BC.

Recent scholarship has rightly been more skeptical about identifying intentionally added fluxes than prior work (see Hauptmann, 2020:245; contra Wertime, 1980:16), as many ores will contain gangue minerals that function in a similar way, creating a "self-fluxing" ore (Hauptmann, 2007:250–251). Intentional addition of fluxes separate from the ore-gangue mixture is also quite distinct in its implications from the intentional selection of self-fluxing ores. Specifically, the latter does not necessarily require a detailed understanding that effective slag formation requires a balanced mixture of discrete materials. While the use of separately-added fluxes is difficult to identify, it is fundamentally important to the development of metallurgy. Crucially, it represents an signficant cognitive step in empirical understanding of the behaviour of materials at high temperature and indicated an ability to control and manipulate these behaviours to achieve a desired result. In this case, the aim is greater metal yield through higher slag fluidity, which results in better slag-metal separation and probably also better shielding of the metal from re-oxidation. In short, distinguishing the accidental from the intentional is a fundamental goal in assessing any technological innovation, and one that is particularly challenging in the absence of written records.

A robust case for intentional addition of flux needs to provide evidence (1) that the material was added to the reaction vessel, (2) that this material is *not* present in the ore, gangue, the fuel, or the fabric of the reaction vessel itself, (3) that this practice was consistent enough to reflect an intentional practice, and (4) that the suspected fluxing material was stockpiled in the metallurgical workshop. The Kvemo Bolnisi site provide strong evidence for all four points. Both bulk chemistry and slag mineralogy show the consistent presence of iron in the furnace, while slag microstructures (especially in SL02) and copper mineral samples show that the iron oxides were introduced to the reaction separately from the ore. Finally, the identification of the hematite sample in the vicinity of the workshop substantiates earlier descriptions of a stockpile of hematite in the workshop.

A few other strong cases of intentional fluxing in copper smelting are known, mostly from the Iron Age or later. At Timna Site 30 (southern Levant), excavations uncovered stockpiles of separately collected manganese oxides in a layer now dated to the late 10th to 9th centuries BC (Rothenberg, 1990:51–52;Ben-Yosef et al., 2012:52). Manganese-rich slags are a common feature of sites in the Timna area and in the wider smelting landscapes of the Wadi Arabah, though (Hauptmann, 2007:181, 249–251) considers earlier-dated manganese slags to be the result of smelting a Mn-containing ore rather than deliberate fluxing with a separate material. In the Iron Age, the evidence of stockpiling manganese oxides makes the case for deliberate fluxing more convincing (Hauptmann, 2020:245). There are also some reports of iron-rich minerals from Iron Age copper mining and smelting districts in the Southern Levant (Eliyahu-Behar et al., 2023:5), and some slags from the area are richer in iron rather than manganese (Hauptmann, 2007:180), but the possible use of iron oxides as deliberate fluxes alongside manganese oxides requires further substantiation. Careful comparison of slags and ore from the Lowveld (South Africa) show that 2nd millennium AD smelting of carbonatite-hosted malachite and azurite ores likely involved silica-rich fluxes (Killick et al., 2016). As melted technical ceramic cannot fully account for the elevated silica in the slags, the authors propose the use of a separately added flux. At a Sican period smelting site in Peru (AD 1030–1180), small pieces of hematite were identified on the site, and there is mention of "finely powdered hematite in the furnace charge" as a possible flux, given the iron content of the slags (36–37 wt% FeO) (Killick and Hayashida, 2022:15). However, hematite and other iron minerals are mentioned in samples associated with a nearby copper mine, so there is perhaps some ambiguity about whether the hematite may have been intentionally added as a separate flux.

