Seeing the forest for the trees: Assessing technological variability in ancient metallurgical crucible assemblages

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Abstract

Metallurgical crucible remains have been found in many archaeological contexts and in varying degrees of preservation. The reconstruction of metallurgical activity through the study of these remains, by means of microscopy and chemical analysis, is undertaken with the aims of understanding technological choices of ancient craftspeople, their use of different raw materials and, by extension, the organisation of production and trade. When large assemblages are available for study, an intra-site comparison of technology and material use within different contexts and throughout time offers interesting perspectives.

Complete crucible examples are rarely found and it is often difficult to reconstruct full crucible profiles based on the fragmented remains. This in turn means that process variability within a single crucible can be hard to assess. Crucible slag is often highly heterogeneous, even within single fragments, enticing analysts to lose themselves in details. Furthermore, the abundance of remains is highly variable, depending on the scale of activity as well as archaeological recovery and preservation, while technological variation within an assemblage can only be detected through study of multiple samples.

Drawing on the analysis of two crucible assemblages, some difficulties and opportunities for technological reconstructions are discussed. Issues related to crucible heterogeneity and inherent process variability are illustrated and a number of interpretative problems arising therefrom are examined. Following a deconstruction of these interpretative issues, some suggestions are made for how, despite methodological difficulties, archaeologically relevant results are obtained where one tries to see the forest for the trees.

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1. Introduction

This paper highlights some issues regarding the study of crucibles used for high-temperature metallurgical operations (Rehren, 2003), illustrated by results from two assemblages studied as part of the first author’s PhD research (published in full elsewhere). Here, particular focus is given to open, internally heated crucibles which interact (strongly) with the crucible charge and represent the predominant pre-Roman crucible technology. Crucible slag is defined here as the combination of vitrified ceramic and various contributions from the crucible charge, such as fuel ash and metal oxides, developed at the interface of the crucible and its charge.

This contrasts with – typically later – externally heated examples, often made of more refractory ceramic (Bayley and Rehren, 2007), such as Roman brass-making (Bayley, 1984), medieval European fire assay (Martín-Torres et al., 2006, 2008) and early Islamic Central Asian steel-making crucibles (Rehren and Papachristou, 2003). In such crucibles, a glaze may form on the exterior and dross is sometimes preserved on the interior, but interior crucible slag is rarely developed. Though this paper focuses in particular on internally heated crucibles, much of the following discussion has bearing on all crucible types.

Crucible studies can be largely subdivided into two categories: investigations of ceramic technology and of metallurgical processes. The former tend to focus on the ceramic fabric, analysing the raw clay and use of temper as well as the crucible design to assess thermal and mechanical properties of the vessels. Thin-section petrography is often used here (e.g. Evely et al., 2012). The latter are aimed at understanding the metallurgical crucible process, and technological choices made therein, as well as uncovering variability in the use of raw materials. Here, a stronger focus is given to the analysis of crucible slag, using mounted sections for reflected light microscopy and SEM–EDS analysis (e.g. Rehren and Kraus, 1999). This metallurgical perspective is adopted here.

Less studied issues are how crucible heterogeneity affects the sampling strategy for a single crucible or an entire crucible assemblage, how it affects the analytical methodology applied to the study of those samples, and what the interpretative issues arising from this heterogeneity and sampling strategies are.

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While such problems are particularly in need of investigation for crucible studies, similar considerations must be made for the examination of metallurgical slag more broadly (e.g. Bourgarit, 2007 and Humphris et al., 2009). This paper aims to complement these studies and stimulate further research on heterogeneity, sampling bias and representativeness in archaeometallurgy.

2. Materials and methods

2.1. Materials

We present material from two case studies to illustrate the variability that can occur both within single crucibles and throughout entire crucible assemblages. The first assemblage is from Qantir–Pi-Ramesse (Egypt, 13th century BC), where crucibles were used for the casting of bronze objects (Pusch, 1990; Rehren et al., 1998; Rademakers et al., 2015). The second crucible assemblage is from Gordium (Turkey, 6th–4th century BC), where bronze and leaded bronzes were alloyed. The archaeological background for these assemblages is omitted here, as the focus of this paper is strictly methodological. Contextual information for the Pi-Ramesse assemblage is presented by Pusch (1990), while Rademakers et al. (in preparation) will discuss the specific context of the Gordian crucibles (see Kealhofer, 2005 for a broader overview of the Gordion excavations), and their technological interpretation.

