Chapter 15

From mine to microbe – the Neolithic copper melting crucibles from Switzerland

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Abstract
The occurrence of chalcopyrite in several late Neolithic crucibles from NW Switzerland and SW Germany has been variously interpreted as indicating evidence for local copper smelting, or being due to post-depositional phenomena. This study uses optical microscopy and a discussion based on textural and micro-stratigraphical arguments to demonstrate that chalcopyrite is a late formation and not indicative of copper smelting. This has significant implications for the technological and archaeological interpretation of these finds, but also illustrates the potential of image-based studies in science-based archaeology.

Introduction
The emergence and spread of metallurgy in Europe is a major concern of archaeological and archaeometallurgical research. In the 1960s scholars such as Renfrew and Branigan focused their attention – and consequently that of others – on the role which metals have played in the development of stratified societies and the emergence of elites, showing off with their access to these new materials. The Balkans and Western Asia are now both known to have had metallurgically competent Neolithic cultures, and issues of technology transfer and autochthonous developments between and within these regions and neighbouring areas are hotly disputed. Comparatively less attention has been placed on the early north-west Alpine metallurgy, although the Neolithic of northwest Switzerland and southwest Germany is characterized by the occurrence of several copper-using and copper-working cultures at a time when all surrounding cultures were still mostly a-metallic and showed no signs of metal working (Strahm 1994).

In particular the Pfyn culture, dating to about 3800 to 3300 BC, shows considerable evidence for metal manufacturing, such as remains of crucibles and casting debris; but crucibles are also known from the subsequent Horgen culture (Fasnacht 1989). Startlingly, evidence for metal working in this region disappears after several hundred years, bringing these cultures back into line with their neighbours. Only after a further half a millennium or so metallurgy emerges again in Central Europe, heralding the beginning of the Bronze Age throughout the Continent. This time, it is a broad and sustained development with no particular emphasis on the Swiss or southwest German regions.

It is against this background that the crucible fragments of the Pfyn culture have attracted attention for more than a century, having been found at a wide range of sites and representing certainly several dozen different vessels. Despite their relative frequency and undeniable significance for our understanding of this truly Neolithic metallurgy, surprisingly little archaeometallurgical research has been done to properly characterise their precise place within the chaîne opératoire of copper metallurgy. Where, between the mine which provided the raw mineral, the various processing steps necessary to produce first copper metal and then useful metal artefacts, and their use, recycling and discard do they belong? One can – and should – debate how much scientific analysis really is necessary to address, possibly answer this question. W. Fasnacht, in a series of papers in the 1990s, has convincingly argued that they are casting vessels, processing existing metal stock; an assumption already manifest in their German name: Gusslöffel translates literally as ‘casting...
sponos’. This interpretation is based on common sense as much as on careful observation, but stands against some results of high-powered instrumental analysis. Others, therefore, have suggested a possible alternative interpretation, based on the presence of copper-iron sulphides identified by X-ray diffraction analysis of some of the metalliferous residue on the inside of several of these vessels. In particular Maggetti et al. (1991) discuss whether the presence of copper sulphides, such as chalcopyrite, bornite and chalcocite, alongside metallic copper, indicates that smelting of sulphidic copper ore took place within these crucibles.

This debate is of major consequence for the interpretation of the Pfyn metallurgy: was it a fully autonomous and possibly independent development, mastering at an early stage the smelting of complex sulfidic copper ore, and if so, why did it disappear again after a few hundred years of apparently sustained exploitation? If, however, these crucibles really are mere melting and casting vessels, with no related evidence for the primary production of copper within the wider cultural context, then one could argue that this was copper manufacturing rather than producing. The metal then had to be obtained from outside the immediate cultural context via a long distance trade link, as no significant occurrence of native copper is known from the region.