In comparison with these other examples, many of which postdate 500 BC, pertain to non-iron oxide fluxes, and/or do not conclusively resolve questions of intentionality, the use of iron oxide fluxes in the late 2nd millennium BC at Kvemo Bolnisi takes on particular significance. The hypothesis that the invention of iron smelting was somehow related to developments in copper metallurgy has long been attractive, as iron and copper frequently co-occur geologically, and copper smelting slags often contain iron in the form of oxides and silicates. Empirical support for this hypothesis has been lacking (Merkel and Barrett, 2000), leading some to question the underlying premise (Liss et al., 2020). While it is now clear that iron metal was not the main product of the Kvemo Bolnisi smelting process, the use of iron oxides fluxes reflects an important cognitive development in metallurgical knowledge. Namely copper metallurgists at Kvemo Bolnisi understood iron oxides as a discrete material. They, or their predecessors, had clearly experimented with hematite in high temperature reduction processes in order to work out the optimal balance for a fluid slag. The Kvemo Bolnisi slags, with chemical compositions plotting near a melting temperature minimum in the SiO_2-FeO-Al_2O_3 phase diagram, reflect the knowledge obtained by the results of this experimentation.

These behaviors, and the cognitive understanding they imply, furnish the underlying conditions for the invention of iron. The most plausible model for the invention of useable iron in an intended copper smelt is that a furnace charge with less copper and more iron was driven to higher reducing conditions. This could occur if the ores derived from the boundary between the gossan and supergene zone of a copper deposit, but it could also occur if a low-grade copper ore charge was "overfluxed" with iron oxides. Under these circumstances, it may have been possible to obtain useable chunks of metallic iron without much copper. It is likely no accident that clear evidence for intentional fluxing in copper smelting correlates with the late 2nd-early 1st millennium BC spread of iron.

One key question that is difficult to answer with certainty is whether the hematite was collected at Kvemo Bolnisi itself (presumably from a different part of the mineralization), or had to be mined separately and brought in from elsewhere. This question has less of a bearing on the question of technical knowledge—it is clear from all the assembled evidence that the hematite was clearly recognized and stockpiled as a discrete and separate additive—but rather on questions of organization and logistics. Circumstantial evidence suggests that the hematite may have come from other mines nearby. Deposits of specular hematite with crystal habit similar to sample HAE are known from neighboring areas further up the valley and in adjacent valleys (Fig. 12). These sites, originally identified in Soviet times and relocated by recent surveys (Erb-Satullo, 2018), have traces of mining that have been attributed to the medieval period (Gzelishvili, 1964). Given the hematite found at Kvemo Bolnisi, one wonders if these deposits were originally exploited much earlier.

The discovery of intentional hematite fluxing at Kvemo Bolnisi prompts a reconsideration of isolated instances of hematite found at Colchian copper smelting sites in western Georgia. Two fragments with platy hematite very similar to the hematite sample from Kvemo Bolnisi were identified at copper smelting sites 41 and 43 (Erb-Satullo, 2016:110,113), radiocarbon dated between the 13th-10th centuries BC (Erb-Satullo et al., 2018). Hematite is also mentioned in excavation reports of a Colchian smelting site in Samegrelo (Khakhutaishvili, 2009 [1987]:101), which was relocated by Erb-Satullo and colleagues in 2014 and almost certainly relates to copper smelting (Erb-Satullo, 2016:323).[1] As discussed above, Colchian copper smelting technology is

[1] Samples of slag from this site (Chogha II/Site 75) were not analyzed, but macroscopically the slags align with the hundreds of other Colchian copper smelting slags analyzed by that project, including those from Chogha I/Site 74, 300m away.