2.2. Sampling

Following macroscopic investigation, samples were cut from these crucibles to obtain flat profile sections, mounted in epoxy resin blocks and left to harden. The mounted sections were then ground using increasingly finer abrasives and polished down to 0.25 μm using diamond paste.

2.3. Analysis

The mounted samples were analysed using reflected light microscopy (Leica DM4500 P LED polarisation microscope) and, after carbon coating to ensure surface conductivity, by SEM (JEOL 8600 Superprobe) for structural and textural characterisation of both crucible ceramic and slag. SEM–EDS analysis (Oxford Instruments EDS attachment and INCA software) was performed to obtain quantitative chemical compositions of particular phases (point-microanalysis) and larger areas. Bulk chemical composition was determined by averaging the analysis of five frames (magnification: 100×) for crucible ceramic and crucible slag respectively (similar to Freestone and Tite, 1986). This procedure was performed for 95 samples (49 from Pi-Ramesse, 46 from Gordion) discussed here.

For the presentation of bulk chemistry, ternary diagrams of SiO₂–Al₂O₃–FeO and SiO₂–Al₂O₃–CaO for crucible ceramic and slag composition were constructed (in each case ignoring all other elements). Full compositional data for both assemblages (Rademakers, 2015) will be published elsewhere.

Handheld portable XRF (pXRF) has been used to qualitatively analyse the cleaned surfaces of Pi-Ramesse crucible fragments on site in Egypt (Innov-X Systems, DP 4000). Three 15 second analyses were performed for each fragment using a 40 kV beam, and the data averaged. The raw intensity spectra (in counts/s) have been used to assess the presence of particular elements by hand (checking for characteristic Kα₁ and Kβ₁–intensities), without converting to concentrations (Dungworth, 2000a). pXRF analysis could not be performed for the full Gordion assemblage, due to accessibility constraints.

3. Results

3.1. Within-crucible variability

The first type of variability that can be identified within crucible assemblages is the variation that occurs within crucibles themselves. The analysis of a single crucible sample does not necessarily capture this variability, and some of the differences seen between samples from different crucibles can often be attributed to variability of the same process. This section sets out the main factors influencing this within-crucible variability and its characteristics.

Several process parameters can vary strongly during metallurgical crucible processes. The most important are redox conditions, temperature and the distribution of charge constituents. The first two are strongly related to changing oxygen supply within the crucible, which in turn is controlled by tuyère placement, continuity in bellowing action and charcoal cover. This oxygen supply is a dynamic factor, producing hotter and cooler regions within a crucible, and more oxidising or reducing conditions in different areas. These zones change through time as crucibles often go through several stages in their use, such as pre-firing, charging, melting/smelting, casting, cooling and reuse.

The possible reuse of crucibles is not treated in depth in this paper, but obviously introduces important interpretative issues. The likelihood of reuse must be assessed for each crucible assemblage through careful examination of all fragments, and its possible effects on the final interpretation must be discussed.

Most of the metallurgical process information is contained in the crucible slag forming through the melting of the inner surface of the crucible. The degree of this melting is a function of operating temperature and the composition and refractoriness of the ceramic. The ceramic properties are highly homogeneous for the assemblages discussed here (Rademakers et al., 2015, in preparation). More heterogeneous ceramic fabrics, common for early crucibles, may induce more heterogeneous melting behaviour. However, most crucibles are highly heterogeneous with regard to vitrification and slag formation despite compositional homogeneity of their fabric. This changing rate of ceramic disintegration stems mainly from variability in process parameters throughout the crucible. The degree to which the ceramic vitrifies and melts in turn influences the amounts of charge constituents that can be encapsulated by the vitrified ceramic, such as charcoal/fuel ash, ore fragments, metal prills and metal oxides, transforming it into crucible slag. None of these constituents are necessarily present in every particular area of the crucible, even if they occur in one area.

