

Mineralogy of slags: a key approach for our understanding of ancient copper smelting processes

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Copper was the first metal to have been smelted (extracted from its ore) some seven thousands year ago in the ancient Near East. For most pre-industrial periods, the documentation of copper smelting *chaîne opératoire* relies mainly on investigations by archaeometallurgists of the metallurgical waste recovered during archaeological excavations, namely the copper slags. Copper slags are mostly an assemblage of crystals of oxides (iron, manganese, *etc.*), olivine (fayalite, *etc.*) and/or pyroxenes embedded in a polymetallic more-or-less glassy matrix. The mineralogy of the slags is directly related to the initial charge and the working conditions prevailing in the pyrometallurgical reactor. This chapter aims to give an overview of how copper slag mineralogy is investigated and the type of information it yields in order to help our understanding of past metallurgies and societies.

1. Introduction

1.1. A short history of copper metallurgy

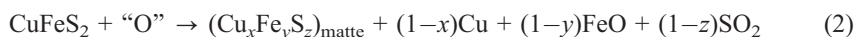
Copper and its alloys were among the earliest valuable and strategic metals used by humans together with gold and silver (Tylecote, 1992; Mille and Carozza, 2009). Copper alloys such as arsenical copper and then tin-copper – also called bronzes – gradually replaced lithic tools and weapons during the Bronze Age (~2000 to 800 BC in Europe), before being replaced in turn by iron and steel during the Iron Age (Tylecote, 1992). Copper alloys, however, were still being widely used afterwards for common ware. Day-to-day items such as vessels, candlesticks, *etc.* began to be mass produced in copper and alloys in Europe from the 13th Century AD onwards (Thomas *et al.*, 2013). From the 15th Century AD to the 19th, artillery manufacture meant that copper and particularly bronze were highly prized materials (Killick and Fenn, 2012). One particularly illustrative example of the strategic importance of bronze cannons, as a guarantee of a safe and sustainable shipping trade, is very thoroughly and nicely depicted for 14th–17th Century Venice (Avery, 2011). From the very beginnings of

their exploitation up to the present time, copper and/or some of its alloys have been associated continuously with a high aesthetic value. Among the most famous examples are the so-called ‘bronze’ statues and statuettes that were produced widely during Antiquity, in medieval Asia, in Africa, as well as in Early modern Europe. By means of splendid inlaid basins, ewers, and candlesticks, the medieval Islamic World spread the shine of bronze and brass all around the world as well.

1.2. Copper smelting: from ore to metal

The most important sources of copper are sulfides, oxides and carbonates (Artioli, 2010). When exploited by humans, these minerals may be called ores (Killick, 2014). Copper ores need to be processed thermally and chemically – ‘smelted’, in order to extract the metallic copper. The processes of copper smelting belong to the field of extractive metallurgy. We will briefly explore the main processes in use during pre-industrial times in the next section. Native copper may also have been present in a number of copper deposits, notably in North America and may have been exploited occasionally by human groups. It must be emphasized that the working of native copper solely by hammering, as done notably at the very beginning of copper metallurgy, refers more to tacit know-how directly inherited from the lithic industry than to the acquisition of new skills and knowledge pertaining to metallurgy, that is the mastering of thermo-chemical and/or thermo-mechanical treatments (extraction of ore, refining, alloying, casting, annealing, *etc.*). Thus, the evidence of copper items within a given chrono-cultural context does not necessarily indicate the mastering of metallurgy (Bourgarit and Mille, 2007).

The aim of copper smelting is to recover metallic copper from its ore. This implies that in most cases two chemical transformations have taken place (Davenport *et al.*, 2002; Lossin, 2003). On the one hand, copper compounds have to be separated from the other species of minerals present in the ore, *i.e.* from gangue material. Iron and/or silica compounds are encountered very frequently in copper deposits (equation 1). On the other hand, copper has to be reduced, either from its oxides or from any other compounds including sulfides (equation 2). In practice, these two chemical events – which may take place at one or several different stages of the smelting process – are thermally activated: at relatively high temperatures for equation 1 (typically ~1200–1300°C) and at lower temperatures for equation 2 (~500–700°C). High temperatures in pre-industrial periods were achieved by burning wood and/or charcoal in more or less elaborate reactors (charcoal beds, bone fire, ceramic vases, built furnaces, *etc.* see Rehder, 2000). Depending on the process, the period and the ore being smelted, a large quantity of waste would have been produced. There is agreement among those studying ancient copper smelting processes that this waste should be referred to as ‘slag’.



