



Crucible technologies in the Late Bronze–Early Iron Age South Caucasus: copper processing, tin bronze production, and the possibility of local tin ores



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ABSTRACT

The South Caucasus was a major center of metal production in the Late Bronze and Early Iron Ages. Nowhere is this more clear than in the hills and mountains in the southeastern Black Sea region (ancient Colchis), where exceptionally large numbers of metal production sites have been found. Chemical and microscopic analysis of slagged technical ceramics at these sites illuminates several aspects of both raw copper and tin bronze alloy production. Copper ores were smelted in a complex multi-stage process designed to extract metal from sulfide ores. Technical ceramics served as containers for a range of different reactions, from the first phase of smelting, in which the copper sulfides were likely consolidated into a matte, though later stages of matte processing and metal copper production in smaller crucibles. In addition, a single crucible fragment, recovered from a late 2nd millennium BC slag heap, demonstrates that tin bronze was created by the direct addition of cassiterite tin ore, probably of alluvial origin, to metallic copper. The crucible's context, the use of cassiterite ore rather than tin metal, and a review of local geology suggests that the tin used in this crucible came from nearby, with the most likely source being the Vakijvari and Bzhuzhi gorges roughly 10–15 km away. While a single fragment does not speak to the regularity of this practice, at the very least it raises the possibility that the Colchian bronze industry was based on local rather than imported tin.

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1. Introduction

Copper and copper-alloy production flourished in the southeastern Black Sea region (modern western Georgia) during the Bronze Age (Abesadze, 1958; Abesadze and Bakhtadze, 2011 [1988]; Tavadze and Sakvarelidze, 1959). The region has a large number of copper ore deposits, and there was substantial ancient copper mining and smelting, especially during the height of the Late Bronze–Early Iron Age Colchis Culture (c. 1500–600 BC) (Erb-Satullo et al., 2014; Gzelishvili, 1964; Khakhutaishvili, 2009 [1987], 2006; Khakhutaishvili and Tavamaishvili, 2002; Mudzhiri, 2011). Large numbers of slagged technical ceramic fragments

have been recovered from copper production sites in the region. Previous analyses of production debris (Erb-Satullo et al., 2014) demonstrated that copper was extracted from sulfide ore deposits in a complex process involving ore roasting, and possibly involving an intermediate stage of matte production. In the present study, the examination of the slagged fragments of technical ceramics allows us to clarify several aspects of the production of raw copper. In addition, the in-depth analysis of one crucible fragment, which has a tin-rich slag on its interior surface, illustrates the techniques of alloying and tin bronze production. Although tin bronze is widely distributed in the South Caucasus by the Middle–Late Bronze Age, the processes of tin acquisition and the spatial organization of bronze production remain open questions (Abramishvili, 2010). A clear understanding of the dynamics of production and trade is a necessary prerequisite for discussing political and economic developments in these societies.

Analyses of technical ceramic slags are supplemented with analyses of metal inclusions in a range of different slags from these

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sites. Several slags without adhering technical ceramic from the same site as the tin-rich sample were also analyzed. The goal of these additional analyses is to confirm that, as suspected from macroscopic observations and comparisons with neighboring sites, the bulk of metallurgical activities related to copper smelting. Taken together, these data clarify several aspects of raw copper production and illuminate how and where the tin bronze was produced.

2. The question of tin supplies in the Near East and the South Caucasus

The search for Bronze Age tin sources, tin ore distribution networks, and tin production debris has a long pedigree. Afghanistan is often cited as a likely source of tin for Mesopotamia (Cleuziou and Berthoud, 1982; Crawford, 1974), though there are some outstanding questions, at least for the Early Bronze Age (Thornton and Giardino, 2012). Direct evidence of 3rd millennium BC tin mining is lacking for this region. Tin mining remains dating to the 2nd millennium BC have been found in Tajikistan and Uzbekistan (Boroffka et al., 2002), as well as Kazakhstan (Stöllner et al., 2011). Early 2nd millennium BC textual evidence from Anatolia and Mesopotamia points unequivocally to the east as a source of tin, but the “sources” named in the texts probably refer to way stations rather than points of origin (Thornton and Giardino, 2012:254; Weeks, 2003:179). Overall, while 3rd millennium BC tin sources are hotly debated, eastern tin sources for Near Eastern bronzes are more widely accepted for the 2nd millennium BC.

Controversy surrounds the discovery of an ancient tin mine at Kestel and its accompanying settlement, Göltepe, in the Taurus mountains of Anatolia (Earl and Özbal, 1996; Yener, 2000; Yener and Goodway, 1992; Yener et al., 1989). Based on analytical and experimental work, researchers argue that tin oxide was reduced to tin metal in crucibles, while alloying took place elsewhere (Earl and Özbal, 1996; Vandiver et al., 1993). Many critiques (Hall and Steadman, 1991; Muhly, 1993; Pernicka et al., 1992) have focused on the low tin content (averaging about 0.2 wt.%) of the remaining ore, the apparent lack of tin bronzes in contemporary local metal assemblages (however, see Lehner and Yener, 2014:544–545 for counterexamples), and early 2nd millennium BC textual evidence for tin importation. Ongoing research suggests that there is still much to learn about ancient tin sources on the Anatolian Plateau (Lehner, 2014; Lehner and Yener, 2014:532; Yener et al., 2015).

The South Caucasus has long been marginalized in the discussion of tin sources for the wider Near East. Nonetheless, references to possible tin deposits in the Caucasus have surfaced from time to time. Early work mentions a source of tin ore in the vicinity of Metsamor, Armenia, and tin-rich slags found on the site itself (Crawford, 1974:242; Mkrtiachan, 1967), but this contrasts with a contemporary report, which states that cassiterite and stannite are found only as insignificant accessory minerals in a few deposits (Akopyan, 1967). Moreover, the only published analytical measurement of a Metsamor slag yielded only 0.005% Sn (Mkrtchyan et al., 1967:72), so it is difficult to confirm the statements about tin ore and tin-rich slags. Several sources mention a possible tin deposit in South Ossetia in the central portion of the Greater Caucasus range (Crawford, 1974:242; de Jesus, 1978:37), but these can be traced back to a single remark in a secondary source (Sulimirski, 1970:230–231). Other scholars are more skeptical of the presence of tin ores anywhere in the Caucasus (Selimkhanov, 1978:57). A recent review of early metallurgy in the Caucasus states that the geological conditions are generally unfavorable for the formation of tin deposits, while acknowledging the possibility of unexplored deposits (Courcier, 2014:580). There are some brief references to tin deposits and tin-bearing slags in both the western-central Greater

and Lesser Caucasus ranges (Bezhanishvili, 1933; Hasanova, 2014:65; Kharashvili, 1958:162–165; Tavadzze and Sakvarelidze, 1959:53). Until now, no production debris from tin processing or tin bronze production in the Caucasus has been analyzed in detail.

Despite a lack of mining and production evidence, significant amounts of tin were clearly circulating in the Caucasus by the 2nd millennium BC, if not earlier. Traditionally, arsenical copper is considered the dominant alloy in the Early Bronze Age, with an increasing reliance on tin bronze during the Middle and Late Bronze Ages (Abramishvili, 1999; Kavtaradze, 1999; Meliksetian et al., 2003; Tedesco, 2006:115, 118). However, tin bronzes do occasionally show up earlier, appearing in a late-Neolithic context at Aruchlo (Hansen, 2012) and at Early Bronze Age Velikent in the North Caucasus (Kohl, 2003; Peterson, 2003). The former case is one of the earliest tin bronze objects found in the Near East (for other, not entirely uncontroversial examples from the Near East and southeastern Europe, see Garfinkel et al., 2014; Radivojević et al., 2014; Radivojević et al., 2013; Šljivar and Borić, 2014). Moreover, even in the Late Bronze–Early Iron Age, tin bronze was not a universal alloy (Abesadze, 1958:58–59, 98–99; Kavtaradze, 1999:86–87). Certainly by the Late Bronze Age, people in the Caucasus used metallic tin and lead–tin alloys, a practice that continued into the Early Iron Age (Khanzadian and Piotrovskii, 1992:68; Prange and Yalçin, 2001; Selimkhanov, 1978). Some hypothesize that the Caucasus region maintained long-distance trading contacts, importing tin, gold, and lapis lazuli from Central Asia in the 3rd millennium BC (Apakidze, 1999; Edens, 1995:60–61). However, the suggestion that Central Asia or the Eurasian steppes served as the main source of tin for the Late Bronze Age Caucasus has some paradoxical corollaries, given the dramatic scale of metal production and increasing frequency of tin bronze in the late 2nd millennium BC. If this were the case, the expansion in the long-distance trade in tin would correspond to the period when the shared metalworking traditions of the preceding Early–Middle Bronze Age – Chernykh’s (1992) Circumpontic Metallurgical Province – took on a more regionalized character in the Caucasus. The result is an implausible, though not impossible, juxtaposition of increasing long distance metal trade with decreasing exchange of metallurgical ideas (Kohl, 2007:122).

Given the lack of well-investigated production evidence for the alloying, mining, or smelting of tin, any evidence of tin processing has the potential to address key questions. First, was tin bronze created by mixing of separately smelted tin and copper metal, by adding tin ore to copper metal, or by direct co-smelting of copper and tin ores (Charles, 1978)? Second, at what stage in the production process did alloying take place? Third, does the context or composition of the production debris suggest a possible source for the tin ore?

3. Technical ceramics at copper production sites in western Georgia

In three field seasons (2010, 2012, and 2014), our project has mapped about 50 copper production sites in the Supsa-Gubazeuli production area (Erb-Satullo et al., 2014) (Fig. 1). Fragments of friable gray technical ceramic with signs of heavy burning and partial melting on their interior concave surfaces were ubiquitous at production sites. Macroscopic examination of these ceramics suggests that they served a number of different purposes. In several cases, pieces of technical ceramic have been fused to the edges of large slag cakes (Fig. 2), while many other slag cakes have traces of vesicular glassy material where the ceramic has broken off. Measurements of 28 slag cakes yielded an average diameter of 24 cm with a standard deviation of 5 cm. The ceramic probably served as a furnace lining, creating a parting layer between the

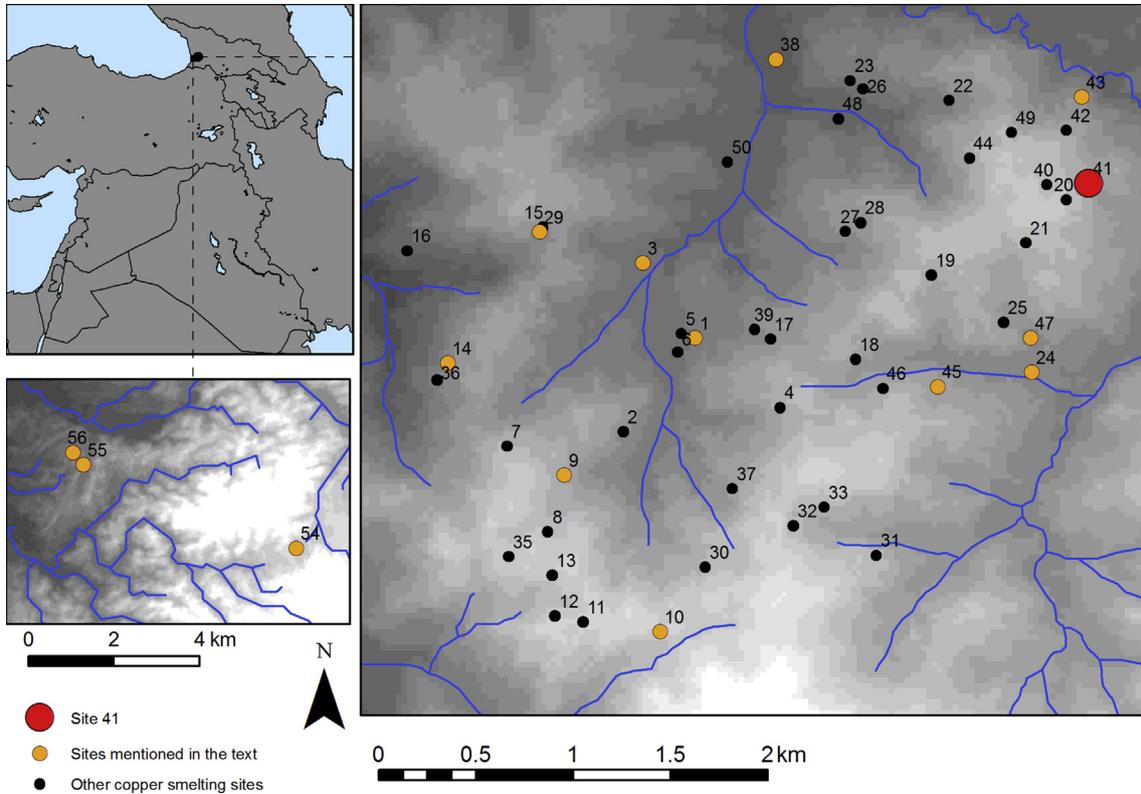


Fig. 1. Map of site locations. Elevation data is from an ASTER DEM (a product of METI and NASA).