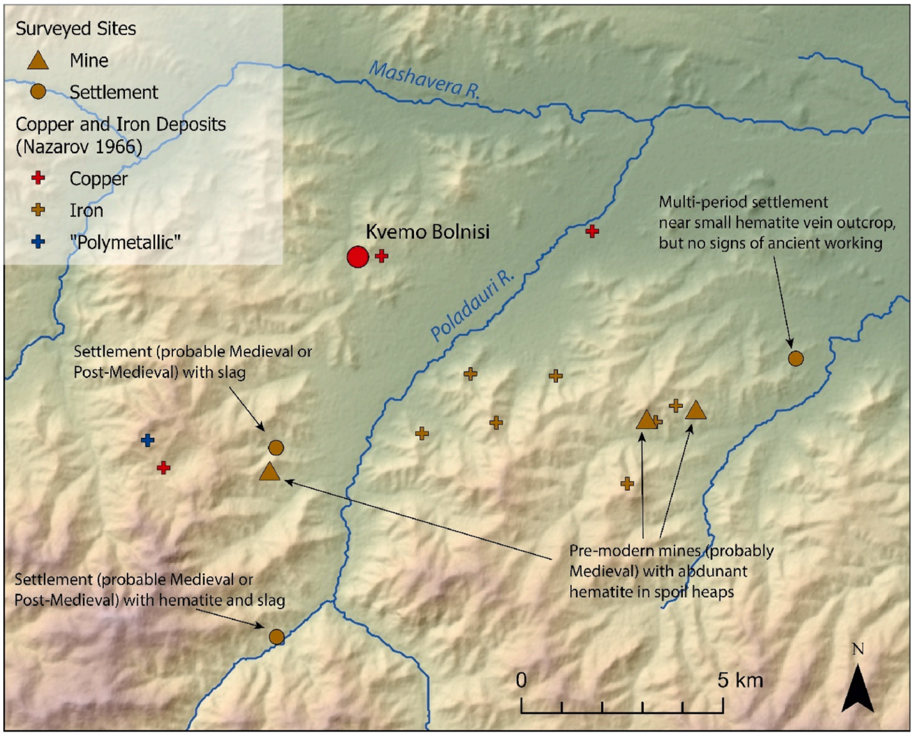

Fig. 12. Sites surveyed by Project ARKK with hematite in the vicinity of Kvemo Bolnisi. Copper and iron deposit locations from Nazarov (1966), should be considered approximate, as they are georeferenced from a smaller-scale map covering a larger area.

clearly quite different from that of Kvemo Bolnisi, so the role of hematite in the smelting process is ambiguous. In Colchis, the use of an iron-bearing copper ore (primarily chalcopyrite, $CuFeS_2$) with iron-bearing accessory minerals (e.g. sphalerite, (Zn,Fe)S) complicates identification of a separately added iron-bearing flux through slag chemistry and mineralogy. As un-smelted copper ores were not found at these sites, we also do not have enough information about the composition of the gangue to determine whether the ore would have been self-fluxing. Nevertheless, the appearance of hematite with similar habit and macroscopic appearance, at multiple contemporary copper smelting sites is suggestive of a common purpose. This hints that collection of and experimentation with iron oxides as a discrete substance (i.e. separate from copper ore) was more widespread among late 2nd millennium BC copper smelters than has been previously recognized.

6. Conclusion

Put succinctly, the copper smelting technology at Kvemo Bolnisi represents a step in the process by which iron oxides became iron ore. While the former is a purely geochemical designation independent of human use, the latter is a technological term referring specifically to raw material used in extractive iron metallurgy. These metallurgical remains reflect an elusive but fundamental shift in the perception and understanding of iron-containing minerals by metalworkers, one that is key to the invention and early innovation of iron. This understanding, combined with empirical disposition required to balance flux and gangue components, makes the next step—experimenting with iron oxides in the absence of copper—less of a cognitive leap. Perhaps this last step was deliberate, or perhaps it occurred unintentionally when a metalworker attempted to smelt a batch of low-grade copper ore. At some point, however, a metalworker must have recognized that, under the right conditions, a new metal could be produced without the need for copper ore.

The evidence for the use of separately added iron fluxes in copper metallurgy has another intriguing implication for the iron-from-copper theory for origins of iron smelting. If iron oxides were deliberately collected from deposits other than the source of copper ore (as may be the case at Kvemo Bolnisi), then copper gossans do not necessarily have to be the source of iron ore for the first iron smelting. Counterintuitively, *iron-poor* copper deposits, like those at Kvemo Bolnisi, could equally have played a role in the invention of iron, by stimulating experimentation with exogenous sources of iron oxide flux to smelt ores that were not self-fluxing.