Another potentially interesting aspect of this question relates to the still-enigmatic scarcity of early smelting slag throughout Central and Northern Europe, and the subsequent hypothesis of a slagless metallurgy (Craddock 1995). Here appeared a chance to literally look into a potential smelting vessel and finding out about the fate of the non-copper components of the ore when it is being smelted. This is particularly relevant in this case, where complex copper-iron sulfides are being put forward as the potential ore rather than the simpler and much richer copper salts such as malachite or atacamite. These latter minerals contain only volatile components besides the copper, rendering a slagless metallurgy just about conceivable, assuming that really pure ore was being smelted. The considerable amount of iron in minerals such as chalcopyrite or bornite, however, reaching up to parity with the copper content, has to be separated during smelting from the copper metal; here, the formation of some kind of slag or dross becomes inevitable, and should leave an archaeologically visible trace.

It is against this range of questions of regional archaeological significance and interest to the history of technology that a set of crucible fragments from northwest Switzerland were analysed; the results of the study are presented and interpreted below.

Materials and Methods

The archaeological literature knows several dozen contexts within the SW German/NW Swiss Pfyn and Horgen cultures yielding crucible fragments (Schlichtherle and Rottländer 1982; Fasnacht 1991). Despite a certain variability of their design, no systematic technological differences have so far been identified between crucibles from the two cultural units, or across the geographical extent of their occurrence. Thus, for the time being they are treated here as a single phenomenon, although later research may well lead to further subdivisions and subsequent re-assessment of the homogeneity of this group.

The archaeometallurgical study followed on from the initial ceramic study by Baumgartner (1982), published in parts by Maggetti et al. (1991). Samples of originally eleven crucible fragments, recovered during excavations of lake shore settlements and now in the care of the Swiss National Museum, became available for analysis. Offcuts of the pieces which were originally sampled for their ceramic composition were kindly provided by M. Maggetti in 1990, originating from Wetzikon (LM 10, LM 11), Wetzikon-Robenhausen (LM 2, LM 8), Stäfa-Uerikon (LM 5, LM 15, LM 16), Meilen-Schelle (LM 7, LM 14), Meilen-Fellmeilen (LM 12) and Gachnang-Niederwil (LM 13). Nine of these samples comprised also vitrified areas and opaque inclusions; LM 12 and LM 13 did not show any metallurgically relevant traces and were not studied further.

The offcuts were used to prepare polished thin sections which were then studied by reflected light microscopy and subsequently by scanning electron microscopy with energy-dispersive spectrometry.

Results

Nine of the samples were investigated, and a detailed description of the observations for each one is given in Rehren (2004). The focus of this current paper is on the archaeologically and metallurgically relevant aspects, and on some methodological issues. Thus, the results are presented in a summarized manner to avoid repetition.

A common feature of these crucibles is their very limited vitrification, which is typically restricted to a thin (typically less than one millimeter) layer on the concave surface of the fragments (Fig. 1). The remainder of the fabric is apparently unaffected by the heat of the metallurgical process(es) which took
place in them, demonstrating that these vessels were heated from above / within. This is the norm for crucibles prior to the Iron Age (Rehren 2003), and does not in itself allow a more specific technological identification of the process(es) involved. In accordance with this, the bodies of the vessels are rather thick, up to several centimeters, and tempered with organic material (Fig. 2). This provides a thermally insulating matrix, clearly beneficial by minimizing heat loss through the body, and limiting to the top-most inner layer the potentially deleterious impact of the highest temperature on the mechanical integrity of the crucibles. Thus, the vessels can be made from ordinary clay with no particularly refractory qualities; the mechanical integrity is maintained even if the inside surface melts completely. This aspect of raw material choice and preparation is explored in more detail by Maggetti et al. (1991) and Maggetti (this volume), who found no indication for the selective use of a particularly refractory clay for the manufacture of these vessels.