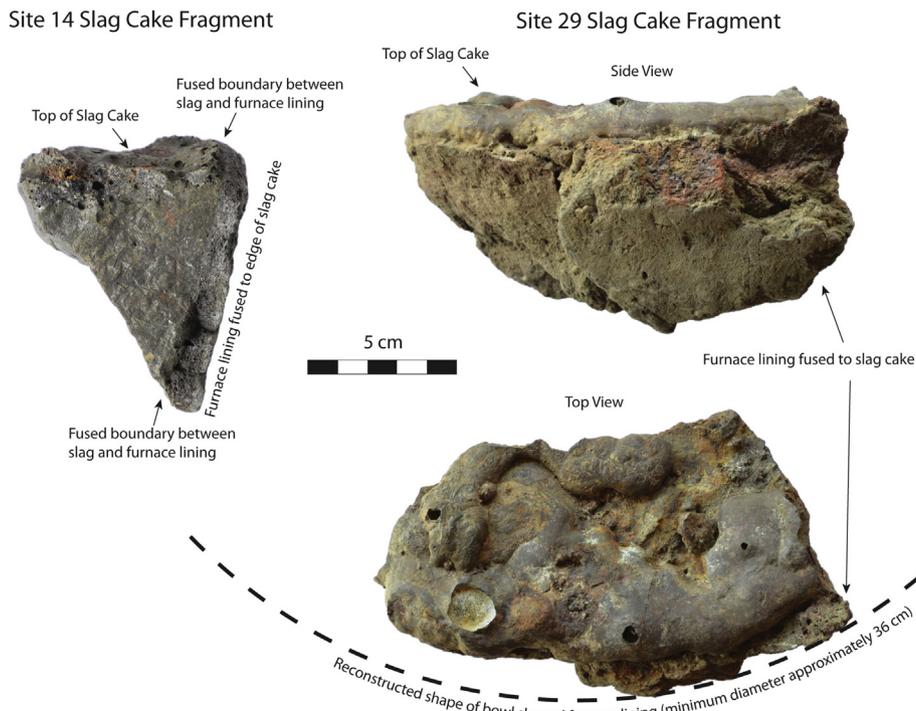


Fig. 2. Dense slag cake fragments from the Supsa-Gubazeuli production area with well preserved pieces of technical ceramic fused to their edges. Most slag cakes are about 20–30 cm in diameter.

sides of the pit furnace and the contents of the furnace. Upon cooling, the contents of the furnace could be dug out and the thick slag cake broken and removed to access the metal-rich phases pooling below.

On the other hand, many technical ceramic fragments are not fused to dense slag cakes, nor do they appear to have broken off from one. Many smaller crucibles reconstructed from rim fragments are too small to contain typical slag cakes, suggesting the

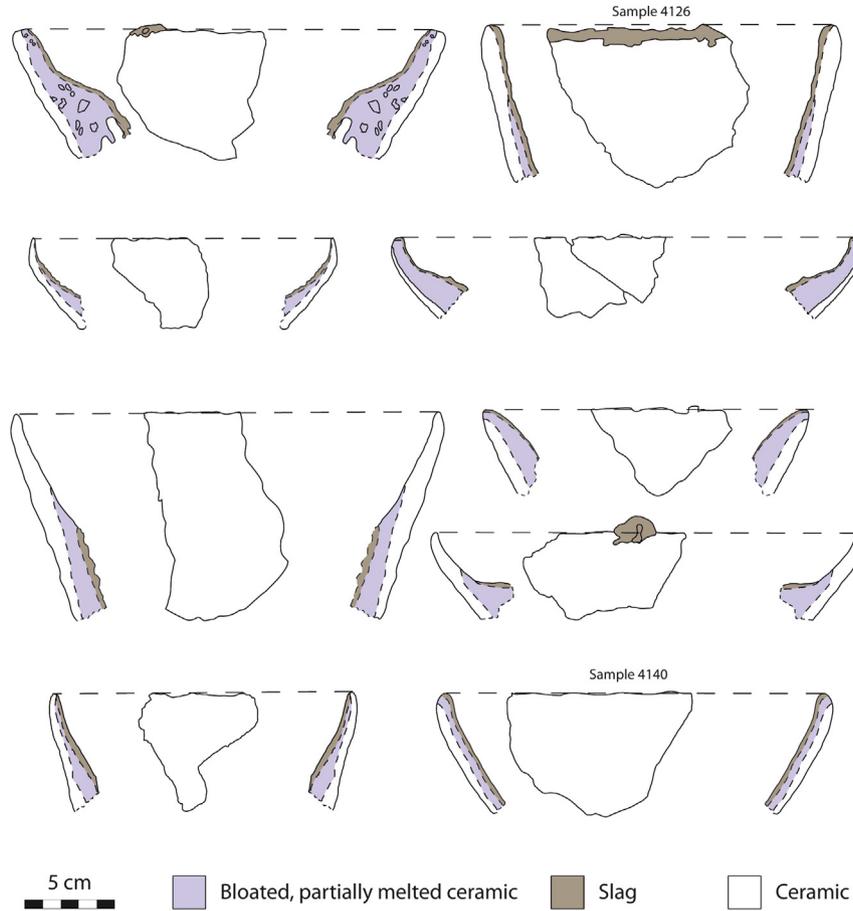


Fig. 3. Selected crucibles from Site 41. Samples which were analyzed by SEM and optical microscopy are labeled.

smaller vessels were used for a different process (Fig. 3). Given their smaller size, they could have been more easily maneuvered when full, and there are several instances where slag has spilled over the rim, perhaps in the process of skimming slag off the surface of the crucible's contents. While the examination of the assemblage as a whole clearly shows these different purposes, not all the slagged fragments of technical ceramic are easily categorized individually as belonging to one process or another. For example, several samples (4103, 4117 and 4508) have a layer of dense slag several centimeters thick, but it is unclear whether they are actually part of a larger slag cake. The tin-rich technical ceramic (sample 4110) is clearly a crucible rim though the fragment is too small to reconstruct the vessel's size or shape (Fig. 4).

Two small 1 × 1 m test excavations at Site 41, conducted in 2012 and 2014 uncovered a densely packed matrix of slag, charcoal, abundant fragments of technical ceramic (including the tin-rich sample), and a few pieces of non-metalurgical pottery. A charcoal sample (*Castanea sativa*) collected from the bottom of the slag heap near the natural clay sub-sediment yielded a date of 1279–1112 calBC (95.4% probability). While some inbuilt age is possible for woody charcoal, the high fuel throughput of smelting means that the old wood effect from long-term storage of cut wood is unlikely (Levy et al., 2004:869). This date is consistent with other similar sites in the vicinity (Gilmour et al., in prep; Khakhutaishvili, 2009 [1987]:105–106).



Fig. 4. Photograph of sample 4110, the tin-rich crucible, showing the whitish prills visible on interior convex surface and a view of the cut section. In both views, the rim of the fragment is towards the center of the image.

4. Analytical methods

In order to determine the function of these gray technical ceramic vessels, polished sections were prepared from 20 samples of slag fused to technical ceramics. Some samples were prepared as polished thin sections to allow for transmitted light microscopy. The samples were analyzed by the lead author using optical microscopy (OM) and scanning electron microscopy (SEM) using an Oxford Instruments INCA X-Sight SEM–EDS. Area analyses were conducted by energy dispersive X-ray spectrometry (EDS) with detection limits of about 0.3 wt.%. The goal was to average over the largest area possible while avoiding large voids, corroded areas, and in the case of slag, unmelted inclusions. For the slag, area analyses were typically about 0.05–0.2 mm², while those carried out on ceramic were around 2–4 mm².

In order to contextualize the tin-rich slagged ceramic, a Bruker Tracer III–V portable X-ray fluorescence (pXRF) spectrometer was used to qualitatively analyze many slagged crucible rim fragments from Site 41, looking for large tin peaks similar to the one seen in the qualitative pXRF spectrum of sample 4110. Measurements were made on the interior slagged surface of all crucible fragments with a minimum of 100-s count intervals. Initially, repeat measurements were done at different points on the same object, but this made little difference, so this step was omitted in later analyses. Additionally, four samples of slag from Site 41 without ceramic adhesions were mounted and analyzed microscopically to confirm that the overall picture of pyrotechnological activities at the site was in line with neighboring copper smelting sites.

Lastly, metallic phases in slags of various types were analyzed by wavelength dispersive X-ray microanalysis (WDS). If tin bronze was produced by co-smelting copper and tin ores, we would

expect metallic prills found in copper smelting slags to contain some tin.

5. Results

5.1. Analysis of slags adhering to technical ceramics

Most slags adhering to technical ceramics contain no tin. These slags are generally similar to slag cakes and spongy amorphous slag fragments found at copper smelting sites (Erb-Satullo et al., 2014). Typically, these slags are dominated by olivines (fayalite–forsterite solid solution series), and frequently contain iron oxides such as magnetite. A range of copper-bearing phases were identified, including copper sulfides and copper–iron sulfides. Iron sulfides are present, but less common, especially in the slag glazes on crucible rims. Many sulfides are in the shape of spherical matte prills that formed in the molten state. Interestingly, metallic copper prills were frequently found in thin slag layers covering technical ceramics, many of which are smaller crucibles (Fig. 5). This contrasts with the relative infrequency of copper prills found in the broader slag assemblage (Erb-Satullo et al., 2014:152).

