CRUCIBLE TECHNOLOGIES IN THE LATE BRONZE-EARLY IRON AGE SOUTH CAUCASUS: COPPER
PROCESSING, TIN BRONZE PRODUCTION, AND THE POSSIBILITY OF LOCAL TIN EXPLOITATION

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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 a 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.

Keywords

Tin; Caucasus; Craft Production; Near East; Late Bronze Age; Early Iron Age; Crucible; Smelting; Ore

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 substantial ancient copper mining and smelting remains, 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]; Khakhutaishvili, 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 copper 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 processes 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 (Cleuziou and Berthoud, 1982; Crawford, 1974), though there are some doubts, 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., in press).

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 slags yielded only 0.005% Sn (Mkrtchyan, et al., 1967:72), so it is difficult to confirm the statements about tin ore in secondary sources. 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 sources are much 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 in the literature 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; Tavadze and Sakvarelidze, 1959:53). Until now, no production debris from tin processing or tin bronze production in the Caucasus has been analyzed in detail.

109 Despite a lack of mining and production evidence, significant amounts of tin were clearly
110 circulating in the Caucasus by the 2nd millennium BC, if not earlier. Traditionally, arsenical
111 copper is considered the dominant alloy in the Early Bronze Age, with an increasing reliance on
112 tin bronze during the Middle and Late Bronze Ages (Abramishvili, 1999; Kavtaradze, 1999;
113 Meliksetian, et al., 2003; Tedesco, 2006:115, 118). However, tin bronzes do occasionally show
114 up earlier, appearing in a late-Neolithic context at Aruchlo (Hansen, 2012) and at Early Bronze
115 Age Velikent in the North Caucasus (Kohl, 2003; Peterson, 2003). The former case is one of the
116 earliest tin bronze objects found in the Near East (for other, not entirely uncontroversial
117 examples from the Near East and southeastern Europe, see Garfinkel, et al., 2014; Radivojević,
118 et al., 2014; Radivojević, et al., 2013; Šljivar and Borić, 2014). Moreover, even in the Late
119 Bronze-Early Iron Age, tin-bronze was not a universal alloy (Abesadze, 1958:58-59, 98-99;
120 Kavtaradze, 1999:86-87). Certainly by the Late Bronze Age, people in the Caucasus used
121 metallic tin and lead-tin alloys, a practice that continued into the Early Iron Age (Khanzadian
122 and Piotrovskii, 1992:68; Prange and Yalçin, 2001; Selimkhanov, 1978). Some hypothesize that
123 the Caucasus region maintained long-distance trading contacts, bringing tin, gold, and lapis
124 lazuli from Central Asia in the 3rd millennium BC (Apakidze, 1999; Edens, 1995:60-61).
125 However, the suggestion Central Asia or the Eurasian steppes served as the main source of tin
126 for the Late Bronze Age Caucasus has some paradoxical corollaries, given the dramatic scale of
127 metal production and increasing frequency of tin bronze in the late 2nd millennium BC. If this
128 were the case, the expansion in the long-distance trade in tin would correspond to the period
129 when the shared metalworking traditions of the preceding Early-Middle Bronze Age--Chernykh's
130 (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, where and when did alloying take place in the production process? Third, does the context of 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) (figure 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 (figure 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 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 most slag cakes, suggesting the smaller vessels were used for a different process (figure 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, on an individual basis, not all the slagged fragments of technical ceramic are easily categorized 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 (figure 4).

Test excavations on Site 41 yielded a large sample of crucible rim fragments, including the tin-rich fragment. Two small 1 x 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, and a few pieces of 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 from the vicinity (Gilmour, et al., in press; 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. In several instances, 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 on the order of 0.05 -0.2 mm², while those carried out on ceramic were around 2-4 mm².