An interesting feature is the evidence for repair, possibly re-use of some of the crucibles. At least in two instances was a second ceramic layer visible, covering an earlier partly vitrified surface (Fig. 3a, b). The metallurgically crucial observation is the presence of copper-iron sulphides, identified in six of the fragments (LM 2, 5, 7, 8, 10 and 11). The same samples contain prills of metallic copper trapped in the vitrified ceramic, almost always in close proximity to the copper sulphides (Fig. 4 and 5). These sulphides, mostly identified as chalcopyrite, although chalcocine and pyrite occur as well, clearly equal those discovered in earlier studies by X-ray diffraction, both in these samples and in others. Their presence is central to the argument for copper smelting.

Figure 1: Cross section through a crucible fragment from Stäfa-Uerikon. Note the very limited vitrification layer near the rim of the vessel, top left. Width of image ca. 3 cm.

Figure 2: Thin section through a crucible fragment from Wetzikon-Robenhausen (Inventory number 32981 of the Swiss Landesmuseum). Note the thick body, and the very limited vitrification layer near the rim of the vessel, top and right. Width of image ca. 3 cm.

Figure 3a, b: Thin section of crucible fragment 36394 from Stäfa-Uerikon. Note the dark outer layer of a different ceramic, covering a previously vitrified surface. Width of thin section ca. 3 cm.
In addition to the chalcopyrite found within the vitrified areas of most crucibles, several fragments have a scatter of small pyrite clusters throughout their ceramic body. Each cluster comprises several dozen tiny crystals, together loosely arranged in a sphere of less than 0.1 mm diameter. Such structures are known in ore petrography as *framboids*, from their perceived similarity to raspberries (in French *framboise*), or petrified bacteria, from their assumed origin (Ramdohr 1975). They are typical of sulphur-bearing anaerobic environments, such as siltstones and slates rich in organic matter. Framboids were found in four or five of the samples (LM 7, 11, 14 and 16, and possibly 10).

**Spatial aspects of sulphide and metal occurrence**

The presence of copper sulfides is restricted to the vitrified parts of the crucibles, as one would expect if they constitute ore remnants, and where they occur in close proximity to the prills of metallic copper and copper oxide dispersed and dissolved in the vitrified matrix (see below). Despite this close proximity to the copper metal, there is, however, an important systematic difference between the spatial arrangement of sulphides and metal. The copper metal is inevitably present as droplets trapped in the vitrified ceramic; the metal was therefore obviously at the same time liquid as the ceramic layer in which it is embedded. The sulphides, in marked contrast, populate the surface of the vitrified ceramic, often lining the inside of gas bubbles which result from the decomposition of the clay minerals during vitrification (‘bloating’ of the ceramic). Most tellingly, cracks in the vitrified ceramic are often cemented by copper sulphides (Fig. 6). Another fundamental difference between copper metal and sulphide inclusions lies in their shape; the metal is inevitably present as prills, i.e. small almost perfect spheres typical of liquid metal solidifying in a viscous surrounding (Fig. 7a, b). In contrast, the sulphides are without exception showing a layered structure wrapping the ceramic matrix, often with a cauliflower-like upper surface and only ever appearing in a spherical shape when filling spaces which clearly are former gas bubbles; semi-filled such bubbles illustrate the gradual process by which they were filled. In effect, and while at present copper metal and copper sulphides co-exist within the very same space, there is a clear stratigraphic separation between the two (Fig. 8). The copper metal can only have been incorporated in the ceramic matrix while it was hot to the level of
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vitrification, while the sulphides can only have been deposited here when the vitrified ceramic was cool enough to allow cracks to form in the glassy parts, and by a mechanism uniformly cladding external surfaces and the inside of bubbles, which are often visibly connected with each other and the surface by a network of cracks.

However, the combination of sulphide inclusions and gas bubbles frequently is found in copper smelting slag (Fig. 9). In those cases, however, the sulphides form prills attached to gas bubbles, which most likely form from the reaction of the sulphide with oxygen provided by the siliceous slag, resulting in the formation of sulphur dioxide and copper metal. These sulphur dioxide bubbles provide the buoyancy necessary to keep the matte prills afloat in the slag; accordingly, matte and gas form two semi-detached spheres, quite different from the concentric spheres of chalcopyrite cladding the inside of air bubbles as is the case in the Pfyn crucibles.