Distinctive, partially-reacted clusters of copper– and iron–bearing compounds were also found in many samples, including several which are clearly smaller crucibles (Fig. 6). Sample 4116 is a small rim fragment of a crucible from Site 41 with a thin layer of slag adhering to the interior surface. While the fragment's small size prohibited a precise reconstruction of the vessel diameter, its shape and thickness shows that it definitely came from a smaller crucible rather than a larger furnace lining. A fragment of partially-reacted copper–iron sulfide (mostly chalcopyrite, but with small amounts of bornite and covellite), iron

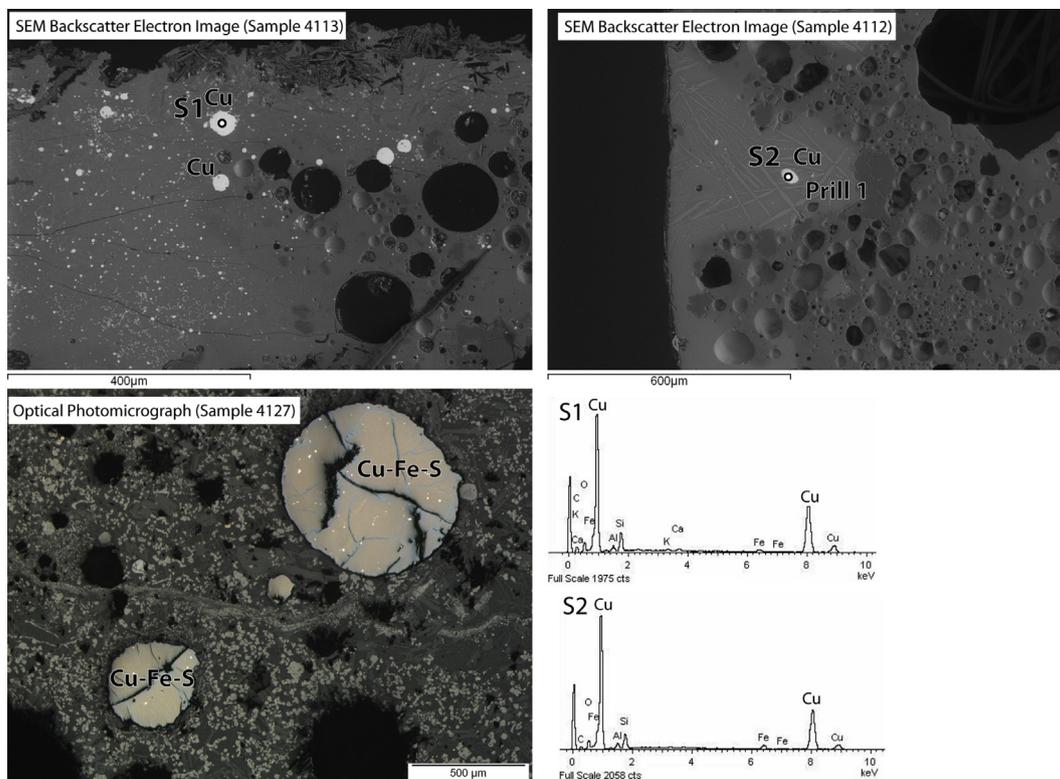


Fig. 5. Copper metal and copper sulfide prills in slagged technical ceramics, along with selected EDS spectra. Samples 4112 and 4113 have small prills of copper metal (Cu) trapped in the slagged surface. The copper prill in the upper right image is prill 1, sample 4112 in the table of WDS analyses (Table 4). The optical photomicrograph of sample 4127 shows two large matte prills (Cu–Fe–S) containing copper, sulfur and a little iron in a matrix of iron oxide (magnetite) and olivine (fayalite) crystals.

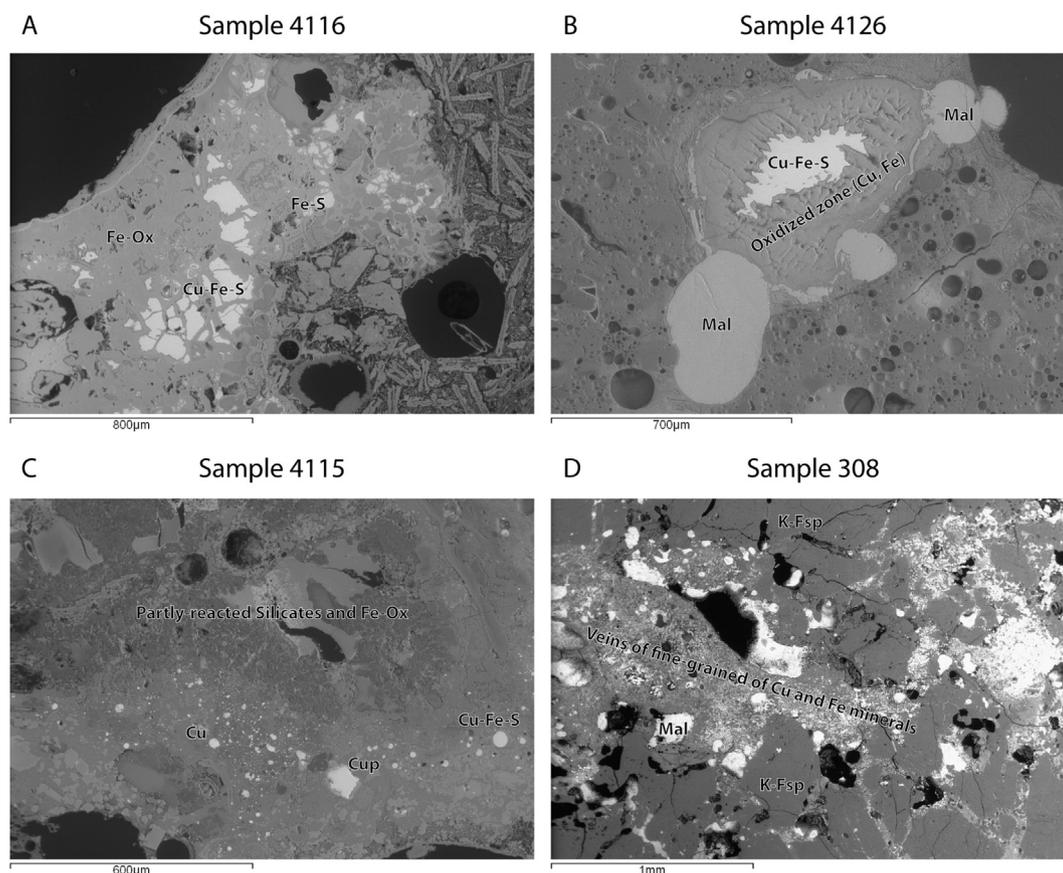


Fig. 6. Partially reacted ore fragments in slagged technical ceramics. Samples 4116, 4126, and 4115 definitely come from smaller crucibles, while the shape of the technical ceramic in 308 was difficult to reconstruct. Abbreviations: Fe–Ox, iron oxide; Fe–S, iron sulfide; Cu–Fe–S, copper–iron sulfide; Cu, copper metal, Cup, cuprite; Mal, malachite; K–Fsp, potassium feldspar.

sulfide (pyrite or pyrrhotite), and hydrated iron oxides was found in the thin slag layer (Fig. 6A). Similar clusters of copper–iron sulfides are found in samples 4126 and 4140, both of which were crucibles whose shape and diameter were possible to reconstruct (Figs. 3 and 6B). These instances can either be interpreted as primary ore fragments or partially roasted pieces of matte from an earlier stage of production, though in the case of sample 4116, the presence of iron sulfide (pyrite or pyrrhotite) argues for the former case.

Other examples are more clearly fragments of ore and gangue, due to their associations with silicate minerals. Sample 4115, a crucible with an everted rim, contained numerous small prills of metallic copper in association with partly melted silicates and iron oxides (Fig. 6C). It is likely that this cluster of minerals is a partially reacted fragment of ore. Sample 308 also contained a large fragment of partially melted potassium feldspar with a vein of copper- and iron-rich compounds. Unfortunately, the size of the reaction vessel from which sample 308 was taken is impossible to reconstruct, but the slag's morphology bears little similarity to dense slag cakes. Taken together, these examples strongly suggest that copper sulfides were added to these crucibles, probably in the form of both processed matte and as (roasted?) ore.

In terms of their bulk chemistry, slags adhering to technical ceramics are similar to those that are not (Table 1, Fig. 7). Slight differences can be easily explained by the fact that slags fused to technical ceramics are likely to have more Si and Al due to the partial melting of the ceramic.

5.2. Analysis of the tin-rich slag adhering to a crucible fragment (sample 4110)

Aside from the whitish prills of corroded tin-bronze, sample 4110 appears macroscopically similar to other crucible rim fragments. On a microscopic scale, the slag layer contains many metal prills ranging in size from $<5\ \mu\text{m}$ up to $700\ \mu\text{m}$ (Fig. 8). The slag layer contains numerous partially reacted inclusions, such as iron oxide, pyroxene (diopside–hedenbergite solid solution series), quartz, and feldspar (alkali and plagioclase) (Figs. 9 and 10). Freshly-crystallized olivines (fayalite–forsterite solid solution series) forming at the edge of the partially reacted iron oxide attest to fairly reducing conditions in the melt (Hauptmann, 2007:22–23). Two partially-reacted grains of cassiterite (SnO_2) were also observed in the portion of the sample closer to the rim. The morphologies of these grains indicate that they were primary additions rather than crystals forming from the melt (Fig. 10). These examples differ from other examples of tin oxide crystals that more clearly formed through preferential oxidation of tin-bronze prills (Fig. 11), in that they are larger and are not directly associated with large metal prills. Moreover, the grain in the upper image of Fig. 10 has a clearly rounded appearance, which is indicative of a partially-reacted mineral (see similar interpretations in Chirikure et al., 2010:1661–1662; Merideth, 1998:155–159; Rademakers et al., in prep). Two partially-reacted grains of rutile (TiO_2) were also identified (Fig. 12) just 2 mm from one cassiterite grain and 3.2 mm from the other. Only one tiny prill of copper sulfide ($\sim 60\ \mu\text{m}$) was identified, in contrast with the sulfide-rich copper smelting slags.

Table 1
Normalized SEM–EDS area analyses of slags on technical ceramics, and of several slags not adhering to technical ceramics. Numbers represent the average of four different area measurements, with the exception of samples 4112 (3 areas) and 4115 (2 areas), which had minimal areas of uncorroded slag. Compositions are reported in normalized oxide wt.%. Numbers in the context column are context numbers for test pits in slag heaps.