1.3. Copper slags: the main material studied

1.3.1. Other sources exploited for the investigation of smelting processes

Most ancient copper-reduction processes are documented exclusively by historical sources, namely excavation of production sites. Written documents are sometimes referred to, but these may cause confusion because the main studies to date deal with prehistoric societies. The 16th Century AD description of a medieval copper smelting process in Bohemia is a good example (Agricola, 1556). Being one of the first technical treatises on the subject published in western Europe, it has long led scholars to misinterpret protohistoric processes (see for example the nice review by Metten, 2003). Ethnographic studies may also shed some light on ancient metallurgical processes (Iles and Childs, 2014) but parallels should be drawn with care. Few such studies have been undertaken so far for copper smelting (Zschoke and Preuschen, 1932; Lewin and Hauptmann, 1984; Herdits, 1993; Bisson, 2000; Anfinset, 2011). Archaeological assemblages commonly provide evidence of metallurgical structures and associated items such as furnaces, ceramic vases, tuyeres and metallurgical *chaîne opératoires* indeed are based mainly on ceramics (Martinón-Torres and Rehren, 2014). More generally, archaeology aims to shed light on the evidence of the spatial organization of the activity (spatial distribution of structures and waste). However, most of the evidence usually records only a small part of the information related to the processes. Moreover, the informative potential of such archaeological material is often severely reduced because of poor conservation: the superstructure of furnaces is a good example of this, being systematically absent from the archaeological record. Therefore, copper slags represent the most interesting source of information with which to work.

1.3.2. Slag description

As noted above, most researchers working on ancient metallurgies have agreed to refer broadly to all waste produced during copper pyrometallurgical processes, including smelting operations, as ‘copper slag’ (Hauptmann, 2014). Bachmann (1982) was the first to set up a typology of ancient copper smelting slags which encompasses more or less all the types encountered at protohistoric to medieval sites (Fig. 1). This typology is still in wide use. In pre-industrial contexts, copper slags usually reveal complex compositions. Their macrostructure ranges from a very heterogeneous aggregate of unreacted minerals bound by a fused phase, up to almost perfectly homogeneous melt (Fig. 2). Due to rapid cooling, the melt generally consists of a fine grained mixture of different phases (Fig. 3). Crystalline phases are usually olivines, (fayalite, Fe_2SiO_4 or tephroite, Mn_2SiO_4), spinel (magnetite, Fe_3O_4 or hercynite, FeAl_2O_4) and pyroxene (*e.g.* hedenbergite, $\text{CaFeSi}_2\text{O}_6$). Cu-based inclusions are frequently present, either as sulfides or as metallic Cu, the latter often being oxidized as copper oxides, carbonates or chlorides. These phases grow in a developed silica- or manganese-based glass.

1.3.3. Slag representativeness

Depending on the production context and on the period, the quantity of slags recovered may vary from a few kilograms to thousands of tons. The first question for

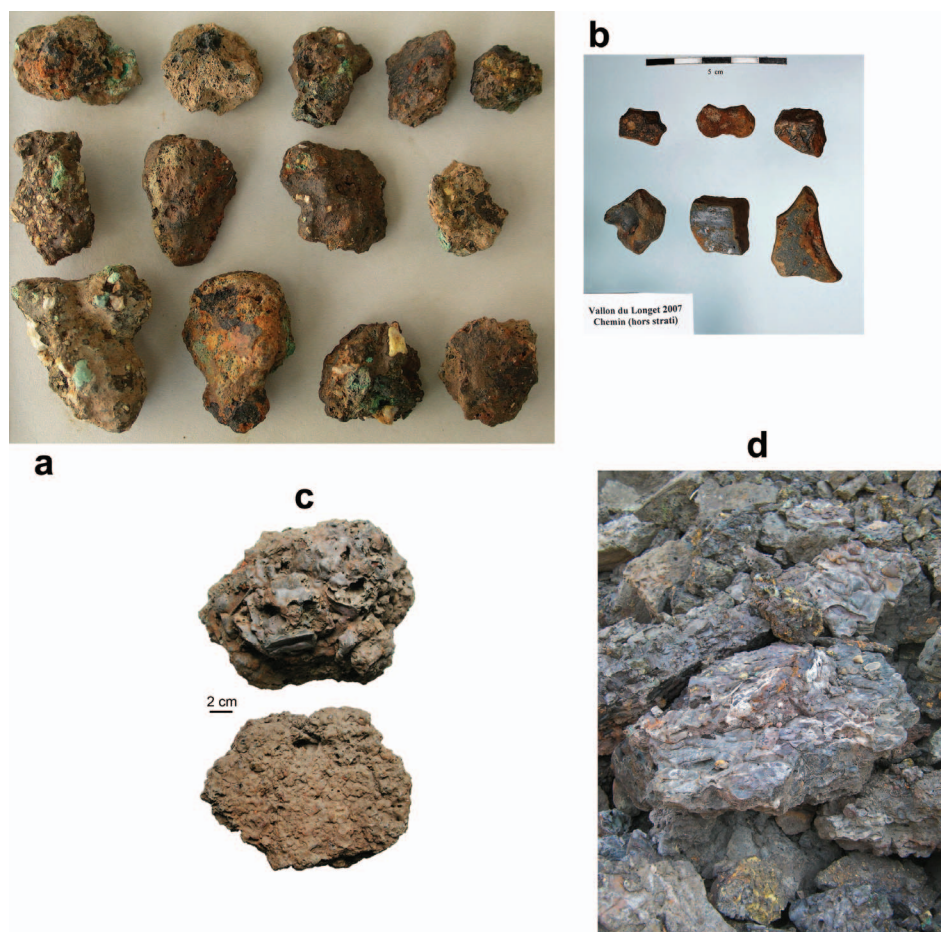


Figure 1. Main types of copper smelting slags recovered so far from pre-industrial sites. (a) Conglomerate slags from Chalcolithic La Capitelle du Broum, France (size \approx 1 cm); (b) plate slags from Early Bronze Age Saint-Véran; (c) coarse slags from Late Bronze Age Luzerna, Trentino; and (d) tapped slags from Roman Skouriotissa, Cyprus.

archaeometallurgists is to decide what these copper slags represent with respect to the process as a whole and its possible evolution during the chronology of a site's occupation. Let us examine two extreme situations.