Textural and phase issues

A further significant aspect is the correct identification of the sulphides present in the Pfyn crucibles. They have previously been identified by XRD as chalcopyrite, and ore microscopy has confirmed this identification. However, chalcopyrite can originate from a number of formation processes. While these processes produce a phase of identical composition and fundamental crystal structure, they often result in quite different morphologies and textures, which are in turn indicative of the respective processes.
The most common texture of chalcopyrite ore relevant to ancient smelting is that of rich hydrothermal ore deposits, where the mineral forms well-developed crystals and aggregates, often intergrown with other sulphides such as pyrite, galena and sphalerite, and gangue minerals such as quartz, barite or calcite. The grain size of these crystals ranges from several centimeters down to a few micrometers, and they are typically either exhibiting their characteristic crystal forms or have more or less straight boundaries with their neighbouring minerals. Ancient smelters apparently preferred more coarse-grained ore which they could more easily concentrate by crushing and sorting, but finer-grained minerals are often intergrown with each other and survive as tailings or other waste materials near the mine and the smelter.

In the material studied here, the chalcopyrite forms layered structures and spheroidal aggregates of needles pointing outwards from a nucleus; the combination of these two textures results in the cauliflower-like pattern which predominates in these samples when the chalcopyrite layer borders on one side to void space. This texture is indicative of low-temperature, often aquatic environments of sulphide deposition, such as are prevalent in certain submarine-exhalative or sedimentary ore deposits (e.g., Ramdohr 1975).

In contrast, matte inclusions, i.e. artificial copper-iron sulphides from metallurgical contexts, have a texture typical of solidification from a melt phase, including the decomposition of a high-temperature solid solution crystal into a matrix of bornite with lamellae of chalcopyrite or vice versa, depending on the exact copper to iron ratio, and eutectoid structures of matte with magnetite, reflecting the iron and oxygen content in the system (e.g., Bachmann 1982). These latter structures are extremely rare in nature, while they are the norm in copper slags and other artificial contexts involving base metal sulphide melts.

**Smelting or melting?**

The investigation so far has demonstrated that there is likely a chronological gap between the incorporation of the copper metal into the vitrified ceramic, which is obviously contemporaneous with the high-temperature activity which took place in these crucibles, and the formation of the chalcopyrite, which has been deposited only after the material had solidified and cracks had formed in the vitrified ceramic. Furthermore, the texture of the chalcopyrite is indicative of a low-temperature formation, probably within an aquatic environment. Thus, there is evidence for the presence during the use of the crucibles for metallic copper, while the chalcopyrite has formed later, probably only during the deposition of the crucibles in the archaeological layers. This temporal division makes it very unlikely that the chalcopyrite represents residual ore of a smelting operation.

A further argument against chalcopyrite smelting is the lack of an enhanced iron oxide level in any of the vitrified material; unpublished EDS analyses of the vitrified ceramic of these crucibles match closely the composition of the un-vitrified ceramic matrix, with the exception of an elevated copper content in the vitrified material. If chalcopyrite ore would have been smelted in these crucibles, one would expect a noticeable increase in the iron oxide content of the siliceous phase, effectively making it a metallurgical slag rather than vitrified ceramic material. Such an increase in iron oxide contents in the siliceous materials on the inside of vitrified crucibles has been found both in Early Bronze Age copper smelting crucibles from Shahri-Sokhta in Iran (Hauptmann et al. 2003) and in Chalcolithic crucibles used to smelt arsenical copper in SE Spain (Müller et al. 2004). While the absence of evidence rarely is evidence for absence, it is difficult to see in this case how chalcopyrite can be smelted to copper without significantly enriching the surrounding melt in iron oxide.