Sample	Site	Context	Sample description	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	K ₂ O	CaO	TiO ₂	MnO	FeO	CuO	ZnO	BaO
307	3	Surface	Small amount of slag on technical ceramic rim sherd	0.3	5.4	9.9	38.0	0.5	0.5	1.8	8.9	bdl	0.3	32.8	1.0	bdl	0.7
308	3	Surface	Thick layer of slag on technical ceramic	0.5	3.0	13.0	37.1	0.5	0.8	2.4	7.4	0.4	bdl	32.9	1.3	bdl	0.6
309	3	Surface	Small piece of dense slag on technical ceramic, possibly part of slag cake	0.5	3.8	12.7	41.1	0.5	0.5	2.0	8.2	0.4	0.3	29.3	0.3	bdl	0.3
1003	10	Surface	Lumps of spongy slag on technical ceramic	0.7	1.4	7.5	27.5	0.3	1.3	0.7	1.1	bdl	0.3	54.0	0.4	4.2	0.7
3806	38	1001	Small amount slag on technical ceramic rim sherd	0.4	4.4	12.0	35.8	0.5	0.4	0.8	9.2	0.3	bdl	35.8	0.5	bdl	bdl
4103	41	Surface	Thick dense slag layer on technical ceramic, possibly part of slag cake	0.9	1.5	12.8	36.4	0.3	1.1	2.3	2.8	0.4	bdl	40.3	0.6	bdl	0.6
4104	41	Surface	Porous slag with abundant partially-reacted inclusions	0.6	1.6	11.3	35.8	0.4	0.8	2.4	2.1	0.5	bdl	39.7	0.5	bdl	4.4
4106	41	1001	Porous slag with abundant partially-reacted inclusions	0.7	1.8	11.2	36.1	0.3	1.2	2.3	3.2	0.4	bdl	41.7	0.4	bdl	0.7
4109	41	Surface	Dense slag, likely part of slag cake	0.5	3.5	9.8	40.7	bdl	1.4	1.6	3.5	0.3	bdl	36.3	bdl	bdl	2.3
4111	41	1001	Porous slag layer on technical ceramic	0.5	2.1	10.0	33.1	0.3	1.0	1.6	5.0	0.3	bdl	43.9	0.9	bdl	1.2
4112	41	1001	Thin slagged layer on technical ceramic rim sherd	0.7	2.6	15.2	43.3	0.6	bdl	2.1	5.1	0.6	0.3	28.5	1.0	bdl	bdl
4113	41	1001	Thin slagged layer on technical ceramic rim sherd	0.7	3.6	13.2	42.0	0.8	bdl	2.4	7.8	0.7	0.3	16.8	11.3	bdl	0.4
4114	41	1001	Porous slag with curvature suggesting it cooled over a tuyère	0.3	1.6	9.0	27.2	0.4	1.5	1.1	1.4	0.3	bdl	56.7	0.5	bdl	bdl
4115	41	Surface	Thin slagged layer on technical ceramic	0.5	2.2	11.8	36.9	0.3	1.3	1.9	5.8	0.4	bdl	38.0	bdl	bdl	1.0
4116	41	Surface	Slagged layer on technical ceramic	0.8	1.8	16.2	42.8	0.4	bdl	2.8	4.5	0.5	bdl	27.3	2.1	bdl	0.8
4117	41	Surface	Thick dense slag layer on technical ceramic, possibly part of slag cake	0.7	2.1	12.8	36.6	0.5	0.6	2.2	4.2	0.4	bdl	36.2	0.6	0.3	2.7
4126	41	2003	Thin slag layer on technical ceramic rim sherd	0.4	1.8	7.1	21.7	0.3	1.4	1.4	1.4	0.3	bdl	62.2	1.9	bdl	bdl
4127	41	2003	Thin slag layer on technical ceramic rim sherd	0.7	1.9	8.1	33.6	0.3	1.0	2.0	3.9	0.3	bdl	46.9	1.1	bdl	0.3
4131	41	2003	Thin slag layer on technical ceramic rim sherd	0.5	2.1	10.6	33.1	0.3	1.3	2.4	3.4	0.5	bdl	44.9	0.7	bdl	0.4
4140	41	2002	Thin slag layer on technical ceramic rim sherd	0.6	4.0	12.2	34.6	0.6	1.7	2.1	3.8	0.3	0.4	38.8	0.3	bdl	0.6
4144	41	2002	Thin slag layer on technical ceramic rim sherd	0.3	4.8	12.4	33.6	0.4	0.9	1.6	3.9	0.5	bdl	40.4	0.9	bdl	0.3
4312	43	1001	Thin slag layer on technical ceramic	0.9	1.4	11.3	33.8	bdl	0.5	1.8	2.5	0.4	bdl	45.3	2.1	bdl	bdl
4508	45	Surface	Thick slag layer on technical ceramic, possibly part of slag cake	1.2	2.2	11.5	36.6	0.3	1.3	2.0	3.5	0.5	bdl	35.7	0.8	3.5	1.0
5402	54	Surface	Thin slag layer on technical ceramic	1.5	1.0	11.3	41.6	bdl	2.7	2.2	1.9	bdl	bdl	26.8	0.3	9.0	1.6

Energy dispersive area analyses were carried out on both the slag (avoiding partially melted inclusions, which included quartz, feldspar, and pyroxenes, along with some iron oxides) and on the ceramic, to allow major and minor element comparisons between the two (Table 2). The composition of the slag is significantly influenced by the melting of the crucible. However, the slag has more iron and tin, and less silicon and aluminum than the ceramic. The elevated iron may derive either from detrital iron oxides or the

iron content of the copper metal added to the crucible. The high calcium content of the slags relative to the ceramic may represent the contribution of fuel ash (Rademakers et al., in prep).

Heavy minerals such as rutile, pyroxene, and iron oxides are suggestive of an alluvial placer ore deposit (Chirikure et al., 2010:1665). However, it is essential to rule out the possibility that the heavy mineral inclusions in the slag come from the partial melting of the technical ceramic. The mineral inclusions in the

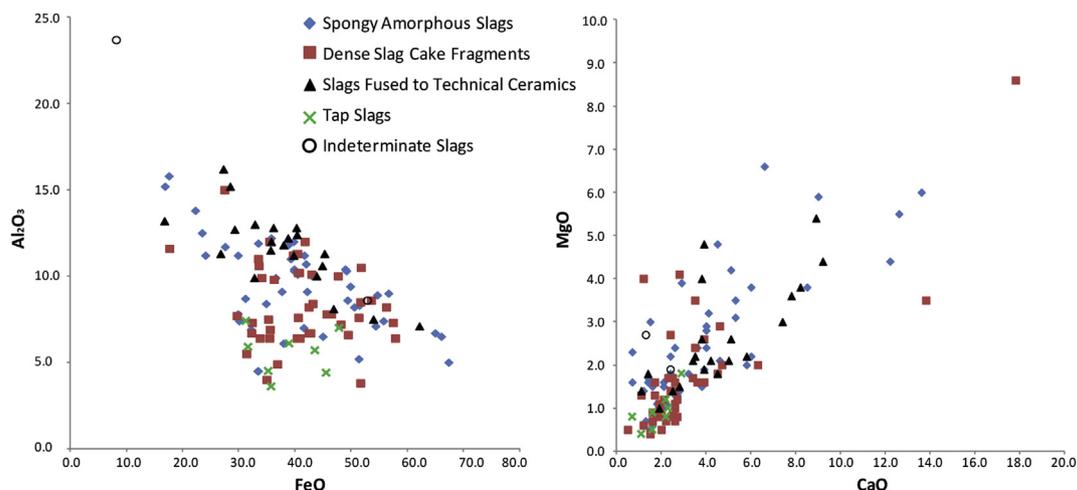


Fig. 7. Plots of Al₂O₃ vs. FeO and MgO vs. CaO for different slag types. Chemical data from Table 1 and Erb-Satullo et al. (2014:Table 4).

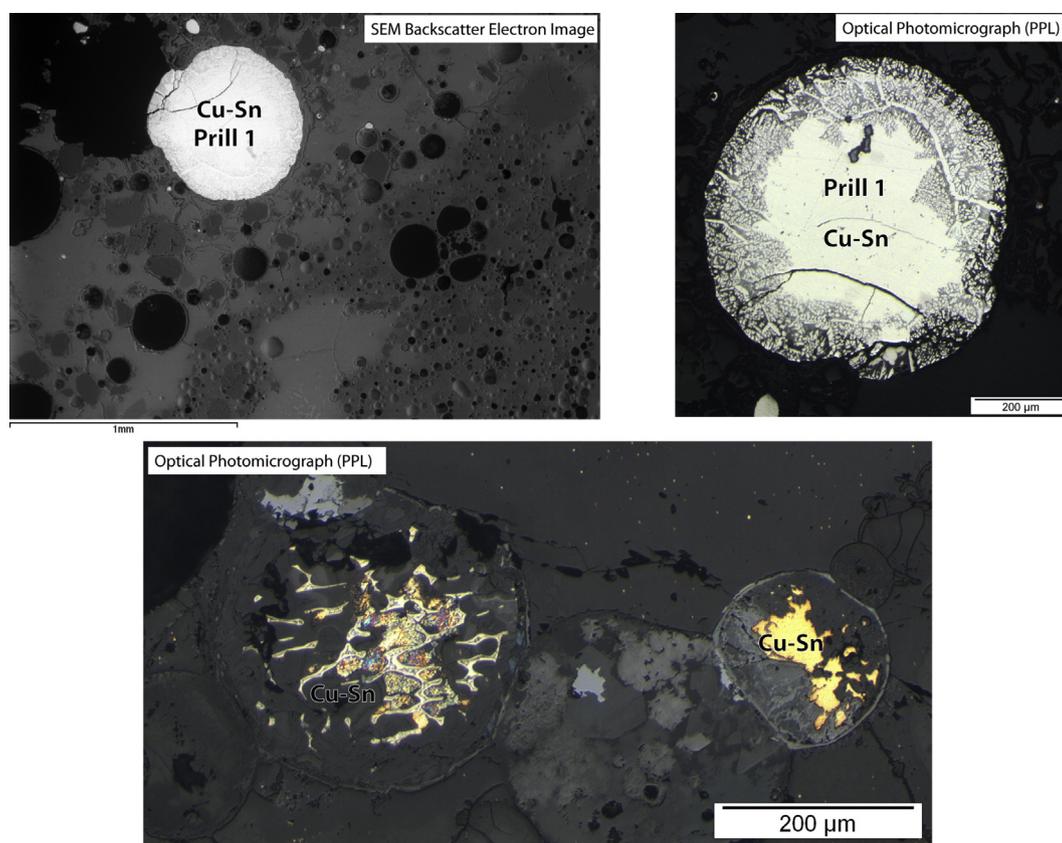


Fig. 8. SEM and OM images of sample 4110, showing tin bronze prills (Cu–Sn), including prill 1 in sample 4110 analyzed by WDS (Table 4). In the lower right area of the SEM image, the boundary between the slag and the vitrified ceramic is visible. Prills in the lower image are heavily corroded, but clearly display different microstructures, indicating variable Sn content.

ceramic fabric consist mostly of quartz and feldspars, with occasional pyroxenes. Iron oxides were also found in the ceramic fabric. However, no instances of rutile or cassiterite were identified. In order to quantify key mineralogical differences, partially-reacted pyroxenes and iron oxides over 200 μm were counted and mineral frequencies per mm² were calculated for the sample prepared for thin section analysis (Table 3). Pyroxenes were found in much higher frequencies in the slag than in the ceramic. The slag layer

also contains some large pyroxenes (>350 μm), which have no counterparts in the ceramic. These comparisons show that pyroxenes were part of the crucible charge. For iron oxides, the frequency differential is smaller, though as mentioned above, the elevated iron in the slag relative to the ceramic may be the result of dissolved iron oxides. In addition, more than half the iron oxides counted in the ceramic layer had spongy morphologies, meaning that they would quickly dissolve or drastically diminish in size if the ceramic were melted. These observations suggest that there are more iron oxides in the slag than one would expect if the relict iron oxides came from the ceramic alone.

5.3. Qualitative pXRF survey of technical ceramic rim fragments

A pXRF survey of 51 additional fragments of technical ceramic collected during the 2012 and 2014 field seasons failed to identify additional samples with large tin peaks comparable to that of sample 4110. While this pXRF survey covered only a small fraction of the total production debris at the site, it shows that tin alloying was only part of a broader range of metal production activities.

5.4. Analysis of slags not adhering to technical ceramics from Site 41

A few slag samples not adhering to technical ceramics were analyzed microscopically to determine whether they were similar to copper smelting slags at neighboring sites. Indeed, these slags align closely in terms of chemistry and mineralogy with the large body of slags analyzed previously (Table 1) (Erb-Satullo et al.,

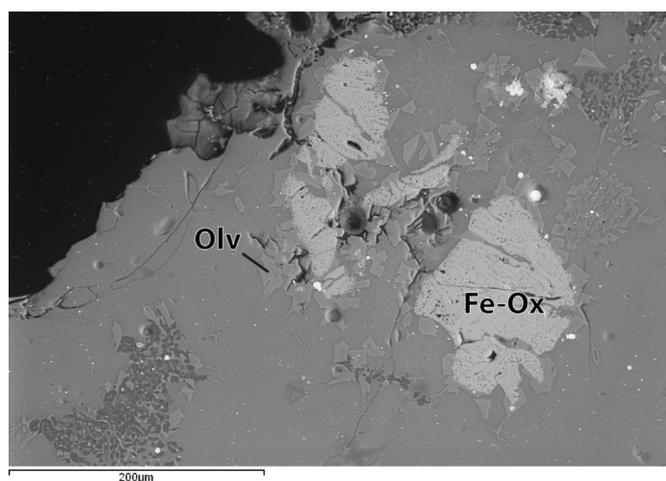


Fig. 9. SEM backscatter image of partially reacted iron oxide (Fe-Ox), along with angular, freshly formed olivines (Olv) in sample 4110.