In order to contextualize the find, 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-second count intervals. Initially, repeat measurements were done at different points on the same object, but this made little difference in the presence or absence of a tin peak, and 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 contained no tin. These slags generally share many similarities with slag cakes and spongy amorphous slag fragments found at copper production 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 were present, but are less common, especially in the slag glazes on crucible rims. Many sulfides are in the form of spherical matte prills forming from the molten state. Interestingly, metallic copper prills were frequently found in thin slag layers covering technical ceramics, many of which are smaller crucibles (figure 5). This contrasts with the relative dearth of copper prills found in much of 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 (figure 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 sulfides (mostly chalcopyrite, but with small components of bornite and covellite), iron sulfides (pyrite, or pyrrhotite), and hydrated iron oxides was found in the thin slag layer (figure 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 (figures 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 gangue minerals. Sample 4115, a crucible with an everted rim, contained numerous small prills of metallic copper in association with a partly melted silicates and iron oxides (figure 6C). The prills are clearly associated with this fragment, and it is likely that the cluster 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 bears little similarity to dense slag cakes. Taken together, these examples strongly show 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, figure 7). Slight differences can be easily explained by the fact that slags fused to technical ceramic 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-rich 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 $<5\text{ }\mu\text{m}$ up to $700\text{ }\mu\text{m}$ (figure 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) (figures 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 crystallizing from the melt (figure 10). These examples differ from other examples of tin oxide crystals that more clearly formed through preferential oxidation of tin-bronze prills (figure 11), in that they are larger and are not directly associated with large metal prills. Moreover, the grain in the upper image of figure 6 has a clearly rounded appearance, which is indicative of a partially-reacted minerals (see similar interpretations in Chirikure, et al., 2010:1661-1662; Meredith, 1998:155-159; Rademakers, et al., in press). Two partially-reacted grains of rutile (TiO_2) were also identified (figure 12) just 2 mm from one cassiterite grain and 3.2 mm from the other. Only one tiny prill of copper sulfide 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 possibly from 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 press).

Because heavy minerals such as rutile, pyroxene, and iron oxides are suggestive of an alluvial placer ore deposit (Chirikure, et al., 2010:1665), 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 ceramic fabric consist mostly of quartz and feldspars, with occasional pyroxenes. Iron oxides are 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 mm^2 were calculated for the sample prepared for thin section analysis (table 3). Pyroxenes were found in much higher densities in the slag than in the ceramic. The slag layer also contains some large pyroxenes ($>350 \mu\text{m}$), 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. Moreover, more than half the iron oxides counted in the ceramic layer were spongy iron hydroxides, which 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 a large and unmistakable tin peaks in the spectra comparable to 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 taking place at the site.

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 test 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 (figure 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 the evidence of a separate matte production phase in which little or no copper metal was created. 36 WDS microanalyses of 18 metal prills in 16 different samples from 8 sites were carried out (table 4). Analysis of three different prills in sample 4110 showed that the tin content in these uncorroded prills ranged from 17-39 wt.%, though this does not mean that the bulk composition of the metal produced was more than 20 wt.% Sn. The iron content of these 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 had 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 had 5.91 wt.% Ni and 1.21 wt.% Ag, respectively. Prills with multiple metallic phases were found only in samples 4707, 101, and 302 (figure 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 had about 8-9 wt.% Cu, with 5-7 wt.% Mo. Since molybdenum-bearing minerals are noted as a component of copper ore deposits in southwestern Georgia (Gugushvili, et al., 2010:335), the presence of molybdenum is not unexpected. The high nickel and cobalt content of the whitish phases in sample 4704 (see table 4) are somewhat surprising, but these metallic phases were small fibrous crystals on the edge of larger sulfide prills (figure 14), and they should not be taken as representative of the smelted copper's overall composition. Importantly, the tin content of all these phases, including several copper prills in slagged technical ceramics from Site 41, was 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 (figure 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 type of ores 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 a couple of 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 dry 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 supports this hypothesis. The proportion of dense type 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 exceedingly sharp--there are dense slag cakes with metallic copper, and not every spongy slag contains copper metal.

Several aspects of copper smelting likely cloud 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 during the first stage

of production. Second, the introduction of leftover siliceous gangue as a flux might introduce small amounts of additional copper-sulfides, and would tend to produce slags with a chemical composition similar to those produced in 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). This would lead to the creation of 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 been 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 in order to limit the re-oxidation of the copper.