In the following: 'Chalcolithic' will be used to designate the period when copper smelting first appeared. At most Chalcolithic sites excavated so far tiny quantities of smelting debris have been recovered: a maximum of a few hundred small pieces weighing several kilograms at the most (Bourgarit, 2007). Several reasons may be put forward. First, Chalcolithic copper production is usually small and is devoted to small implements intended for a restricted circle of consumption (Mille and Carozza, 2009).

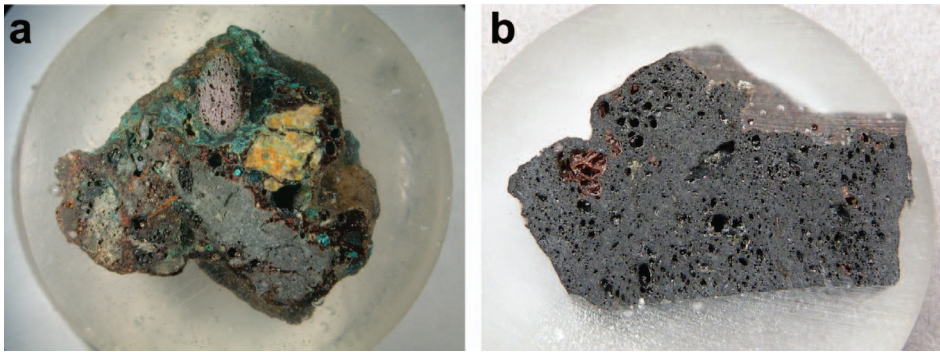


Figure 2. Two extreme cases of copper-slag macrostructures on bulk polished sections (daylight macrophotography). (a) Unreacted minerals in a conglomerate slag from Chalcolithic La Capitelle du Broum, and (b) homogeneous melt in a plate slag from Early Bronze Age Saint-Véran (size of image \approx 2.5 cm).

Second, slags are usually too viscous for proper copper separation, thus requiring crushing to recover the entrapped copper prills. The resulting minute slag pieces or even fine slag sand can easily escape the archaeological record (Bourgarit and Mille, 2005). Whether crushed or not, slags may disappear during burial mechanisms including corrosion. Such mechanisms are usually well documented by archaeologists, whereas copper slags are usually quite chemically inert in most burial environments, although selective corrosion may occur at the rims (Carozza *et al.*, 2010). Third, slags may be recycled as seen in a number of slag-tempered ceramics. This phenomenon is nevertheless quite rare and easily quantifiable. It has also been proposed that slags may

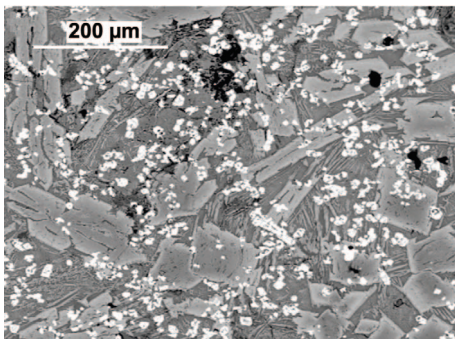


Figure 3. Typical copper-slag microstructure as seen by SEM (backscattered electrons) on a plate slag from Saint-Véran, French Alps: Mg-fayalite appears here as zoned polyhedra with a rim depleted in Mg; grains of magnetite (white) and dendritic augite-like clinopyroxenes (dark grey) are also present.

be reintroduced in the charge with fresh ore as catalyst. Such recycling should reappear in the archaeological record... as slags. Another possible reason for the small quantity of slags recovered is that smelting sites may be seasonal, *i.e.* ephemeral. This has been proposed for an Early Bronze Age site in the Alps (Bourgarit *et al.*, 2008), where the amount of slag (\sim 100 kg) was estimated to have been produced over a period of 4–8 months. This does not apply to all sites. For example, the 500 slag items ($<$ 1 kg) recovered during one excavation campaign at a Chalcolithic site in southern France (Fig. 1) could not have been produced by more than one or two smelting runs (Bourgarit and Mille, 2005). Finally, when combined, these

hypotheses may explain only partly the minute quantities of slags recovered: opened some decades ago, the debate has not evolved much beyond this point (Craddock, 2007). One extreme hypothesis is that the earliest smelting operation used to work high-grade ore thus producing few slags, if any. ‘Non-slaggering’ processes are evoked; the few slags recovered would thus stem from trial and error which would represent in the smelting process either a lower-grade ore or a less carefully beneficiated ore. Consequently, more gangue elements would need to be removed. Ultimately, the question remains: what do the few slags recovered represent? Whatever the explanation, the relative homogeneity of the slag corpus under study in terms of both typology and composition will guarantee its archaeological consistency, and thus its meaning. What meaning? In the extreme case of trial and error products, it may be assumed that the few slags recovered would represent the upper limit of the current skills and know-how.