Some aspects of these proposed invention models require further confirmation. Given the lack of absolute radiocarbon dates from the Kvemo Bolnisi workshop and for the chronology of iron innovation in the region, there is a degree of imprecision about the chronological relationship between the two. If the Kvemo Bolnisi workshop dates somewhat later than Gzelishvili's proposed late 2nd millennium BC date, it may post-date the early stages of iron adoption in eastern Georgia. However, it is highly suggestive that the earliest evidence for the deliberate use of iron oxide fluxes in copper metallurgy correlates in broad terms with the appearance of smelted iron, both in the Caucasus and possibly also in the southern Levant. Kvemo Bolnisi was likely not the only LBA-EIA copper smelting site in the Near East where iron oxides were deliberately used as flux. Rather, the significance of the results derive from the circumstances of site (with smelting activities directly adjacent to the mine, and ore almost totally lacking in iron), which has produced one of the earliest *unambiguous* cases for deliberate use of iron oxide fluxes. Recall, by way of comparison, the more ambiguous find of hematite at a copper smelting site in Colchis mentioned above. In that case, the potential deliberate addition of iron oxide fluxes is obscured by the use of iron-bearing copper ores (primarily chalcopyrite, $CuFeS_2$). As more 2nd millennium BC copper smelting sites become known, it will be essential to investigate the possible deliberate use of iron oxide fluxes, wherever the data allow.

Debates about the invention of iron will likely continue until we have accumulated more data on the geography, chronology, and technology of early iron smelting activities. That stage is clearly some way off. Encouragingly, research at Kvemo Bolnisi shows that the investigation of currently known sites has much to contribute to debates about the links between the bronze and iron technologies and their impact on iron innovation. More generally, this work shows how the analysis of production remains not only reconstructs technological behaviors, it can also address questions of knowledge, perception, and intent. These are dimensions of ultimate significance for the study of innovation in ancient materials technologies, and indeed, for many subjects of archaeological investigation.

CRediT authorship contribution statement

Nathaniel L. Erb-Satullo: Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Bobbi W. Klymchuk:** Writing – review & editing, Visualization, Investigation.

Data availability statement

Data on analyses of slags, ores, and fluxes is provided in the supplementary information and in an open access dataset published on the Harvard Dataverse (Erb-Satullo and Klymchuk, 2025).

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Nathaniel Erb-Satullo reports financial support was provided by British Institute at Ankara. Nathaniel Erb-Satullo reports financial support was provided by American Research Institute of the South Caucasus. Nathaniel Erb-Satullo reports financial support was provided by Teschmacher Fund (Harvard Department of Anthropology). Nathaniel Erb-Satullo reports financial support was provided by Gerda Henkel Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

Akhvlediani, N., 2001. On the dating of burial no. 13 in the Beshtasheni burial-ground. Anc. Civiliz. Scythia Sib. 7, 273–285.

Ben-Yosef, E., Shaar, R., Tauxe, L., Ron, H., 2012. A new chronological framework for Iron Age copper production at Timna (Israel). Bull. Am. Sch. Orient. Res. 367, 31–71.

Ben-Yosef, E., Tauxe, L., Levy, T.E., 2010. Archaeomagnetic dating of copper smelting site F2 in the Timna Valley (Israel) and its implications for the modelling of ancient technological developments. Archaeometry 52, 1110–1121.

Eliyahu-Behar, A., Ben Dor, Y., Brauns, M., Shulman, O.A., Avni, Y., Killebrew, A.E., Tirosh, O., Yahalom-Mack, N., 2023. "A land whose stones are iron."—Iron ore sources in the Southern Levant. Front. Environ. Archaeol. 2.

Erb-Satullo, N.L., 2016. Metal Production in the Land of the Golden Fleece: Economic Organization and Technological Change in the South Caucasus, 1500-500 BC. Harvard University. PhD Unpublished PhD Dissertation.

Erb-Satullo, N.L., 2018. Patterns of settlement and metallurgy in late Bronze-Early Iron Age Kvemo Kartli, southern Georgia. In: Anderson, W., Hopper, K., Robinson, A. (Eds.), Finding Common Ground in Diverse Environments: Landscape Archaeology in the South Caucasus. OREA, Austrian Academy of Sciences, Vienna, pp. 37–52.

Erb-Satullo, N.L., 2019. The innovation and adoption of iron in the ancient Near East. J. Archaeol. Res. 27, 557–607.

Erb-Satullo, N.L., 2022. Towards a spatial archaeology of crafting landscapes. Camb. Archaeol. J.

Erb-Satullo, N.L., Gilmour, B.J.J., Khakhutaishvili, N., 2014. Late Bronze and Early Iron Age copper smelting technologies in the South Caucasus: the view from ancient Colchis c. 1500-600 BC. J. Archaeol. Sci. 49, 147–159.