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. This complex chaîne opératoire allowed metalworkers to maximize their yield by extracting copper from sulfide 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

405 unlikely, since the smelting process leaves these crucibles in a vitrified weakened state
406 unsuitable for re-use. Moreover, copper left over from an earlier smelt would likely dissolve in
407 the slag rather than coalesce into large prills. A second possibility, that the crucible was used for
408 melting recycled tin bronze, fails to explain the unreacted cassiterite, heavy minerals associated
409 with placer deposits, and the high tin content of some prills.

410 A third possibility is that the crucible was used to create tin-bronze by mixing metallic tin
411 with molten copper. However, it is very unlikely that the tin oxide clusters identified as relict ore
412 grains could have originated from the oxidation of tin or tin-bronze metal. This explanation also
413 does not account for the presence of partially-reacted heavy minerals. The final, most likely
414 explanation is that tin ores, probably of placer (alluvial) origin, were directly combined with
415 copper metal in a reducing atmosphere, a process known as cementation. This is the simplest
416 explanation for the presence of both the cassiterite grains and detrital heavy minerals: they are
417 simply the residue of the original ore charge.

418 Similar production debris has been documented elsewhere. Alloying by cementation is
419 proposed for a set of LBA crucibles from Pi-Ramesse in Egypt, which also contain relict grains
420 of cassiterite and prills of high-tin bronze (Rademakers, et al., in press). In southwestern Iberia,
421 Valério et al. (2013) argue for the direct addition of cassiterite to a crucible charge, though in this
422 case, the presence of unreacted copper minerals suggests co-smelting rather than cementation.
423 Morphology is crucial, since tin metal and bronze can oxidize to produce freshly formed tin
424 oxide phases in a slag (figure 11) (Rademakers, et al., in press; Rehren, 2001). In the case of the
425 crucible from Site 41, the argument for cementation is further bolstered by the identification of
426 other relict heavy mineral, 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 copper smelting sites. 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 (figure 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. 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 western 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 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 press), 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 raw cassiterite ore, 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 on 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 through a separate dry-roasting stage.

At least one ceramic crucible was used to create tin bronze. The analysis of this crucible raises 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 ore give weight to the hypothesis of relatively nearby tin sources. An examination of local geology suggests that the Bzhuzhi and Natanebi gorges, 10-15 km to the south and farther up into the lesser Caucasus mountains 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 data from the tin alloying crucible, coupled with a review of the archaeological and geological literature, suggests we must seriously consider the possibility that local exploitation of local tin was an important component of west Georgian metal production. 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 trade from the east in late 2nd and early 1st millennium BC western Georgia. 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.

7. Acknowledgements

The authors would like to thank Richard Newman (Boston Museum of Fine Arts) for assistance with the scanning electron microscopy and WDS microanalysis. Frederik Rademakers, Thilo Rehren and Edgar Pusch kindly provided us with an in press version of their paper on the alloying crucibles from Pi-Ramesse, which provided some very useful comparanda. Aslihan Yener and colleagues generously furnished us with an in press copy of their upcoming Antiquity paper. David Killick, Christopher Thornton, and Thilo Rehren all provided very helpful feedback on the interpretation of the crucible. Special thanks go to Thomas Fenn, Noa Corcoran-Tadd, and 2 anonymous reviewers for providing helpful comments and critiques. Amiran Kakhidze

540 (Batumi Archaeological Museum), Emzar Kakhidze (Batumi Maritime Academy), Anthony
541 Gilmour, and Marc Cox were instrumental in helping to organize and carry out the fieldwork in
542 western Georgia. Dana Challinor identified the radiocarbon sample from Site 41. This research
543 was supported by the awarding of a National Science Foundation Graduate Research Fellowship
544 (DGE0644491 and DGE1144152) to Nathaniel Erb-Satullo. Fieldwork and research were funded
545 with a National Science Foundation Doctoral Dissertation Improvement Grant (BCS-1338893) to
546 Nathaniel Erb-Satullo, as well as additional grants from the British Academy (SG100285),
547 National Geographic Society (GEFNE30-11), the Harvard Davis Center for Russian and
548 Eurasian Studies, the Harvard Anthropology Department, and the Jens Aubrey Westengard Fund.
549

550 Figure Captions

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

553 *Double column size*

554

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

558 *Double column size*

559

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

562 *Double column size*

563

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

567 *Double column size*

568

569 Figure 5. Copper metal and copper sulfide prills in slagged technical ceramics, along with
570 selected EDS spectra. Samples 4112 and 4113 have small prills of copper metal (Cu) trapped in
571 the slagged surface. The copper prill in sample 4112 is the Prill 1, sample 4112 in the table of
572 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.