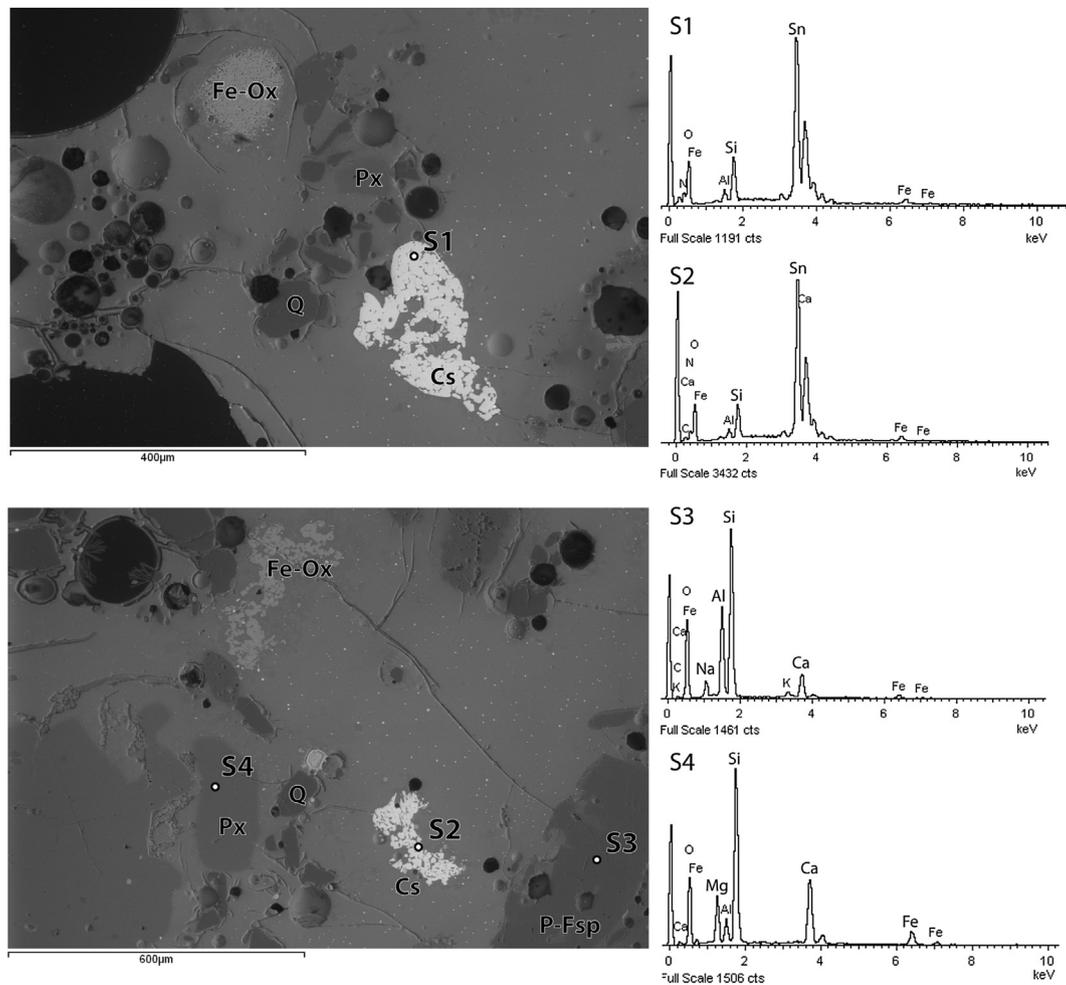


Fig. 10. SEM backscatter images of sample 4110, showing partially reacted cassiterite (Cs), iron oxide (Fe-Ox), pyroxene (Px), quartz (Q) and plagioclase feldspar (P-Fsp), along with associated EDS point spectra. Small white dots are tiny prills of tin bronze. Note the rounded edges, particularly indicative of partially reacted cassiterite, in the grain in the upper image.

2014). The main mineralogical phases identified in the slags were iron silicates (mostly fayalite), iron oxides (mostly magnetite) and sulfides of copper and iron (Fig. 13). These slags confirm that raw copper production was practiced at Site 41, as at numerous neighboring sites.

5.5. WDS microanalysis of metal prills in slags from the Supsa-Gubazeuli production area

Copper prills are relatively rare in slags from the Supsa-Gubazeuli production area, a feature suggesting good slag-metal separation and possibly a separate matte production phase in which little or no copper metal was created. 36 WDS microanalyses were carried out on 18 metal prills in 16 different samples from 8 sites (Table 4). Analysis of three different prills in sample 4110 showed that the tin content in these uncorroded prills ranged from 17 to 39 wt.%, though this does not mean that the bulk composition of the metal produced was more than 20 wt.% Sn. The iron content of sample 4110 prills is low, with the exception of the prill 2 measurement (3.01 wt.%), which might include elements from the slag matrix due to the small size of the prill relative to the beam diameter. Measurements of arsenic in the range of 0.5–1 wt.% are atypical for other metal prills analyzed in this study, though Cu–As and Cu–Sn–As alloys are common in metal objects (Abesadze and Bakhtadze, 2011 [1988]:346–361). The higher arsenic content

might indicate that the copper was recycled metal, but it may simply be due to variability in local ore sources.

The rest of the samples analyzed by WDS came from slags of various types either from Site 41 itself or from sites a few kilometers away. Most came from spongy amorphous slags or slagged technical ceramics, and most prills have only one visible metallic phase, occasionally with small sulfide inclusions. These prills typically consist of 97 wt.% or more of Cu, with the balance mostly iron. Two exceptions are the prills from sample 901 and 4144, which have 5.91 wt.% Ni and 1.21 wt.% Ag, respectively. Prills with multiple metallic phases were found only in samples 4704, 101, and 302 (Fig. 14). In the latter two cases, the metallic prills consisted of a copper-rich and an iron-rich phase, which formed due to the limited solid solubility of iron in copper. In both cases, the iron-rich phase have about 8–9 wt.% Cu and 5–7 wt.% Mo. Since molybdenum-bearing minerals are a component of copper ore deposits in southwestern Georgia (Gugushvili et al., 2010:335), the presence of molybdenum is unsurprising. The high nickel and cobalt content of the whitish phases in sample 4704 (see Table 4) is somewhat unexpected, but these metallic phases were small fibrous crystals on the edge of larger sulfide prills (Fig. 14), and they should not be taken as representative of the smelted copper's overall composition. Importantly, besides those in sample 4110, the tin content of all these phases, including several copper prills in other slagged technical ceramics from Site 41, is never greater than

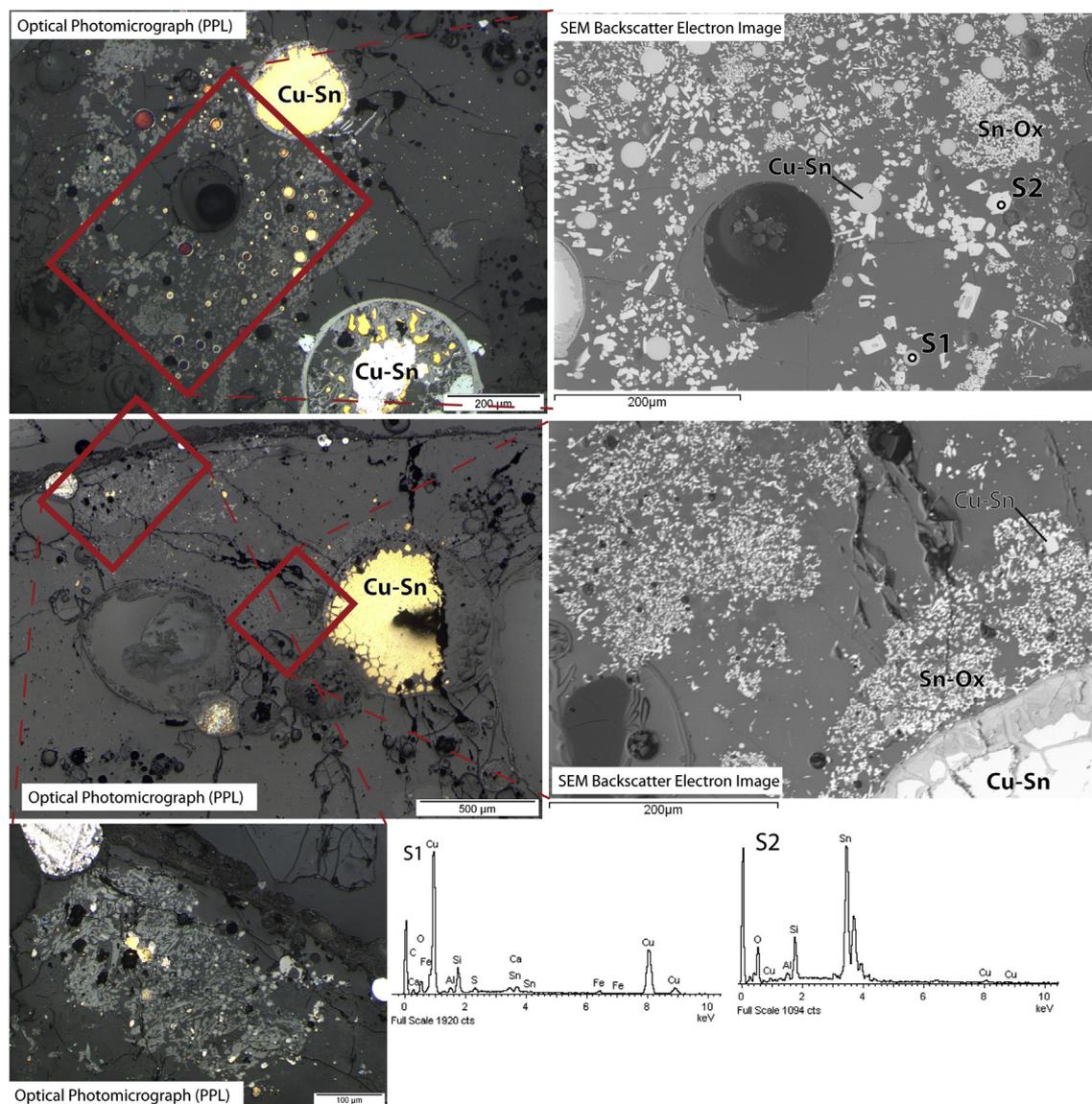


Fig. 11. Optical photomicrographs and SEM backscatter images of sample 4110, showing bronze prills (Cu–Sn) and associated tin oxide crystals (Sn–Ox), with relevant EDS spectra. The dispersed, feathery masses of small crystals associated directly with bronze prills were likely formed through preferential oxidation from the bronze prills in the molten state. A possible exception is the cluster magnified in the bottom left, which, though mostly re-crystallized and containing small tin bronze prills dispersed within it, has a relatively well defined shape.

0.06 wt.%. This demonstrates that alloying must have taken place in a separate step after the production of raw copper.