Given the large number of slags, other issues may arise. For example, the huge Roman slag heaps in the Troodos mountains, Cyprus – the largest known so far in the ancient World – enclose millions of tons of slag, each lump of which weighing several hundreds of grams (Fig. 1). Such large slag deposits were produced centuries ago (in Roman times), probably over a large time span (several centuries). Due to possible reworking, displacements, *etc.*, the current structure of the heaps may not reflect the original one, thus rendering interpretation of stratigraphic dating difficult. Absolute dating of slags would be one solution to help sorting. Archaeomagnetism represents a promising route (Shaar *et al.*, 2011). Some preliminary work has been carried out by thermoluminescence on the quartzite of a slagged sherd of tuyere (Hauptmann and Wagner, 2007). Also, ^{14}C dating may be applied to entrapped charcoal pieces. However, absolute dating of slags is not common practice, notably because of the cost. Moreover, the chronological resolution may not always be sufficient. A marked variability of smelting residues from coeval workshops cannot be excluded (Humphris *et al.*, 2009). A large sample may appear as the best solution, but how large? In Cyprus, the 80 slags sampled from three different late Roman heaps revealed a large variability (Georgakopoulou and Kassianidou, 2013). Several hundred pieces were probably examined, requiring rapid and inexpensive selection methods. A number of such methods are applied routinely by archaeologists: typology, colour, density, *etc.* For the Cyprus story, all the Roman slags appear to belong to the same tapped-slag type and probably exhibit similar densities. Colour does not seem to be relevant either (Kassianidou, 2003). Handheld X-ray fluorescence may offer an intermediate solution, having been developed for analogous modern purposes (*e.g.* metal sorting prior to recycling).

2. A brief historiography of archaeometallurgical studies of copper smelting

2.1. When and where?

It is not within the scope of the present chapter to draw a comprehensive historiography; for a general view see Craddock (1995), Killick (2001, 2014). There are a few markers.

Theodore Wertime's expedition in 1968 in Afghanistan, Iran and Turkey marked the first large-scale attempt to survey ancient copper smelting sites – among other places involved in pyrotechnical activities (Arab and Rehren, 2004a,b). One of the main aims of the expedition was to document the very beginning of copper extractive metallurgy which was thought to have arisen in those areas under survey. For several reasons the expedition did not yield the expected results. Almost simultaneously, large-scale excavations were carried out in the Timna mining and metallurgical district of Israel (Rothenberg, 1990). These represent the first focused studies of ancient copper mining and smelting processes. A short time after, another big project was started in the nearby Faynan valley in Jordan (Hauptmann, 2007), leading to one of the most comprehensive studies on copper mining and smelting carried out to date. The large time span covered by the numerous sites excavated allowed the evolution of copper smelting to be established, from its very beginning (Chalcolithic, *i.e.* 4th millennium BC in this region) up to the early Islamic period. Simultaneously, the Eastern Alps were examined thoroughly, mainly for Bronze Age occupations (end of 3rd to 1st millennium BC, see Weisgerber, 2004). The British Isles have provided the field with major milestones as well, although the main interest here has been copper mining rather than smelting (Timberlake, 2003; O'Brien, 2004). The Iberian Peninsula has also yielded interesting data regarding the beginning of copper extractive metallurgy (Rovira and Montero-Ruiz, 2013). It is stressed that protohistoric periods (Bronze and Iron Ages) have been and are still being studied much more than the following periods including Roman and medieval times. The geographical distribution of copper smelting sites being excavated is also very uneven, the main efforts being directed to the Near and Middle East, the Alps and the Mediterranean. In comparison, studies in Eurasia and in eastern and northern Europe are rare. Africa, east Asia and the Americas are underexplored despite recent attempts notably in Japan, China, Mexico and Chile (Yoshikawa *et al.*, 2006; Maldonado and Rehren; 2009; Mei, 2009; Mille *et al.*, 2013; Zori *et al.*, 2013; Mei *et al.*, 2015; Figueroa *et al.*, 2018).

2.2. Why?

The aims of the copper-slag investigations have been evolving depending on the teams involved and archaeological contexts. Three goals may be targeted. One primary objective is to determine whether copper smelting has been carried out or not. In a number of cases this may not be straightforward; we will come to this in Section 4. The types of ore smelted including their provenance may also be an objective of slag investigation, particularly when smelting sites are far from the mines. This is notably the case at the beginning of copper metallurgy in Eneolithic Trentino (Cierny *et al.*, 2004) and Chalcolithic Faynan Valley (Hauptmann, 2007). Finally, the aim is to characterize the copper smelting processes. The main working conditions to be documented are the nature of the charge being smelted (*e.g.* deliberate mixture of ores, addition of fluxing agents, *etc.*), the thermal cycles, the atmosphere(s), and the duration of the different steps. This may start by understanding the nature of the physical and chemical mechanisms involved (reduction of copper, formation of the different compounds, *etc.*).