Erb-Satullo, N.L., Gilmour, B.J.J., Khakhutaishvili, N., 2015. Crucible technologies in the late Bronze-Early Iron Age South Caucasus: copper processing, tin bronze production, and the possibility of local tin ores. J. Archaeol. Sci. 61, 260–276.

Erb-Satullo, N.L., Gilmour, B.J.J., Khakhutaishvili, N., 2017. Copper production landscapes of the South Caucasus. J. Anthropol. Archaeol. 47, 109–126.

Erb-Satullo, N.L., Gilmour, B.J.J., Khakhutaishvili, N., 2018. The ebb and flow of copper and iron smelting in the South Caucasus. Radiocarbon 60, 159–180.

Erb-Satullo, N.L., Gilmour, B.J.J., Khakhutaishvili, N., 2020a. The metal behind the myths: iron smelting in the southeastern Black Sea region. Antiquity 94, 401–419.

Erb-Satullo, N.L., Jachvliani, D., Kakhiani, K., Newman, R., 2020b. Direct evidence for the co-manufacturing of early iron and copper-alloy artifacts in the caucasus. J. Archaeol. Sci. 123, 105220.

Erb-Satullo, N.L., Klymchuk, B.W., 2025. Optical and scanning electron microscopy data on slags and mineral samples from kvemo bolnisi. Harvard Dataverse. https://doi.org/10.7910/DVN/4CDMOH.

Gzelishvili, I.A., 1964. Zhelezoplavil'noe Proizvodstvo v Drevney Gruzii. Metsniereba, Tbilisi.

Hamilton, N.E., Ferry, M., 2018. ggtern: ternary diagrams using ggplot2. J. Statis. Software Code Snippet. 87, 1–17.

Hauptmann, A., 2007. The Archaeometallurgy of Copper: Evidence from Faynan, Jordan, Natural Science in Archaeology. Springer, Berlin.

Hauptmann, A., 2020. Archaeometallurgy – Materials Science Aspects. Springer, Cham.

Ho, J.W.I., Erb-Satullo, N.L., 2021. Spatial investigation of technological choice and recylcing in copper-base metallurgy in the South Caucasus. Archaeometry 63, 1306–1326.

Inanishvili, G., 2007. About the history of iron production in Georgia. Metalla 14, 1–62.

Khakhutaishvili, D.A., 2009[1987]. The Manufacture of Iron in Ancient Colchis, BAR International Series 1905. Archaeopress, Oxford.

Killick, D., Hayashida, F., 2022. Copper smelting and refining in the Pampa de Chaparrí, Lambayeque, Peru, ca. 1030–1180 cal AD. J. Archaeol. Sci. 148.

Killick, D., Miller, D., Thondhlana, T.P., Martinón-Torres, M., 2016. Copper mining and smelting technology in the northern Lowveld, South Africa, ca. 1000 CE to ca. 1880 CE. J. Archaeol. Sci. 75, 10–26.

Knapp, A.B., Kassianidou, V., 2008. The archaeology of late Bronze Age copper production: Politiko Phorades on Cyprus. In: Yalçin, Ü. (Ed.), Anatolian Metal IV, Bochum Vereinigung Der Freunde Von Kunst Und Kultur Im Bergbau, pp. 135–147. Bochum, Germany.

Koucky, F.L., Steinberg, A., 1982. The ancient slags of Cyprus. In: Muhly, J.D., Maddin, R., Karageorghis, V. (Eds.), Acta of the International Archaeological Symposium on Early Metallurgy in Cyprus, 4,000-500 BC, Larnaca, Cyprus 1-6 June 1981. Pierides Foundation, Nicosia, pp. 117–137.

Lehner, J.W., 2017. Innovation and continuity of metal production and consumption during the early Iron Age at Boğazköy-Hattuša. In: Schachner, A. (Ed.), Innovation Versus Beharrung: Was Macht Den Unterschied Des Hethitischen Reichs Im Anatolien Des 2. Jahrtausends V. Chr.? Deutschen Archäologischen Instituts Istanbul, Istanbul.

Levy, T.E., Ben-Yosef, E., Najjar, M., 2012. New perspectives on Iron Age copper production and society in the Faynan Region, Jordan. In: Kassianidou, V., Papasavvas, G. (Eds.), Eastern Mediterranean Metallurgy and Metalwork in the, Second Millennium BC. Oxbow Books, Oxford, pp. 197–214.