6. Discussion

6.1. Technical ceramics used for copper smelting

In our recent paper on copper smelting technology (Erb-Satullo et al., 2014), it was difficult to interpret the significance of the two dominant categories of slag, one consisting of dense slag cake fragments, with the other consisting of spongy amorphous slag masses, slag drips, and small lumps. Careful macroscopic and microscopic examination of slagged technical ceramics helps to resolve these outstanding questions. Dense slag cakes are likely the product of an initial phase of copper smelting, in which ore and gangue were smelted, producing a sulfide matte and probably some metallic copper. This process produced the large dense slag cakes, which show evidence of extended heating, but also contain some

large fragments of partially-reacted ore (Erb-Satullo et al., 2014, Fig. 7A). The matte from this initial production stage was probably then processed further in smaller crucibles, perhaps with an intervening stage of roasting. The charge was likely fluxed, probably using siliceous gangue left over from ore beneficiation, which contained small pieces of sulfide minerals. This flux would react with iron oxidizing from the matte to produce a slag. Because of their smaller size, the crucibles could have been moved between the deep pit furnaces and the more open roasting platforms (Erb-Satullo et al., 2014:156), allowing for better control of oxidizing and reducing atmospheres. Slags were skimmed or poured off the surface of the melt, producing the spongy, amorphous slag with charcoal impressions on the bottom (Fig. 15). Most of these spongy slags do not have the classic ropey flow textures of tap slags, since they were rather viscous and often contain partially reacted gangue minerals, fluxes, etc. The small number of more typical tap slags noted previously (Erb-Satullo et al., 2014:150–151), are likely the result of the same slag-skimming process, but a combination of

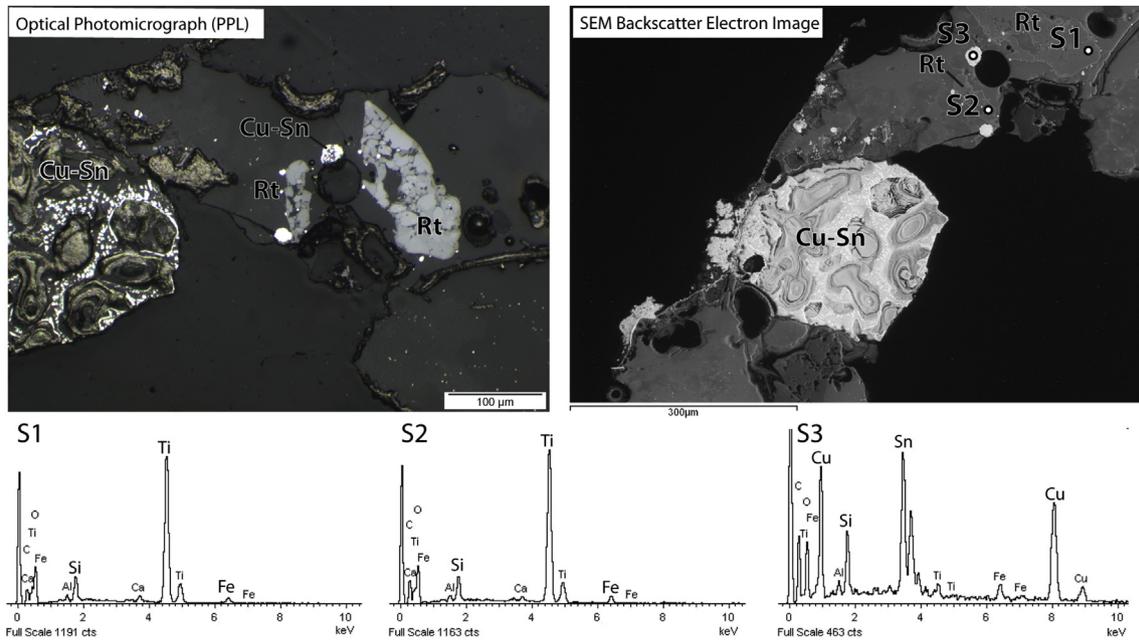


Fig. 12. Optical photomicrograph and SEM backscatter image of sample 4110 showing two partially reacted rutile crystals (Rt) and a large corroded prill of tin-bronze (Cu–Sn), with relevant associated EDS spectra.

Table 2

SEM–EDS area analyses of slag and ceramic portions of sample 4110, the crucible with tin-rich slag. Values are given in normalized oxide wt.%, with the exception of Cl, which is given in elemental wt.%. Detection limit was estimated conservatively at 0.3 wt.%. Abbreviations: bdl – below detection limit.

Location	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	Cl	K ₂ O	CaO	TiO ₂	MnO	FeO	NiO	CuO	ZnO	SnO ₂	PbO
Slag	0.7	3.5	10.7	47.1	0.8	bdl	bdl	2.3	8.2	0.5	0.3	16.8	bdl	0.8	bdl	8.3	bdl
Slag	1.1	3.6	11.1	47.6	0.7	bdl	bdl	2.5	9.0	0.6	0.4	17.2	bdl	0.4	bdl	5.7	bdl
Slag	1.1	4.8	10.0	46.5	0.7	bdl	bdl	2.2	11.4	0.7	0.5	18.7	bdl	0.4	bdl	3.1	bdl
Slag	1.1	4.3	10.5	45.7	1.4	bdl	bdl	1.7	14.8	0.6	0.7	17.9	bdl	0.4	bdl	0.8	bdl
Ceramic	0.8	2.6	20.8	57.6	0.5	bdl	0.7	2.8	1.7	0.9	bdl	11.2	bdl	bdl	bdl	bdl	0.3
Ceramic	1.3	2.0	20.7	59.1	0.8	0.5	0.9	3.1	1.4	0.8	bdl	9.4	bdl	bdl	bdl	bdl	bdl
Ceramic	1.5	2.3	19.5	59.9	bdl	bdl	bdl	3.3	1.9	0.8	bdl	10.1	bdl	bdl	bdl	0.4	0.3
Ceramic	1.0	2.2	20.1	60.3	0.3	bdl	0.6	2.5	1.2	1.2	bdl	10.5	bdl	bdl	bdl	bdl	bdl

temperature and slag composition gave them greater fluidity. The fact that most if not all of these “tap slags” are rich in zinc suggests that the type of ore may have played a role as well.

Whether this increased fluidity was an intentional goal is difficult to say, though there are other hints of slight variation within the framework of the copper smelting process sketched above. At least one furnace excavated in the Soviet-period was built into a hillside with one side open, allowing slag to be removed directly from the furnace, and several others differ slightly from the basic pit furnace structure (Khakhtaiashvili, 2009 [1987]:61, 65, 69–72,

Table 3

Counts and densities of partially-reacted iron oxides (Fe-Ox) and pyroxenes (Px) over 200 microns in the slag and the ceramic portions of sample 4110, as identified by optical microscopy. The iron oxide count may include other partially reacted minerals of similar reflectance (ilmenite, rutile, etc). Iron oxide count for the ceramic is likely inflated by the presence of porous iron hydroxides inclusions, which would probably dissolve if the ceramic were melted. Some low-birefringence pyroxenes were identified by microchemical analysis, but these were not included in the count because they could not be distinguished reliably from other minerals by optical methods.

	Area (mm ²)	Fe-Ox count	Px count	Fe-Ox frequency (cts/mm ²)	Px frequency (cts/mm ²)
Slag	75.07	3	8	0.040	0.107
Ceramic	313.47	9	6	0.029	0.019

78–79). In our current fieldwork, a few examples of rather large masses of spongy slag were found, possibly indicating attempts to carry out the second stage using larger reaction volumes.

The process of removing slag may have been repeated several times, as each progressive phase further enriched the copper matte at the expense of iron. The final conversion to copper metal may have taken place after the copper-rich matte was roasted in solid state, or it may have occurred through interactions between copper oxides, forming at the surface of the matte after all the iron had been removed, and the remaining copper sulfides (Rostoker, 1975:312). The higher frequency of copper metal prills in thin slag glazes on smaller crucibles provides further indication that the final production of metallic copper took place in these vessels.

Qualitative comparisons of mineral phases in spongy and dense slags also support this hypothesis. The proportion of dense slag cakes with abundant metallic copper prills is smaller than the proportion of spongy slags with metallic copper. This suggests that the dense slags are the product of an earlier stage of production, when little copper metal had formed. Admittedly, these mineralogical differences are not very sharp – there are dense slag cakes with metallic copper, and not every spongy slag contains copper metal.

Several aspects of copper smelting likely obscure sharp mineralogical and chemical differences between slag types. First, partly-roasted or naturally-oxidized ores added to the initial phase of smelting may have resulted in some copper metal being produced

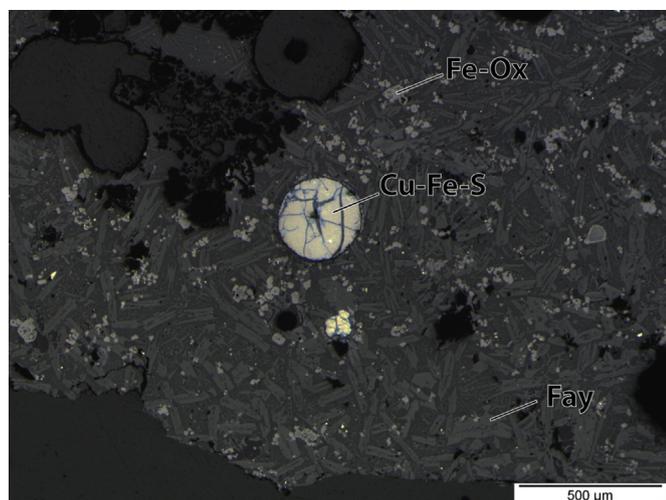


Fig. 13. Optical photomicrograph of a spongy amorphous slag from Site 41 (sample 4106), showing a matte prill comprised mostly copper–iron sulfides (Cu–Fe–S) with some bluish copper-sulfides, in a matrix of fayalite and magnetite. This slag was probably formed by skimming off the surface of a crucible's molten charge.

during the first stage of production. Second, the introduction of left over siliceous gangue as a flux might introduce small amounts of additional copper sulfides, and would tend to produce slags with chemical compositions similar to those produced in the earlier stage. Third, slag skimmed from crucibles early in the second phase of smelting would likely have little metallic copper compared to slags which were removed at the end of the process, when most of the copper had been converted to its metallic state (for a similar argument about slag composition and timing of removal, see Chiarantini et al., 2009:1634). Removal of molten material early in the crucible stage would produce spongy crucible skimming slags with no copper metal and some more iron-enriched copper sulfides. Finally, a small number of amorphous slags may have formed in the upper reaches of the furnace during the initial reduction, and some dense slags may be produced at the end of the final stage of production, if the copper metal in the crucible was left to cool under a 1–2 cm thick layer of slag.

While some details of the production process remain unclear, it is increasingly difficult to argue against a multi-stage production process involving the intermediate production of matte while still accounting for all the evidence. On the other hand, a multi-stage matte smelting operation explains a wide range of both archaeological and analytical data. By using this complex chaîne opératoire

Table 4

Normalized WDS microanalysis of metallic prills in slags from the Supsa-Gubazeuli production area. Compositions in italics were determined by EDS. Detection limits for WDS are approximately 0.03–0.05 wt.% depending on the element, and 0.3 wt.% for EDS. Abbreviations: bdl – below detection limit; nm–not analyzed. Slag types: A – amorphous spongy slag, probably produced by skimming off crucibles; D – dense slag cake fragment; STC – Slagged technical ceramic; I – indeterminate, used for slags which are difficult to categorize. In this case, sample 4313 is glassy, highly vesicular, and contains many copper metal prills. It is probably from skimming off a crucible, but it has an atypical appearance.