In oxidising areas of the crucible, some of the metal in the charge can oxidise. In the case of copper, contaminants such as iron, cobalt, nickel and arsenic or alloying elements such as tin, lead and zinc are burnt off before the copper itself oxidises (Ellingham, 1944; see Dungworth, 2000a and Kearns et al., 2010). If this happens in an area with a sufficiently developed liquid slag layer, the metal oxides can be incorporated into that slag layer and provide highly distorted information on the nature of the original metal melted in a crucible. Under more reducing conditions, metal prills can be trapped nearly unaltered in the slag, reflecting the original metal composition more closely. The relative proportions of molten ceramic, fuel ash, metal oxides and metal inclusions in the crucible slag can vary highly from one part of the crucible to the next. When no slag is formed, some of these metal oxides typically gather on top of the molten charge as a dross layer.

As a first example, a crucible fragment from Pi-Ramesse is shown in Fig. 1. This fragment is slagged along its entire profile, and differences can already be noted by visual inspection. Closer to the rim (top) the slag layer is fairly regular and thin and its reddish surface is quite flat. Lower down, however, the slag thickness increases and is more variable, and the dark grey slag exhibits a more irregular surface with visibly corroded copper-based prills.
Microscopic inspection reveals the slag at the rim area to be mainly composed of vitrified ceramic, fluxed by fuel ash and with only minor copper content (Fig. 1, top right). The slag forming at the lower body, in contrast, is strongly enriched in copper and tin, as well as iron and cobalt. This iron and cobalt occur as spinel \((\text{Fe,Co})(\text{Fe,Al})_2\text{O}_4\) with \(\pm 6\) wt. % Co) in the crucible slag, and probably originate from the partial oxidation of contaminated copper (Fig. 1, bottom right). Differences in redox-conditions and material presence produced this different slag enrichment in the two zones (Table 1) and resulted in their different macroscopic appearance. An important observation here is that the Pi-Ramesse assemblage contains many fragments that consist only of either the upper rim area or the lower body area, and therefore do not allow the comparison of both zones within one sherd. Considered in isolation, analysis of the rim in Fig. 1 only reveals fuel ash contributions and the limited presence of copper (not bronze), and does not allow interpretation beyond ‘copper-related metallurgy’. The lower body tells a different story: it points to ‘bronze-related metallurgy’, with the use of copper contaminated by iron and cobalt.

A second example from Pi-Ramesse is shown in Fig. 2, where two samples have been taken from a small rim fragment. They show a similar type of crucible slag as seen in the previous example near the rim: vitrified ceramic with tiny embedded metal prills. For the top sample, all prills were composed of almost pure copper, with up to 1 wt.% iron. In the bottom sample, all prills had a radically different composition, averaging around 30 wt.% copper, 40 wt.% nickel, 15 wt.% cobalt and 15 wt.% iron. Despite being taken only 2 cm apart, these samples present very different evidence of what must have been the same process and, viewed in isolation, would again lead to divergent interpretations.

Fig. 3 shows a crucible fragment from Gordion, for which three samples (A–B–C) along the profile were taken for analysis. The rim sample (A) exhibits limited slagging, and most of the interior is simply vitrified ceramic. A few tiny prills occur further away from the rim (towards the lower body), which are iron- and arsenic-rich bronze, but the bulk slag metal content is low (Table 2). In the intermediate sample (B), the slag is more developed (though not everywhere) and more metal prills are present. These are mainly pure copper prills with minor iron content, while the slag contains large amounts of tin oxide, malayaita (CaSnO\(_4\)) and copper (chloride) oxides. Finally, the lower body sample (C) presents the thick crucible slag at the bottom of the fragment. Here, two layers exist: the deeper slag layer is similar to sample B (with iron-rich bronze prills), while a dross layer is deposited on its surface, which is dominated by various metal oxides (including lead oxide). The bulk slag metal content in sample B is higher than that of sample A, but lower than that measured in sample C (Table 2), which is reflective of the high metal oxide content in the dross, rather than the elevated presence of metallic prills. Though these dross layers can be helpful in identifying alloy types melted in a crucible, metallic prills rather than metal oxides are required to better assess the actual alloy composition. Fuel ash contributions and iron contamination of the crucible slag are lower for samples A and B than for sample C.