Liss, B., Levy, T.E., Day, J.M.D., 2020. Origin of iron production in the Eastern Mediterranean: osmium isotope and highly siderophile element evidence from Iron Age Jordan. J. Archaeol. Sci. 122.

Lutz, J., Pernicka, E., Wagner, G.A., 1994. Chalkolithische Kupferverhüttung in Murgul, Ostanatolien. In: Wartke, R.-B. (Ed.), Handwerk Und Technologie Im Alten Orient. Philipp von Zabern, Mainz, pp. 56–66.

Mederer, J., Moritz, R., Zohrabyan, S., Vardanyan, A., Melkonyan, R., Ulianov, A., 2014. Base and precious metal mineralization in Middle Jurassic rocks of the Lesser Caucasus: a review of geology and metallogeny and new data from the Kapan, Alaverdi and Mehmana districts. Ore Geol. Rev. 58, 185–207.

Merkel, J.F., Barrett, K., 2000. 'The adventitious production of iron in the smelting of copper' revisited: Metallographic evidence against a tempting model. Hist. Metall. 34, 59–66.

Nazarov, Y.I., 1966. Osobennosti Formirovaniya i Prognoz Glubinnykh (Skrytykh) Mestorozhdeniy Mednokolchedannoy Formatsii Yuzhnoy Gruzii. Nedra, Moscow.

Pigott, V.C., 2003. Iron and pyrotechnology at 13th century-late Bronze Age-Tel Yin'nam (Israel): a reinterpretation. In: Stöllner, T., Körlin, G., Steffens, G., Cierny, J. (Eds.), Man and Mining-Mensch Und Bergbau: Studies in Honour of Gerd Weisgerber on Occasion of his 65th Birthday, pp. 365–375. Deutsches Bergbau-Museum, Bochum.

Radivojević, M., 2015. Inventing metallurgy in western Eurasia: a look through the microscope lens. Camb. Archaeol. J. 25, 321–338.

Rothenberg, B., 1990. Copper smelting furnaces, tuyeres, slags, ingot moulds, and ingots in the Arabah: the archaeological data. In: Rothenberg, B. (Ed.), The Ancient Metallurgy of Copper, Institute for Archaeo-Metallurgical Studies, Institute of Archaeology. University College London, London, pp. 1–77.

Sdralia, A.-M., Kassianidou, V., Rehren, T., 2023. Late Roman copper smelting in Polis Chrysochous, Cyprus. J. Archaeol. Sci.: Report 48, 103889.

Sulava, N., Gilmour, B., Rezesidze, N., Chagelishvili, R., Beridze, T., 2020. Met'alurgiis ts'armoshoba da ganvitareba mtian k'olkheti (lechkhumi) (The Origin and Development of Prehistoric Copper Metallurgy in Mountainous Colchis (Lechkhumi)). Georgian National Museum, Tbilisi.

Veldhuijzen, H.A., 2009. Red hot: the smithy at Tel Beth-Shemesh. Near E. Archaeol. 72, 129–131.

Veldhuijzen, H.A., Rehren, T., 2007. Slags and the city: early iron production at Tell Hammeh, Jordan and Tel Beth-Shemesh, Israel. In: La Niece, S., Hook, D., Craddock, P. (Eds.), Metals and Mines: Studies in Archaeometallurgy. Archetype Publications, London, pp. 189–201.

Wertime, T.A., 1980. The pyrotechnological background. In: Wertime, T.A., Muhly, J.D. (Eds.), The Coming of the Age of Iron. Yale University Press, New Haven, pp. 1–24.

Workman, V., Maeir, A.M., Dagan, A., Regev, J., Boaretto, E., Eliyahu-Behar, A., 2020. An Iron IIA Iron and bronze workshop in the lower City of tell es-Safi/Gath. Tel Aviv 47, 208–236.

Yahalom-Mack, N., Gadot, Y., Eliyahu-Behar, A., Bechar, S., Shilstein, S., Finkelstein, I., 2014. Metalworking at Hazor: a long-term perspective. Oxf. J. Archaeol. 33, 19–45.