Sample	Site	Prill	Spot#	Slag type	Prill description	P	S	Ti	V	Cr	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Sn	Sb	Pb	Bi
101	1	1	1	A	copper-rich phase	na	na	na	bdl	na	4.03	0.14	0.08	95.66	0.17	bdl	na	bdl	bdl	bdl	bdl	bdl
101	1	1	2	A	copper-rich phase	na	na	na	bdl	na	2.93	0.06	0.06	96.95	0.16	bdl	na	bdl	bdl	bdl	bdl	bdl
101	1	1	3	A	copper-rich phase	na	na	na	bdl	na	3.27	0.05	0.05	96.45	0.06	0.06	na	bdl	bdl	bdl	bdl	bdl
101	1	1	4	A	copper-rich phase	na	na	na	bdl	na	4.13	0.07	0.12	95.52	0.09	0.04	na	bdl	bdl	bdl	bdl	bdl
101	1	1	5	A	copper-rich phase	na	na	na	bdl	na	4.27	0.04	0.08	95.48	0.13	0.06	na	bdl	0.04	0.05	bdl	bdl
101	1	1	6	A	iron rich phase	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>84.10</i>	0.98	0.39	9.44	0.08	0.05	4.96	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na	na
101	1	1	7	A	iron rich phase	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>82.59</i>	0.93	0.44	8.45	0.09	<i>bdl</i>	7.37	na	<i>bdl</i>	<i>bdl</i>	na	na
101	1	1	8	A	iron rich phase	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>84.49</i>	1.01	0.51	7.97	<i>bdl</i>	<i>bdl</i>	5.94	na	<i>bdl</i>	<i>bdl</i>	na	na
101	1	1	9	A	iron rich phase	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>84.83</i>	0.92	0.44	8.63	<i>bdl</i>	0.04	5.02	na	<i>bdl</i>	<i>bdl</i>	na	na
302	3	1	1	A	copper phase in copper prill	na	<i>bdl</i>	na	na	na	3.04	0.15	0.20	96.39	0.15	0.06	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
302	3	1	2	A	separate Fe metal phase	0.03	0.05	na	na	na	83.82	2.07	1.18	7.89	<i>bdl</i>	0.03	4.93	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
304	3	1	1	D	copper prill	na	0.12	na	na	na	0.90	<i>bdl</i>	<i>bdl</i>	98.94	<i>bdl</i>	<i>bdl</i>	na	0.05	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
901	9	1	1	A	copper prill	na	na	na	na	na	2.50	<i>bdl</i>	5.91	91.46	0.06	0.08	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
3807	38	1	1	A	copper prill	na	<i>0.30</i>	na	na	na	0.05	<i>bdl</i>	<i>bdl</i>	99.59	0.06	<i>bdl</i>	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
3807	38	2	1	A	copper prill	na	0.10	na	na	na	0.21	<i>bdl</i>	<i>bdl</i>	99.55	0.09	<i>bdl</i>	na	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	na
3808	38	1	1	A	copper prill	na	na	na	na	na	1.63	0.10	0.11	97.86	0.18	<i>bdl</i>	na	0.07	0.05	<i>bdl</i>	<i>bdl</i>	na
4110	41	1	1	STC	dendrite in large prill	na	na	na	na	na	<i>bdl</i>	0.12	0.05	66.67	<i>bdl</i>	0.42	na	<i>bdl</i>	32.53	0.16	0.05	na
4110	41	1	2	STC	eutectoid in large prill	na	na	na	na	na	0.03	0.29	0.03	73.79	0.05	0.99	na	0.05	24.68	0.09	<i>bdl</i>	na
4110	41	1	3	STC	average over dendrites and eutectoid	na	na	na	na	na	0.04	0.19	0.05	70.77	<i>bdl</i>	0.73	na	<i>bdl</i>	28.10	0.12	<i>bdl</i>	na
4110	41	2	1	STC	very small prill (2 μm diameter)	na	na	na	na	na	3.01	0.09	0.19	79.73	0.1	<i>bdl</i>	na	<i>bdl</i>	16.87	<i>bdl</i>	<i>bdl</i>	na
4110	41	3	1	STC	average over dendrites and eutectoid	na	na	na	na	na	0.03	0.09	0.08	59.77	<i>bdl</i>	0.68	na	0.05	39.22	0.07	<i>bdl</i>	na
4112	41	1	1	STC	copper prill	na	0.22	na	na	na	1.17	0.03	0.37	98.11	0.04	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.05	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
4112	41	1	2	STC	copper prill	na	0.16	na	na	na	1.24	0.02	0.43	97.91	0.11	<i>bdl</i>	<i>bdl</i>	0.08	0.05	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
4115	41	1	1	STC	copper prill	na	0.39	na	na	na	2.65	0.03	<i>bdl</i>	96.62	0.06	0.07	0.05	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.1	<i>bdl</i>
4126	41	1	1	STC	copper prill	na	0.11	na	na	na	0.92	0.04	<i>bdl</i>	98.83	<i>bdl</i>	<i>bdl</i>	0.06	<i>bdl</i>	0.06	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
4127	41	1	1	STC	copper prill	na	0.08	na	na	na	1.37	<i>bdl</i>	0.13	98.29	0.08	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.06	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
4144	41	1	1	STC	copper prill	na	0.04	na	na	na	2.05	0.02	0.06	96.55	0.04	<i>bdl</i>	<i>bdl</i>	1.21	0.04	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
4313	43	1	1	I	copper prill	na	na	na	na	na	<i>bdl</i>	<i>bdl</i>	0.05	99.95	<i>bdl</i>	<i>bdl</i>	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
4313	43	2	1	I	copper prill	na	na	na	na	na	0.27	<i>bdl</i>	<i>bdl</i>	99.55	0.05	0.08	na	0.05	<i>bdl</i>	<i>bdl</i>	na	na
4501	45	1	1	A	copper prill	na	<i>bdl</i>	na	na	na	0.22	<i>bdl</i>	0.12	99.59	0.08	<i>bdl</i>						
4704	47	1	1	D	copper-rich phase	na	na	na	na	na	0.05	0.02	0.08	99.69	0.10	<i>bdl</i>	na	0.06	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
4704	47	1	2	D	whitish metallic phase	na	na	na	na	na	2.29	0.76	11.52	85.32	0.06	0.06	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
4704	47	2	1	D	copper-rich phase	na	na	na	na	na	0.17	0.03	0.05	99.69	<i>bdl</i>	<i>bdl</i>	na	0.05	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
4704	47	2	2	D	whitish metallic phase	na	na	na	na	na	38.47	11.15	41.63	8.74	<i>bdl</i>	<i>bdl</i>	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na
4707	47	1	1	A	copper prill	na	na	na	na	na	0.03	<i>bdl</i>	0.10	99.57	0.06	0.04	na	0.07	<i>bdl</i>	<i>bdl</i>	0.13	na
4707	47	1	2	A	copper prill	na	na	na	na	na	0.03	<i>bdl</i>	0.06	99.91	<i>bdl</i>	<i>bdl</i>	na	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	na

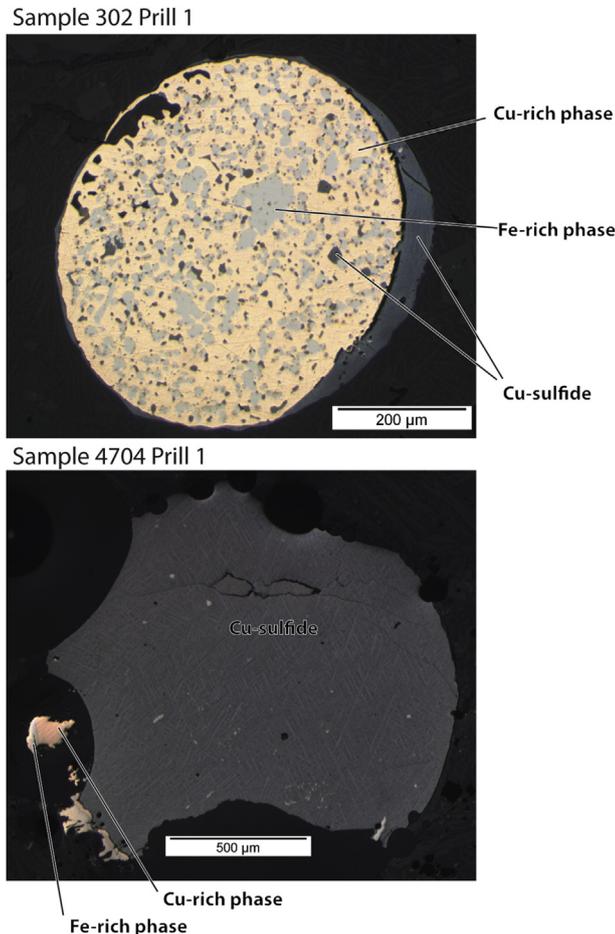


Fig. 14. Complex metallic phases found in west Georgian slags. The prill from sample 301 is very similar to that the one analyzed in sample 101, while prills 1 and 2 in sample 4704 have a very similar appearance.

to extract copper from sulfides, metalworkers were able to increase their metal yield and exploit a wider range of ores.

6.2. Methods of alloying

Analysis of the tin-rich crucible, in combination with WDS microanalysis, demonstrates that alloying was distinct from smelting. There are four conceivable explanations for the tin-rich slag and crucible. The first, rather improbable possibility is that a crucible used to smelt copper was then re-used to smelt tin in a separate episode. The crucible reuse hypothesis is highly unlikely, since the smelting process leaves these crucibles in a vitrified weakened state unsuitable for re-use. Moreover, copper left over from an earlier smelt would likely dissolve in the slag rather than coalesce into large prills. The second possibility, that the crucible was used for melting recycled tin bronze, fails to explain the unreacted cassiterite, the heavy minerals associated with placer deposits, and the high tin content of some prills.

A third possibility is that the crucible was used to create tin-bronze by mixing metallic tin with molten copper. However, it is very unlikely that the tin oxide clusters identified as relict ore grains could have originated from the oxidation of tin or tin-bronze metal. This explanation also does not account for the presence of partially-reacted heavy minerals. The final, most likely explanation is that tin ores, probably of placer (alluvial) origin, were directly combined with copper metal in a reducing atmosphere, a process known as cementation. This is the simplest

explanation for the presence of both the cassiterite grains and detrital heavy minerals: they are simply the residue of the original ore charge.

Similar production debris has been documented elsewhere. Alloying by cementation is proposed for a set of LBA crucibles from Pi-Ramesse in Egypt, which also contain relict grains of cassiterite and prills of high-tin bronze (Rademakers et al., in prep). In southwestern Iberia, Valério et al. (2013) argue for the direct addition of cassiterite to a crucible charge, though in this case, the presence of unreacted copper minerals suggests co-smelting rather than cementation. Morphology is crucial, since tin metal and bronze can oxidize to produce freshly formed tin oxide phases in a slag (Fig. 11) (Rademakers et al., in prep; Rehren, 2001). In the case of the crucible from Site 41, the argument for cementation is further bolstered by the identification of other relict heavy minerals, a feature not documented in other possible cases.

There is some disagreement about the feasibility of making tin bronze by adding cassiterite to molten copper. Several sources suggest that bronze produced by this method would be of lower quality (Moorey, 1999:252), with tin content reaching a maximum of about 1% (Maddin et al., 1977). Another source points out potential problems with controlling tin content (Muhly, 1985:278). However, alloying by cementation is actually more efficient, since it reduces the number of production stages, and therefore the tin loss to the slag (Charles, 1978:27).