Double column size

Figure 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.

Double column size

Figure 7. Plots of Al_2O_3 vs. FeO and MgO vs. CaO for different slag types. Chemical data from table 1 and Erb-Satullo et al. (2014:table 4).

Double column size

Figure 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.

Double column size

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

Single column size

596

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

601 *Double column size*

602

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

609 *Double column size*

610

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

614 *Double column size*

615

616 Figure 13. Optical photomicrograph of a spongy amorphous slag from Site 41 (sample 4106),
617 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 the off the surface of a crucible's molten charge.

Single column size

Figure 14. Complex metallic phases found in west Georgian slags. 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.

Single column size

Figure 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/skimmmg the off the surface of molten crucibles charges.

Double column size

Figure 16. Geological Map of southwestern Georgia, showing location of Site 41, the Bzhuzhi and Vakijvari gorges, and other modern towns and cities. Geological data from Nazarov (1966). Hillshade produced from ASTER DEM (a product of METI and NASA).

Double column size

Table Captions

Table 1. Normalized SEM-EDS area analyses of slags on technical ceramics, and several additional 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 area of uncorroded slag. Compositions are reported in normalized oxides wt. %. Numbers in the context column are context numbers for test pits in slag heaps.

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.

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.

663

664 Table 4. Normalized WDS microanalysis of metallic prills in slags from the Supsa-Gubazeuli
665 production area. Compositions in italics were determined by EDS. Detection limits for WDS are
666 approximately 0.03 to 0.05 wt.% depending on the element, and 0.3 wt.% for EDS.

667 Abbreviations: bdl-below detection limit; nm-not analyzed. Slag types: A-amorphous spongy
668 slag, probably produced by skimming off crucibles; D-dense slag cake fragment; STC-Slagged
669 technical ceramic; I-indeterminate, used for slags which are difficult to categorize. In this case,
670 sample 4313 is glassy, highly vesicular, and contains many copper metal prills. It is probably
671 from skimming off a crucible, but it has an atypical appearance.

672

673

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Table 1

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 cermic	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