As for most of the studies dealt with in this volume, these three ‘technical’ objectives are underlined by a number of issues raised by the archaeology and history. How is copper production organized (*e.g.* as a household activity performed in the domestic sphere or as more specialized systems)? What is the whole *chaîne opératoire* including ore prospection and destination of final product? How are technological choices made, if at all? Is it possible to reconstruct a technological lineage? The smelting strategy is constrained by one or several factors including technological, social, economic, political as well as cultural. Moreover, the complexity of the processes may constitute an accurate record of innovation and/or inventions, *i.e.* of technological transfers between human societies. In the last two decades a number of Anglo-Saxon archaeologists and archaeometallurgists have monopolized the social anthropological questioning on copper smelting and more generally on ancient copper metallurgies (Budd and Taylor, 1995; Ottaway, 2001; Kienlin, 2014; Thornton, 2014; White and Hamilton, 2014). Ironmaking has generated a number of papers as well (Charlton *et al.*, 2010, 2013b). It is beyond the author’s competence to comment on these works, and on the scepticism sometimes expressed about the Anglo-Saxon approaches (Killick and Fenn, 2012). Note also the interesting (French) work carried out on late prehistoric lithic and ceramic technologies (Rouillard *et al.*, 2007; Pelegrin, 2009; Roux, 2010, 2013).

2.3. Who?

Our understanding of all the ancient copper-production modes is a matter of interdisciplinary collaboration involving archaeologists, historians and a number of different specialists from natural sciences. That said, the researchers working on the smelting processes belong to a well defined discipline called archaeometallurgy (Rehren and Pernicka, 2008; Killick and Fenn, 2012; Killick, 2015). So far, most studies have been carried out by European teams. Though the USA has hosted some of the first archaeometallurgists (C.S. Smith, R. Maddin, J. Muhly), none of them has ever worked on copper smelting. American archaeometallurgists working on copper smelting are still few in number. China, Japan and some South and Central American countries have only recently entered the field.

Who are these archaeometallurgists? Mineralogists have always been very active in the field. This is easily understandable as the study of ancient copper reduction processes relies mainly on the investigation of complex mineral assemblages, *i.e.* copper slags. As far as metallurgical processes are involved, metallurgists have also naturally been involved since the very beginning. Archaeologists are also involved of course. Increasingly, the younger generation of investigators has benefited from a mixed background in both archaeology and material sciences. This may appear as a drawback because the basic knowledge in mineralogy and metallurgy is diluted, whereas the materials (slags) and processes to be examined are often very complex. Yet the high quality of a number of recent papers tends to invalidate this pessimistic view.

2.4. How?

Once the slags are sorted according to their typology (size, form, colour, texture) and density, their investigation follows more or less standard mineralogical protocols, from petrographic studies of thin sections to investigations of mounted thick sections and samplings, including elemental analysis and powder X-ray diffraction (Hauptmann, 2007, 2014). To our knowledge, only two attempts – both promoted by Gilberto Artioli – have been made so far to quantify the crystalline phases by Rietveld refinement of the diffraction diagrams (Bourgarit *et al.*, 2008; Addis *et al.*, 2016). Due to the complexity of the diagrams, the precision on quantification is often rather poor. Yet it is often adequate for understanding production modes. In the two aforementioned cases this quantification has proven to be determinant (see Section 4). Scanning electron microscopy (SEM) and microanalysis systems have gained importance in slag studies, not only in helping to identify mineral phases, but also in characterizing chemical compositions of amorphous phases and pointing out chemical segregations such as zoning. Yet, one may regret that SEM examinations and analysis are slowly replacing the less time and money-consuming petrographic observations. Less common analytical approaches such as Mössbauer spectrometry (Moesta *et al.*, 1984; Metten, 2003), Fe-K-edge X-ray absorption near edge structure (XANES) and high-wavelength resolution WDS electron microprobe (Burger *et al.*, 2010) have been carried out in order to quantify the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the bulk or in particular phases. Note that, to the author's knowledge, grouping of slags using statistical treatments on elemental composition as has been done for iron smelting (Charlton *et al.*, 2013a) has never been carried out before.

Metallurgical approaches and notably those dealing with modern slag systems mostly inspired by the steel industry (VDEh, 1995) are underrepresented in the archaeometallurgical literature. The best example of this may be seen in the scarcity in the archaeometallurgical literature of simple empirical methods for determining the physical and chemical properties of ancient slags such as melting temperature and viscosity (Lutz *et al.*, 1988). This brings us to thermodynamics and kinetics calculations. Theoretical approaches are used at various levels to assess some of the working conditions. The main working conditions are temperature, atmosphere, initial charge composition, slag viscosity and process duration. How these parameters are deduced from slag investigations will be detailed in the next section. Yet, the chemical systems and reactions involved in the smelting processes are often too complex for fully satisfactory thermodynamics and kinetics calculations because of the heterogeneity of ancient slags and because the systems are commonly far from thermodynamic equilibrium. The experimental simulation route may open complementary avenues. Various aims are targeted (Doonan and Dungworth, 2013). Small-scale model experiments carried out in laboratories focus on specific aspects of the chemical reactions and working conditions. As far as we know, few such experiments have been published to date (Neuninger *et al.*, 1970; Tylecote, 1974; Moesta, 1983; Rostoker *et al.*, 1989; Pollard *et al.*, 1991; Bourgarit *et al.*, 2004; Burger *et al.*, 2010). Full-scale models – often carried out in the field – are much more common and have been used