The evidence for alloying of tin bronze at a copper smelting site is somewhat surprising. Many chunks of unalloyed copper – in the form of lumps or fragments of roughly-shaped plano-convex ingots – have been found in hoards in western Georgia. By comparison, tin bronze ingots are relatively rare (Abesadze and Bakhtadze, 2011 [1988]:362–365). These results imply that metalworkers frequently transported copper from smelting sites in its unalloyed state. The lack of artifact molds on smelting sites, coupled with their relative frequency at settlement sites (Apakidze, 2009:Table 51; Mikeladze, 1990:26; Mikeladze and Khakhutaishvili, 1985:Table 4), tends to confirm the interpretation that the final stages of artifact formation took place away from sites of raw metal production. The tin-rich crucible from Site 41 complicates this picture. Although the regularity of this practice is unknown, the evidence for cementation may explain why chunks of raw tin metal have not been found in hoards.

6.3. Evidence for local exploitation of tin ores to produce bronze

The tin bronze cementation crucible at Site 41 is thus far a unique case. We cannot say for sure whether it represents the regular method of bronze production or an atypical case. However, a consideration of the regional geology, the context of the find, and the technology of production strongly favors the conclusion that the tin ore used in this crucible came from a deposit in western Georgia.

At first glance, the mostly intermediate igneous geology of southwestern Georgia does not appear to be suitable for tin mineralization, which tends to be associated with acidic igneous rocks (Fig. 16). The Adjara-Trialeti zone is characterized by island-arc geology formed during the closing of the Tethys Sea (Gugushvili et al., 2010). The region is dominated by Eocene andesites, through which intrusions of dioritic and syenitic compositions have penetrated (Nazarov, 1966). Copper, lead, zinc, and molybdenum deposits are commonly associated with these intrusions (Gabunia, 1933; Gugushvili et al., 2010). While tin ores are not major components of these deposits, there are reports of their presence. Tavazde and Sakvarelidze mention approximately 20 places in western Georgia where tin ores have been found (1959:53). Many are in Abkhazia and other parts of the Greater

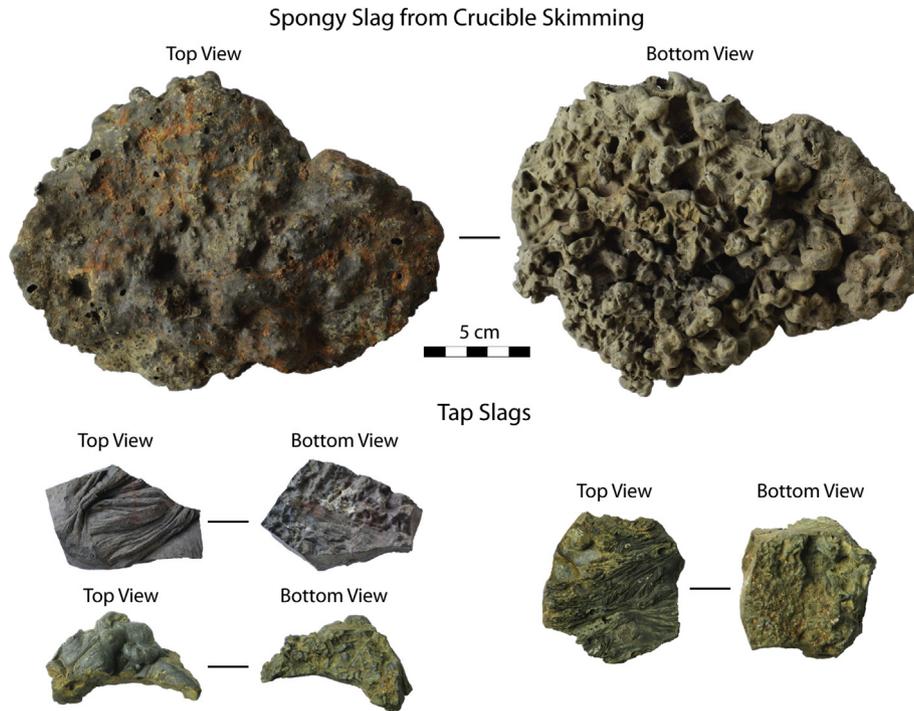


Fig. 15. Spongy slag (Site 24) and more typical tap slags with flow textures. The upper left tap slag is from Site 29, the lower left one is from Site 56, and the one on the right is from Site 55. Both spongy slags and tap slags were likely formed from the same process of pouring/skimming off the surface of molten crucible contents.

Caucasus range with acidic igneous rocks (see [Adamia et al., 2010](#); [Adamia et al., 2011](#):500–501). Significantly, they also report the presence of cassiterite ore in the Bzhuzhi and Vakijvari gorges, only 10–15 km from Site 41 ([Tavadze and Sakvarelidze, 1959](#):53). While the primary deposits are described as subeconomic in modern terms, fluvial action may have created small, relatively enriched pockets of placer ore, which could have been exploited by ancient miners. The crucible from Site 41 also gives added weight to

[Tavadze's and Sakvarelidze's \(1959:53\)](#) reports of tin-bearing slags near these west Georgian deposits. Though these reports do not include analytical data or dating evidence, they raise the possibility that the Site 41 crucible may not be an isolated exception.

The archeological context of the find also supports the notion of a nearby ore source. It makes little sense for tin ore from a distant source to be brought out to a small, relatively out-of-the-way smelting site, when it is clear that secondary melting and casting

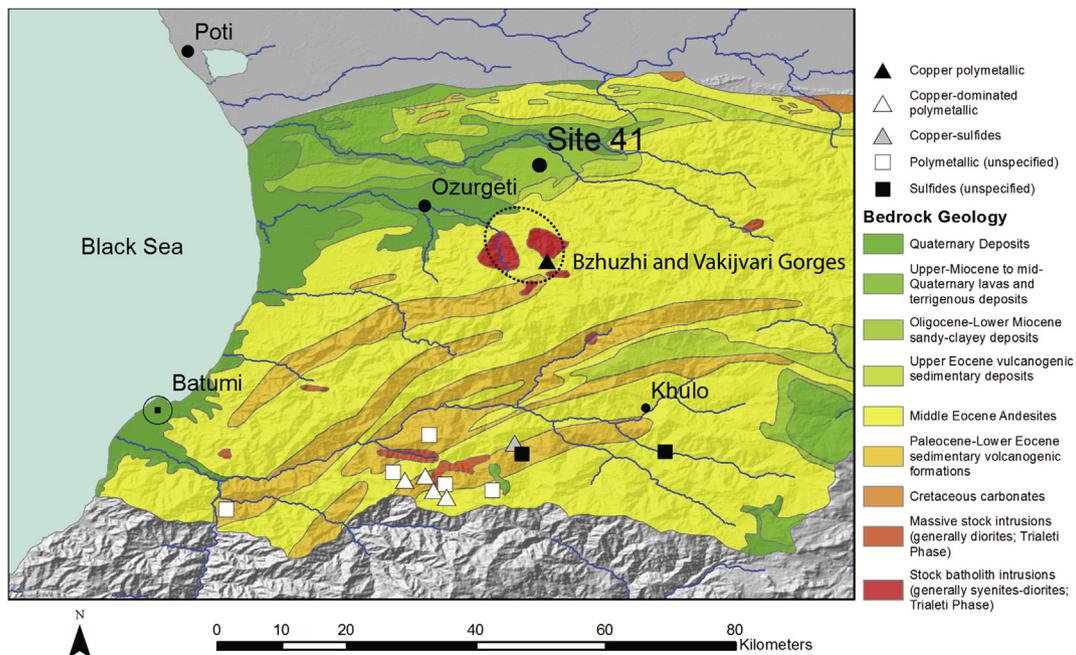


Fig. 16. Geological map of southwestern Georgia, showing location of Site 41, the Bzhuzhi and Vakijvari gorges, and modern towns and cities. Geological data from [Nazarov \(1966: Appendices 3, 5\)](#). Hillshade produced from ASTER DEM (a product of METI and NASA).

were carried out in coastal settlement sites (Apakidze, 2009:Tables 11, 51; Mikeladze, 1990:26; Mikeladze and Khakhutaishvili, 1985:26–27, Table 36). Because tin traded over long distances would probably arrive first in the more populated coastal and riverine areas, it would make much more sense simply to alloy tin with copper at settlement sites immediately before casting into artifacts. A far more likely scenario is that, in this instance, the tin ore was brought directly from a relatively nearby mine to the smelting/alloying site, probably along with the copper ores used for smelting. Only then would the products of smelting and alloying be transported elsewhere for casting and forging into weapons, tools, and other items.

The use of tin ore rather than tin metal is also suggestive of a relatively local ore source. Several scholars have argued that it is unlikely that raw tin ore was transported long distances (Maddin et al., 1977:45; Moorey, 1999:252). Because cassiterite is roughly 20 wt.% oxygen, and ancient smelting processes were far from 100% efficient, a given amount of tin metal weighs less than the ore required to make it. Admittedly, the transport of placer cassiterite over some distance is not totally implausible. Cassiterite was likely brought to workshops in urban Pi-Ramesse in the Nile Delta (Rademakers et al., in prep), while the nearest possible ore sources are in the Eastern Desert (Muhly, 1985:283; Muhly, 1993:244; Wertime, 1978). Although these deposits are several hundred kilometers away from Pi-Ramesse, the Nile considerably lessens transport times, and they are certainly closer than alternative sources (e.g. Central Asia). The context in which the crucible was found, the use of placer cassiterite, and a reconsideration of the local geology all point to a local tin source.

7. Conclusions

Ceramic reaction vessels were used for a variety of purposes at Late Bronze–Early Iron Age metal production sites in western Georgia. Some were used to contain large slag cakes, likely produced during the early stages of the production process. These vessels were too large to manipulate when filled with molten slag, so they were probably left to cool in the furnace at which point their contents would have been removed. Copper sulfide matte produced in this initial stage would then be processed further in smaller crucibles which could be moved in and out of the furnace with a lower risk of breakage. Slag floating on the surface was repeatedly skimmed off, producing the ubiquitous spongy amorphous slags. Throughout this process, matte would be progressively enriched in copper and depleted in iron. Eventually, copper-rich iron-poor matte was reduced to copper, either through oxide–sulfide interactions in the molten state or after a separate roasting stage.

At least one ceramic crucible was used to create tin bronze. The analysis of this crucible has some intriguing potential implications for the organization of metal production and the possibility of local ore sources in the Caucasus. Evidence for alloying using cassiterite ores diversifies the picture of production activities taking place at these relatively isolated smelting sites. Moreover, the archaeological context of the crucible and the use of cassiterite give weight to the hypothesis of relatively nearby tin sources. An examination of local geology suggests that the Bzhuzhi and Vakijvari gorges, 10–15 km to the south, are likely sources, consistent with the crucible's findspot at a foothills site. The crucible is thus far an isolated case, though it casts previously unsubstantiated claims of tin-rich slags (Tavadze and Sakvarelidze, 1959:53) in a new light. The evidence for the diversity of production pathways, as demonstrated by the contrasting conclusions from the crucible and the chemical data on ingots in hoards, is particularly interesting. Only by examining such production debris in detail can we understand

the economic systems that produced such massive quantities of tin bronze in the Caucasus.

The new evidence from the tin alloying crucible, coupled with a review of the archaeological and geological literature, suggests we must seriously consider the possibility that exploitation of local tin was an important component of metal production in the Caucasus. It is too early to say whether local tin mining could have supplied the bulk of tin required for Colchian bronzes, but this remains a plausible possibility. There is certainly more evidence for local exploitation than for large-scale long distance imports from the east in the late 2nd and early 1st millennium BC. Perhaps models for technological and social change based on the LBA–EIA eastern Mediterranean, which prominently feature dependence on such long-distance networks of exchange, are less applicable to the Caucasus and neighboring regions. Indeed, while this period did herald some significant social and technological developments, they must be considered on their own terms.

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