Table 2

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

Table 3

	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

Table 4

Sampl	Site	Prill	Spot #	Slag Typ	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	bdl	bdl	bdl	bdl	84.10	0.98	0.39	9.44	0.08	0.05	4.96	bdl	bdl	bdl	na	na
101	1	1	7	A	iron rich phase	na	bdl	bdl	bdl	bdl	82.59	0.93	0.44	8.45	0.09	bdl	7.37	na	bdl	bdl	na	na
101	1	1	8	A	iron rich phase	na	bdl	bdl	bdl	bdl	84.49	1.01	0.51	7.97	bdl	bdl	5.94	na	bdl	bdl	na	na
101	1	1	9	A	iron rich phase	na	bdl	bdl	bdl	bdl	84.83	0.92	0.44	8.63	bdl	0.04	5.02	na	bdl	bdl	na	na
302	3	1	1	A	copper phase in copper prill	na	bdl	na	na	na	3.04	0.15	0.2	96.39	0.15	0.06	na	bdl	bdl	bdl	bdl	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	bdl	0.03	4.93	bdl	bdl	bdl	bdl	na
304	3	1	1	D	copper prill	na	0.12	na	na	na	0.90	bdl	bdl	98.94	bdl	bdl	na	0.05	bdl	bdl	bdl	na
901	9	1	1	A	copper prill	na	na	na	na	na	2.50	bdl	5.91	91.46	0.06	0.08	na	bdl	bdl	bdl	bdl	na
3807	38	1	1	A	copper prill	na	0.30	na	na	na	0.05	bdl	bdl	99.59	0.06	bdl	na	bdl	bdl	bdl	bdl	na
3807	38	2	1	A	copper prill	na	0.10	na	na	na	0.21	bdl	bdl	99.55	0.09	bdl	na	na	bdl	0.04	bdl	na
3808	38	1	1	A	copper prill	na	na	na	na	na	1.63	0.10	0.11	97.86	0.18	bdl	na	0.07	0.05	bdl	bdl	na
4110	41	1	1	STC	dendrite in large prill	na	na	na	na	na	bdl	0.12	0.05	66.67	bdl	0.42	na	bdl	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	bdl	na
4110	41	1	3	STC	average over dendrites and eutectoid	na	na	na	na	na	0.04	0.19	0.05	70.77	bdl	0.73	na	bdl	28.10	0.12	bdl	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	bdl	na	na	16.87	bdl	bdl	na
4110	41	3	1	STC	average over dendrites and eutectoid	na	na	na	na	na	0.03	0.09	0.08	59.77	bdl	0.68	na	0.05	39.22	0.07	bdl	na
4112	41	1	1	STC	copper prill	na	0.22	na	na	na	1.17	0.03	0.37	98.11	0.04	bdl	bdl	na	0.05	bdl	na	bdl
4112	41	1	2	STC	copper prill	na	0.16	na	na	na	1.24	0.02	0.43	97.91	0.11	bdl	bdl	0.08	0.05	bdl	bdl	bdl
4115	41	1	1	STC	copper prill	na	0.39	na	na	na	2.65	0.03	bdl	96.62	0.06	0.07	0.05	bdl	bdl	bdl	0.13	bdl
4126	41	1	1	STC	copper prill	na	0.11	na	na	na	0.92	0.04	bdl	98.83	bdl	bdl	0.06	bdl	0.06	bdl	bdl	bdl
4127	41	1	1	STC	copper prill	na	0.08	na	na	na	1.37	bdl	0.13	98.29	0.08	bdl	bdl	bdl	0.06	bdl	bdl	bdl
4144	41	1	1	STC	copper prill	na	0.04	na	na	na	2.05	0.02	0.06	96.55	0.04	bdl	bdl	1.21	0.04	bdl	bdl	bdl
4313	43	1	1	I	copper prill	na	na	na	na	na	bdl	bdl	0.05	99.95	bdl	bdl	na	bdl	bdl	bdl	bdl	na
4313	43	2	1	I	copper prill	na	na	na	na	na	0.27	bdl	bdl	99.55	0.05	0.08	na	0.05	bdl	bdl	na	na
4501	45	1	1	A	copper prill	na	bdl	na	na	na	0.22	bdl	0.12	99.59	0.08	bdl	bdl	bdl	bdl	bdl	bdl	bdl
4704	47	1	1	D	copper-rich phase	na	na	na	na	na	0.05	0.02	0.08	99.69	0.10	bdl	na	0.06	bdl	bdl	bdl	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	bdl	bdl	bdl	bdl	na
4704	47	2	1	D	copper-rich phase	na	na	na	na	na	0.17	0.03	0.05	99.69	bdl	bdl	na	0.05	bdl	bdl	bdl	na

Figure 1

Figure 1 Greyscale

Figure 2

Site 14 Slag Cake Fragment

Site 29 Slag Cake Fragment

Figure 2 greyscale

Site 14 Slag Cake Fragment

Site 29 Slag Cake Fragment

5 cm

Figure 3

Figure 3 greyscale

Figure 4

Figure 4 greyscale

Figure 5

Figure 5 greyscale

Figure 6

Figure 7

Figure 7 greyscale

Figure 8

Figure 8 greyscale

Figure9

Figure 10

Figure 11

Figure 11 greyscale

Figure 12

Figure 12 greyscale

Figure 13

Figure 13 greyscale

Figure 14

Sample 302 Prill 1

Sample 4704 Prill 1

Sample 302 Prill 1

Sample 4704 Prill 1

Figure 15

Spongy Slag from Crucible Skimming

Top View

Bottom View

Tap Slags

Top View

Bottom View

Top View

Bottom View

Top View

Bottom View

Figure 15 greyscale

Spongy Slag from Crucible Skimming

Top View

Bottom View

5 cm

Tap Slags

Top View

Bottom View

Top View

Bottom View

Top View

Bottom View

Figure 16

Figure 16 greyscale