since early on in the history of archaeometallurgy (Gowland, 1912; Coghlan, 1939/1940; Böhne, 1968; Tylecote and Merkel, 1985; Zwicker *et al.*, 1985; Merkel, 1990; Herdits, 1993; Ambert *et al.*, 1997; Woelk *et al.*, 1998; Rovira, 1999; Bourgarit *et al.*, 2002; Lorscheider *et al.*, 2003; Yoshikawa *et al.*, 2006; Timberlake, 2007; Catapotis *et al.*, 2008; Hanning *et al.*, 2010). They generally choose to reconstruct either part or the whole process with the aim of understanding the economic and social environment (production rates, organization of the workshop, human skills, *etc.*). The term ‘experiential’ has been proposed for experiments focusing on the role of the human in the process, while ‘experimental’ simulations are devoted more to the study of the scientific aspects (Jeffery, 2004). Depending on the rigour of the approach (problem, set-up, publication), the data stemming from these numerous simulations may be of variable quality.

3. Main working conditions documented by slag investigation

3.1. Temperature

In modern industrial processes, and especially in the steel industry, there are two types of basic methods for measuring melting characteristics of a slag, namely the pressure drop method and the slag atlas method (VDEh, 1995; Dash *et al.*, 2012). In the archaeometallurgical field, minimal temperature is estimated mainly by plotting bulk composition of major elements into phase diagrams (Fig. 4). As pointed out by Hauptmann (2014), because the charge often only melted gradually and sometimes only partially it is informative to follow the phase diagram by increasing the temperature. Yet it must be kept in mind that the slag we observe *post mortem* is the result of a decrease in temperature leading to complete solidification. Because minor

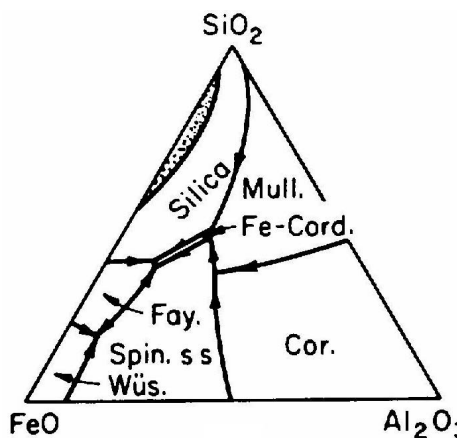


Figure 4. Ternary system FeO–Al₂O₃–SiO₂ showing different phases at thermodynamic equilibrium.

elements are not taken into account, and because thermodynamic equilibrium is rarely reached these calculations yield only a rough approximation. The archaeometallurgical community is now well aware of that (see the very interesting discussion in May 2014 on the archmetals web forum hosted at Oxford University (arch.oucs.ox.ac.uk/detail/95684/index.html) after a comment on a paper by Young and Poyner (2012). Note that a recent experimental study on lead smelting by the iron reduction process has shown that chalcopyrite, CuFeS₂, may play a key role in fostering the formation of fayalite, Fe₂SiO₄, at temperatures below the fayalite liquidus (Liu *et al.*, 2015). When present, chemical zoning

offers a complementary way to infer temperature. Moreover, not only minimal but also maximal temperatures may be estimated in that way. Zoning occurs quite often for olivine in the fayalite–forsterite system, with an enrichment of the forsteritic component at the rim (Fig. 3). Temperatures at different Bronze Age sites in the Alps were thus shown to range between 1200 and 1350°C (Fig. 5) (Bourgarit *et al.*, 2008; Burger, 2008; Addis *et al.*, 2016). The estimates are far from precise, but they are generally adequate for understanding ancient processes. The main question here is how were such temperatures reached? The different technological answers (wind-furnaces, hand- or feet-powered bellows, blowpipes, quality of insulation, *etc.*) actually lead to the same temperature range. To date archaeology has proven to be the best way to document the heating technology.