**The origin of the chalcopyrite**

It is relatively straightforward to exclude copper smelting, based on the microscopic evidence presented; this leaves, however, the necessity to explain the presence of significant amounts of chalcopyrite within the metallurgically relevant areas of the crucibles. The occurrence of chalcopyrite in nine out of eleven samples is clearly a significant observation, given that these eleven samples were initially taken with a ceramological study in mind, not a metallurgical one. On the other hand, it is a phenomenon apparently characteristic of the Pfyn crucibles; I am not aware of any other copper crucibles having been reported to possess such chalcopyrite layers.

The key to their understanding lies in the particular texture, identified earlier as indicative of a low-temperature, possibly aquatic, origin, in combination with the small framboid aggregates of pyrite crystals which were found dispersed throughout several samples. We know that the crucible fragments were excavated from lake settlements, where they were embedded for millennia in the silty sediments. These sediments were often anaerobic, as is indicated by the
frequent preservation of organic material such as wood, which makes them archaeologically very exciting. In these anaerobic conditions thrive bacteria which base their metabolism on the processing of sulphurous compounds, resulting in the deposition of metal sulphides as a metabolic waste product.

Without having explored in detail the biochemical mechanism responsible, it is reasonable to assume that the slow corrosion of the metallic copper trapped in the vitrified parts of the crucibles, together with the release of iron ions from the weathering glass matrix, provided a supply of metal ions into the surrounding aquatic anaerobic environment, where these ions reacted with the sulphide ions provided by the bacteria to precipitate as chalcopyrite. In those parts of the crucibles where no copper metal was present, and hence no copper ions available, we accordingly find only pyrite aggregates. The much increased quantities of sulphide precipitation in the vitrified areas compared to the not vitrified parts of the crucibles most likely results from the much increased release rate of metal ions due to the increased corrosion rate of the vitrified ceramic compared to the non-vitrified ceramic.

So what?
The hypothesis of copper smelting can be safely ruled out for the Neolithic crucibles of the Pfyn culture. Instead, a much more convincing alternative model is proposed to explain the presence in these vessels of chalcopyrite together with copper metal. This shift in interpretation has several ramifications, two of which I want to stress in this context; one relates to the archaeological interpretation, while the other is of methodological concern.

Firstly, the presence of metal artefacts and the apparently local ability to melt and cast copper demands a discussion of the origin of the metal as much as that of the metallurgical skill. It is beyond the scope of this paper to speculate on either of these, but it is clear that the former is probably best addressed in the context of a typical metal provenancing study, using lead isotope ratios and trace element studies (Rohl and Needham 1998). The relatively rich data sets available for the period, particularly for the Balkans as one of the main potential supply regions (Pernicka et al. 1993, 1997), should make this a feasible task. The other is more difficult to address scientifically; too little comparative data is available at present to consider ‘technological styles’ or similar approaches to distinguish between potential directions of transfer of knowhow. It may suffice here to suggest that the Pfyn metallurgy was probably based on imported copper metal, obtained probably via a long-distance trade link which at some point in time failed, spelling the end to this secondary metallurgy. A similar case of a regional metallurgy being based on imported copper alone is known i.e. from contact period Canada, with the Inuit manufacturing a range of implements from European brass kettles (Moreau and Hancock 1996).

An important aspect of this study, significant well beyond the immediate chronological or regional framework, is the apparent strength of optical methods, common sense and an open mind when considering the seemingly firm and indisputable results obtained by advanced scientific instruments. Archaeology is a historic science where relative and absolute time are important factors, while many scientific approaches are based on the actualistic paradigm that time has no influence on the validity of measurements or laws of nature. Despite this, science-based archaeological approaches have to consider the impact implicit in the chronological dimension of archaeology. The situation present now is the cumulative result of different processes, and these have to be seen in a quasi-stratigraphic sequence. Any instrumental analysis will only describe the status quo, without chronological depth. This is equally important for issues of technological processes lasting only minutes or hours, and for the effects of corrosion and post-depositional changes taking place over several millennia. Of the many analytical methods nowadays available to the archaeometrist, image-based approaches are still best suited to take into account aspects of contemporaneity and sequentiality.

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