When comparing the copper, tin and lead content in all analysed rim and body fragments (where ‘body-rim’ means body fragments taken near the crucible rim, as opposed to lower body fragments), a trend becomes evident: body fragments are generally more highly enriched in metal (oxides) than rim fragments (shown for Gordion in Fig. 4). However, this trend is by no means a strict rule, and high variability exists. The highest lead oxide content, for example, is measured in a rim fragment.

These observations confirm that rim fragment slag often consists mostly of vitrified ceramic, fluxed by fuel ash, and is generally less informative than lower body slag, which was in contact with the crucible charge. For these body fragments, the variable redox- and temperature conditions and distribution of charge components modify the type of evidence available (e.g. metal content, different oxide phases). When sampling a crucible fragment, the chosen location will therefore strongly influence the informative nature of analytical results, and complete disclosure of the crucible process is rarely obtained from a single sample. Post-depositional effects such as differential corrosion and fracturing can further bias the representativeness of a fragment for understanding ancient metallurgical processes.

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>Na(_2)O</th>
<th>MgO</th>
<th>Al(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>P(_2)O(_5)</th>
<th>K(_2)O</th>
<th>CaO</th>
<th>TiO(_2)</th>
<th>FeO</th>
<th>CuO</th>
<th>SnO(_2)</th>
<th>CoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic</td>
<td>2.0</td>
<td>2.2</td>
<td>13</td>
<td>66</td>
<td>0.6</td>
<td>1.9</td>
<td>3.2</td>
<td>1.5</td>
<td>8.3</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Slag (rim)</td>
<td>1.4</td>
<td>3.6</td>
<td>13</td>
<td>53</td>
<td>0.7</td>
<td>1.9</td>
<td>13.8</td>
<td>1.9</td>
<td>8.9</td>
<td>0.7</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Slag (lower body)</td>
<td>5.0</td>
<td>3.1</td>
<td>9</td>
<td>46</td>
<td>1.5</td>
<td>1.9</td>
<td>13.1</td>
<td>1.9</td>
<td>11.8</td>
<td>2.1</td>
<td>3.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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3.2. Assemblage-wide variability

Two main types of variability can be expected within crucible assemblages. The first is due to the variability inherent to the crucible process, as discussed in the previous section. The second type is introduced by the variable technological choices ancient craftspeople made, which are sometimes reflected in the crucible slag. This involves the variation in techniques, as well as variation in raw materials used in the metallurgical process. Here archaeologists can address questions such as: did ancient metallurgists stick to one ‘recipe’ or draw from several technological options? Were raw materials from several sources used? Is there any variation in these choices through time or various production contexts? Obviously, such questions have higher archaeological significance than the detailed understanding of process variability, described above, which probably played a minor role for the ancient metallurgist.

In this section, the example of bronze production is used to illustrate this concept. The main techniques of choice are:

1. Alloying of two fresh metals (copper and tin)
2. Cementation (copper metal with tin ore)
3. Co-smelting (copper and tin ore)
4. Recycling (possibly involving addition of fresh metal (or tin ore)).

Their differentiation in actual archaeological finds has received relatively little attention in archaeometallurgical studies (but see Pigott et al., 2003; Rovira, 2007), but was recently investigated in detail for Pi-Ramesse (Rademakers et al., 2015). In addition to
choices of technique, variability due to the use of different raw materials can be expected as well. Here, the identification of materials from different origins (geologically, economically, culturally) does not necessarily represent a conscious choice by the metallurgist. Finally, though variability in techniques and materials can occur across an assemblage, this is obviously not always necessarily the case.

The main problem for identification of technological variation lies in the nature of the available evidence. This can be illustrated by the typical process indicators as preserved in crucible slag that allow identifying different bronze production techniques. Active alloying, as opposed to the mere recycling of existing bronze, can lead to the production of high-tin prills (Crew and Rehren, 2002; Rehren, 2001) with δ-, ε- and/ or η-phase bronze (Rademakers et al., 2015). Though these prills allow exclusion of ‘technique 4’ from the list above (i.e. recycling), they offer no distinction between the ‘techniques 1–3’. During cementation and co-smelting (‘techniques 2–3’), however, it is possible for mineral grains from the ore to be trapped in the crucible slag and excluded from further participation in the metallurgical process. As such, residual mineral grains can allow the distinction between the ‘techniques 1 and 2–3’.