3.2. Atmosphere

In the usual working temperature range (1200–1350°C), copper smelting takes place within two main redox systems. First, the Cu system: Cu^+ and/or Cu^{2+} have to be reduced to Cu. Second, depending on the gangue, the Fe or Mn system controls the formation of the slag, as frequently exemplified by the quartz, fayalite and magnetite (QFM) buffer equilibrium (equation 3). Both temperature and oxygen fugacity control these two systems. The latter is influenced mainly by the CO/CO_2 ratio prevailing in charcoal-powered smelting reactors. The main objective of archaeometallurgists when trying to infer the CO/CO_2 ratio is to reconstruct the height of the charcoal column in the reactor, and consequently the height of the reactor itself (Rehder, 1999). As a

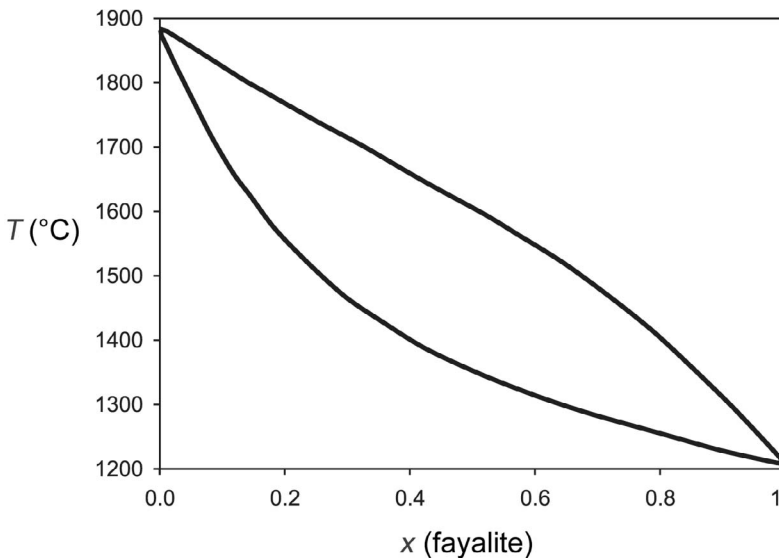


Figure 5. Quasi-binary phase diagram forsterite–fayalite $(1-x)\text{Mg}_2\text{SiO}_4 + x\text{Fe}_2\text{SiO}_4$, (after Klimm and Ganschow, 2005).

reminder, furnace superstructures – if they ever existed – are systematically absent from the archaeological record.

Because most copper is removed from the slag, Fe or Mn oxides are the only available indicators of the redox conditions (although delafossite, $\text{Cu}^+\text{Fe}^{3+}\text{O}_2$, has been the main indicator of oxidizing conditions in early copper slags (Bourgarit, 2007)). In most studies, the redox conditions are estimated by looking at particular equilibria such as the aforementioned quartz, fayalite and magnetite (QFM) buffer equilibrium (equation 3). Usually, the equilibrium conditions are related unequivocally to oxygen fugacity using T - f_{O_2} Ellingham diagrams (Fig. 6). Because equilibrium is rarely reached, a better approach is to quantify the different iron-bearing phases and deduce the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the bulk (Burger *et al.*, 2010). Mössbauer spectrometry is the best method for this. Remember that the high-temperature composition may have been altered significantly during cooling, although laboratory experiments have shown that the cooling rate has no influence (Burger, 2008). That said, the equilibrium approximation is actually not problematic when high precision is not required.

This may become problematic, however, if both sulfide and oxide copper compounds are in the smelted charge. In addition to the three gases CO , CO_2 and O_2 , two other species have to be taken into consideration, namely S and SO_2 (Krismer *et al.*, 2013). Furthermore, experimental simulations and Mössbauer measurements (Burger *et al.*, 2010) have shown that the solid oxygen brought about by CuO exerts the main control

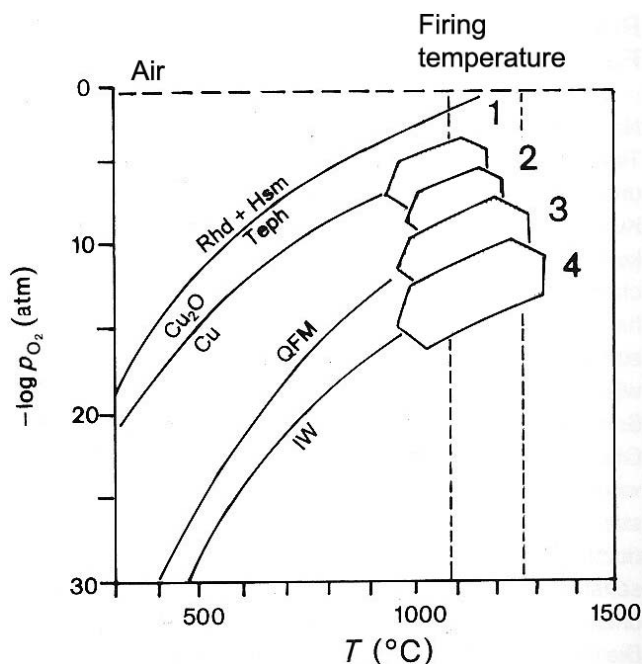


Figure 6. T - $\log f_{\text{O}_2}$ diagram for several redox systems including $\text{Cu}_2\text{O}/\text{Cu}$ and quartz/fayalite/magnetite (QFM) (after Hauptmann, 2007).

on the reactions with respect to O_2 . This is easily conceivable given the difference in molar volumes of these O-bearing compounds. At 1200°C , the molar volume of O_2 is $\sim 10^5 \text{ cm}^3$; it is $< 20 \text{ cm}^3$ for CuO . In other words, in the same volume one may put almost 10^4 times more atoms of O if one chooses to insert CuO instead of O_2 ! For the experiments, the partial pressure of oxygen (pO_2) was forced in the system by a draft of CO/CO_2 ; the amount of solid oxygen/solid sulfur (O/S) was controlled by a mixture of malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ /chalcopyrite CuFeS_2 . The main results are shown in Table 1. As an example, the same slag with a global amount of 35 wt.% Fe^{3+} could be obtained either under an imposed $pO_2 = 10^{-10}$ and a molar ratio O/S = 2.5, or at $pO_2 = 10^{-4}$ and O/S = 2. Thus, a small difference in the composition of the charge yields a change in equilibrium oxygen partial pressure of six orders of magnitude! If inferred solely from the oxidation state of Fe, the real redox conditions prevailing in the furnace can be incorrect.



