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 sulphide ores. Technical ceramics served as containers for a range of different reactions, from the first phase of smelting, in which the copper sulphides 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 sulphide 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
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 (Gleizou 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, Çöltepe, 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 flow tin content (averaging about 0.2 wt.%) of the remaining ore, the apparent lack of tin bronzes in contemporary local metalworking traditions (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.

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 castings (Fig. 2), while many other slag castings have traces of vesicular glassy material where the ceramic has broken off. Measurements of 28 slag castings 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
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
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-metallurgical 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).
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 adherences 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–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

![SEM Backscatter Electron Image (Sample 4112)](image)

![Optical Photomicrograph (Sample 4127)](image)

**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.
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 μm up to 700 μm (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 (SnO₂) 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 (TiO₂) 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 (~60 μm) was identified, in contrast with the sulfide-rich copper smelting slags.
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 slag...
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.,
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
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
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 (Khakhutaishvili, 2009 [1987]:61, 65, 69–72, 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.

Table 2

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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 hydroxide 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.

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<th>Px count</th>
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<td>9</td>
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</table>

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.
during the first stage of production. Second, the introduction of left
dense slags may been produced at the end of the
process involving the intermediate production of matte while still
accounting for all the evidence. On the other hand, a multi-stage
slagging operation explains a wide range of both archaeo-
logical and analytical data. By using this complex chain opératoire

![Image](image-url)

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.

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.

<table>
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<th>Sample</th>
<th>Site</th>
<th>Prill</th>
<th>Spot#</th>
<th>Slag type</th>
<th>Prill description</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Mo</th>
<th>Ag</th>
<th>Sn</th>
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<td>na</td>
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</table>

Table 4 (continued)

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 vitriolic 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 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 copper minerals suggesting 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 Adjaro-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 (Cavunia, 1933; Gugushvili et al., 2010). While tin ores are not major components of these deposits, there are reports of their presence. Tavadze 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
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...
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 objects.

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 about 10 km east of the Eastern Desert (Muhlly, 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 Bzuhuzi and Vakiivari 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 Salvarelidze, 1958:52) 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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