The problem here is that these phases are not the intended end products of the metallurgical operation: high-tin prills and residual ore are the result of processes that were not completed. Under ‘ideal conditions’, these process indicators are not preserved in crucible slag at the end of the operation, and cannot always be expected to be found in a crucible sample taken for analysis. Furthermore, many phases are ambiguous and inconclusive towards identifying technological choices. Low-tin prills, for example, could indicate the production of a low-tin bronze, but equally result from the recycling (and partial burning) of medium-tin bronze. Similarly, accicular, high temperature tin oxide crystals can be formed in a crucible following any production technique (Dungworth, 2000b; Rademakers and Farci, in preparation).

Recognising variability in raw material use is equally difficult. For the case of copper added to a crucible, a general distinction can be made between ‘clean’ and ‘contaminated’ copper. ‘Contaminated copper’ is typically raw copper which has not been (thoroughly) refined after the primary smelting stage. Depending on the type of ore that was smelted, this copper can contain elements such as iron, cobalt, nickel, arsenic, tin or lead that were reduced during smelting and incorporated in the copper. Alternatively, raw copper could be contaminated by remnant primary smelting slag, when poor separation was achieved during the smelting process (Hauptmann et al., 2002) or when slag was intentionally added to copper ingots, in an attempt to cheat when trading the copper. Most contaminants oxidise preferentially to copper and will burn off into the crucible slag first. Enrichment of the crucible slag in these oxides, therefore, can be used as an indicator for the use of different raw materials across a crucible assemblage. Furthermore, it offers the possibility to relate crucibles to final artefact chemistry.

There is, however, again a problem here. While a distinction can sometimes be made between ‘clean’ and ‘contaminated’ raw materials used in different crucibles, it is important to remember that contaminants are only oxidised into the crucible slag under oxidising conditions. These environments are not necessarily present in every crucible (area) and, as a result, the relevant metal oxides are not always present in each sample taken from a crucible.

Therefore, the absence of certain process indicators, technical or material, is often not sufficient to exclude certain technological choices from the interpretation of an assemblage. Due to the inherent process variability witnessed within each crucible, the absence of evidence can usually not be taken as the evidence for absence. Only when the researcher has investigated sufficiently large sample numbers can more confidence in an overall interpretation be achieved. Regardless, conservativeness is usually the appropriate interpretation attitude.

When looking at the changes in bulk chemistry between crucible ceramic and slag for the Pi-Ramesse crucibles (Fig. 5, top), some variation within the assemblage can be noted. A relative increase of the crucible slag in lime occurs for all crucibles, and correlates to an increase in other fuel ash constituents, particularly magnesia and phosphate. The spread from low to high lime enrichments reflects within-crucible variability: all crucibles were presumably placed under a similar charcoal cover during operation, but some crucible areas received higher fuel ash contributions than others.

For about 2/3 of the samples, no slag enrichment in iron can be noted, whereas about 1/3 of the samples exhibit varying degrees of iron enrichment. This enrichment is most likely due to the use of contaminated (raw) copper, and the spread from low to high enrichment is a result of within-crucible variability as well as variable raw copper iron content. Therefore, some of the crucible samples without notable iron enrichment could similarly have contained ‘contaminated copper’, for which iron was not oxidised into the crucible slag in the sampled part of the crucible.

Fig. 5, bottom, shows the same ternary diagrams, distinguishing between rim and body crucible fragments. Some clear differences can be noted between rim and body fragments, as could be expected from remarks made in the previous section. Higher lime slag enrichments typically occur for body fragments, though some rim fragments show moderate to high enrichments too. This reflects a fairly equal distribution of fuel ash throughout the crucibles. Slag enrichment in iron, however, occurs almost exclusively for body fragments and is low for the rim fragments where it occurs. This reflects one of the primary factors for within-crucible variation: the spatial distribution of charge constituents. Closer to the crucible rim, less or no copper is available to exchange contaminants with the crucible slag. An important consequence of this

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![Fig. 4. Boxplot of bulk copper, tin and lead oxide content in 46 Gordion crucible fragments (16 rim, 6 body-rim and 24 body fragments; SEM-EDS data).](image-url)
A perhaps elementary observation is that the deduced importance of 'contaminated' raw copper use is skewed for the full assemblage, and should be based only on the analysis of body fragments. For Pi-Ramesse, this means that in reality about half of the crucibles show iron enrichments, indicative of the use of 'contaminated' copper (out of which ±15% are additionally contaminated with cobalt/nickel, indicating a different raw material).

4. Discussion

The two previous sections have identified three main issues, fundamental to the study of crucible assemblages. Firstly, strongly variable slag formation is possible within a single crucible: crucible slag is a palimpsest, reflecting the changing conditions through space and time inside the crucible. This can result in different slag types in various zones of the crucible, with typically strong discrepancy between rim and lower body areas. Secondly, variable use of techniques and raw materials can exist within the assemblage as a whole, reflective of different technological choices made by the ancient craftspeople. This variation in the crucible remains, however, can be hidden by the process-inherent variation that is superimposed on it. Furthermore, not all techniques and raw materials provide diagnostic evidence to begin with, and obviously, such technological variations do not exist for every assemblage. Thirdly, multiple technological pathways must always be considered when assessing crucible remains. On the one hand, a single process can produce a range of crucible slag types due to varying crucible conditions. On the other hand, a range of processes can result in very similar crucible slag types.

The degree to which these issues affect crucible slag formation strongly varies, of course. One of the critical factors influencing the degree of slag formation is crucible refactoriness. Poorly refractory crucibles typically form thick slag layers as their fabric disintegrates at high temperatures. This enables the mechanical trapping of charge fragments (e.g. charcoal, ore and metal fragments) and the incorporation of contaminants into the slag through chemical interaction. In more refractory crucibles, this melting of the ceramic fabric is less pronounced, as for example in the Gordion crucibles. Though these are not supremely refractory crucibles (like those reported in Martinón-Torres et al., 2006, 2008; Rehren and Papachristou, 2003 and Thornton and Rehren, 2009), slag layers are significantly less developed than for the Pi-Ramesse.
crucibles, despite their similar mode of use. This is illustrated in Fig. 6, where only a minor (but significant) shift between crucible ceramic and slag bulk composition can be noted. An important result of limited slag formation is the absence of an exchange medium for the crucible charge into which contaminants can be burnt off. When iron-rich copper is used, for example, this iron will oxidise and, in the absence of a crucible slag phase, collect as a dross layer on top of the crucible charge together with other metal oxides. Upon casting, such dross layers are either manually removed, or are deposited as a thin layer on top of a limited area of the crucible slag. Such dross layers are often encountered in the Gordian crucibles, and are typically enriched in iron and other metal oxides several times more strongly than the crucible slag. It should be noted that these dross layers, due to the absence of a protecting glassy slag phase, are typically more susceptible to post-depositional corrosion or mechanical loss than regular crucible slag. This further illustrates the impact of crucible refractoriness on the evidence available to the archaeological scientist.

The best tool to address these issues is an adapted, considerate sampling strategy. This must follow a thorough visual inspection of the entire assemblage to assess fabric homogeneity and variable slag formation. Ideally, extensive sampling should be undertaken to assess variability within crucibles and discover variation within the assemblage with confidence. In reality, of course, sampling is constrained by limitations in time or budget, export regulations and curatorial considerations. For such cases, the results presented in this paper have shown that lower body fragments are generally more informative than rim fragments to reconstruct technology and material use, and thicker, more developed slag is more likely to capture process indicators. This corresponds to what most analysts have probably been doing intuitively for decades: go for the ‘juicy’-looking slag. Our results finally provide a more scientific basis to follow those instincts. Nonetheless, it is important to stress that no strict regularity exists and ‘juicy’ samples might not be as informative as they look. Furthermore, a strong ‘nugget effect’ exists for technological process indicators: you may capture a particularly informative inclusion in your sample, or miss it by a hair. Finally, it is possible that a single fragment does capture a large amount of the process-inherent variability. Here, thermodynamically incompatible conditions can sometimes be seen occurring in close proximity, highlighting the absence of equilibrium conditions in most crucibles (e.g. Müller et al., 2004), and the importance of kinetics in slag formation.

The use of alternative analytical techniques can open further perspectives towards quickly assessing variability in crucible assemblages.

Fig. 6. Ternary diagrams showing bulk compositions for 46 Gordian crucible fragments, distinguishing between normal (red) and aberrant (orange) ceramic and normal (blue) and aberrant (turquoise) slag (SEM–EDS data). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Histogram showing relative change in bulk iron content between ceramic and slag measured by SEM–EDS (left) and ratio of iron to titanium in crucible slag measured by pXRF (right). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)
The use of pXRF has been tested for the qualitative analysis of the Pi-Ramesse crucible assemblage. Without discussing the complete results in detail, two examples are shown here. In Fig. 7, left, the relative change

\[
\Delta \frac{\text{FeO}}{\text{Al}_2\text{O}_3} = \frac{\text{FeO}_{\text{slag}}}{\text{Al}_2\text{O}_3_{\text{slag}}} - \frac{\text{FeO}_{\text{ceramic}}}{\text{Al}_2\text{O}_3_{\text{ceramic}}}
\]

in bulk iron content between crucible ceramic and slag is shown, as measured by SEM–EDS analysis of 49 samples. The largest group of samples (about 2/3, in blue) shows a normal distribution around zero, indicating no iron contamination. The second group (about 1/3, in purple) shows increased iron content relative to alumina, indicative of the use of an iron-contaminated copper source (same as seen in Fig. 5). Aluminium peak intensities are not easily measured by pXRF; hence, a similar ratio (using the iron and titanium K\(\alpha\) intensities measured in crucible slag) has been used for in-the-field analysis, as shown in Fig. 7, right, based on the analysis of the entire Pi-Ramesse crucible assemblage of 1042 fragments by pXRF. The same pattern emerges, indicating a large group of ‘clean slag’ and a smaller group of iron-contaminated slag. Though less clearly defined for the pXRF data, it is much more easily obtained and provides the same assemblage-wide pattern. Within-crucible variation can equally be investigated using pXRF, as shown by example in Fig. 8, where the copper and tin content for rim and body fragments respectively is compared. Though increased content in both metals can be noted for both fragment types, the incidence of greater enrichments is much more clearly defined for body fragments, in similar proportions as noted by SEM–EDS analysis of mounted samples. These examples show the potential for pXRF in fast qualitative analysis of entire assemblages to pick up large trends, though its efficacy should be further tested for other assemblages. As a final important note, it is pointed out that pXRF analysis of crucible fragments does not always correspond on a one-to-one basis with SEM–EDS analysis of the same fragment. Here the ‘nugget effect’ as an extreme example of the heterogeneity of individual crucible fragments can produce different results depending on the relatively small area analysed by the pXRF beam. For this reason, pXRF analysis yields better results as a qualitative screening method applied to entire assemblages, while for individual samples, SEM–EDS analysis provides more reliable data.

5. Conclusion

This paper has illustrated the slag variability within metallurgical crucibles, resulting from the combined effects of within-crucible and assemblage-wide process variability. The common reality of crucible heterogeneity and its effects on sampling, analysis and interpretation have hitherto not been systematically addressed in the literature. Here, suggestions have been made for adapted sampling strategies, and the need for adjusted interpretation based on limited sampling was highlighted. The possible effects of missing evidence must be acknowledged and it is advisable to attempt reconciliation of all observations as reflections of a single process wherever possible. This applies both to the interpretation of a single sherd, as well as to that of all samples taken across an assemblage. Only when process-inherent variability cannot account for observed variations should differentiation in techniques and raw materials be considered.

Further controlled experimental work to elucidate ambiguous slag phases (e.g. Rademakers and Farci, in preparation, on tin oxide crystal variability), the effects of crucible reuse on slag formation and composition, and many other issues will open new perspectives in this debate, initiated by a confounding archaeological reality. Despite the many problems discussed here, a full appreciation of crucible variability will...
allow archaeologically relevant interpretations to emerge from the details, like the forest through the trees.

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