3.3. Charge composition

The example above shows how important it may be to document properly the initial composition of the charge. A model has thus been proposed to estimate the amount of oxidic vs. sulfidic copper in the initial charge (Burger *et al.*, 2010). Besides the control of redox conditions, the ideal charge composition should obey another constraint: to balance the quantity of those elements forming the slag. Following the example of Fe, the ideal slag composition is the fayalitic one, Fe_2SiO_4 , *i.e.* two Fe for one Si. To discover whether copper smelters did manage to master the slag composition is a crucial issue for archaeologists and historians. This marks the beginning of productive extractive metallurgy. It is usually quite an easy question for archaeometallurgists to answer. Bulk chemical elemental analysis of slags is a quick way to distinguish between erratic and optimal compositions, as seen when comparing the silica-saturated Chalcolithic slags and the much more fluid Early Bronze Age fayalitic slags (Fig. 8).

Table 1. Global relative amount of Fe^{3+} (%) in laboratory experimental copper smelting slags according to the charge composition (chalcopyrite/malachite expressed as a molar O:S ratio) and the oxygen partial pressure in the atmosphere. Measurements by Mössbauer spectroscopy confirmed by Rietveld refinement.

Log (pO_2)	O:S					
	0	0.8	2	2.5	3	4
-3			63		>66	100
-4	0	7	35	60	>66	100
-7			24		>66	100
-10				36	>66	100

Remember, though, that the complex systems encountered in the slags often prevent the compositions from being plotted in relevant diagrams.

Behind this rather simple task of measuring an elemental composition, a more complex question hides: how was slag composition mastered? Theoretically, there are two main possibilities. On the one hand, the ore and its gangue may happen to yield a near-to-optimum composition which may just need some adjustments by careful beneficiation. To the author's knowledge, there is no archaeological evidence showing unequivocally that this was the only way to control the slag composition, although evidence showing the importance of ore beneficiation is abundant. On the other hand, adding of exogenous material may be carried out in the melt. At the Early Bronze Age Saint-Véran site, French Alps, numerous fragments of riebeckite ($\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}(\text{Si}_8\text{O}_{22})(\text{OH})_2$) have been found at one such smelting site. Because of both the distance from the riebeckite deposits and the size and quantity of the fragments recovered, this mineral is thought to have been brought there intentionally (Rostan and Malaterre, 1994) as a fluxing agent due to its silica content. Unpublished preliminary laboratory-scale experiments tend to show that the soda plays no significant role, although soda may promote removal of sulfur through the mechanism of *kernröstung* (Rosenqvist, 2004). Another means of fluxing is to use sacrificial ceramic tuyeres which have been shown to be applied intentionally to provide the necessary chemical input for early iron smelting in Jordan (Veldhuijzen, 2003). Contrary to the two previous examples, the large, exogenous Ca and Mg contents in the Chalcolithic slags of Roque Fenestre, Southern France (Bourgarit and Mille, 1997) were shown not to be deliberate additions. The resulting slag compositions were indeed erratic and far from any low-temperature eutectic. Yet Ca and Mg proved to follow systematically the dolomite stoichiometry. This has shown that dolomite was entering the melt, and therefore that the local furnaces – which are absent from the archaeological record – were more than simple holes in the ground: they did have rock walls (made out of the local rock, namely dolomite).

3.4. Process duration

Process duration is crucial for estimating the production rate. The duration depends mainly on two factors, namely the separation rate of the final product from the slag, and the slag cooling rate. To our knowledge the only attempt so far to quantify separation rates of the final product (mainly molten copper sulfides and metallic copper inclusions) from the slag was carried out by Addis *et al.* (2016). Therefore, the sinking velocity or buoyancy was calculated as a function of slag viscosity. Viscosity was assessed from the bulk chemical composition following a semi-empirical model (Lutz *et al.*, 1988). Other models and methods are available (VDEh, 1995). Depending on the type of slags recovered (see Section 4), minimum process duration periods of 2 h to >2 days were inferred.

Cooling temperatures can be assessed by the morphological texture of olivines and spinels (Donaldson, 1976) (see Fig. 9). Archaeometallurgical studies reporting on this are rare (Hess, 1998; Anguilano *et al.*, 2002; Manasse and Mellini, 2003; Artioli *et al.*,

2005; Burger, 2008; Addis *et al.*, 2016). At Saint-Véran, the slags exhibit an original columnar morphology of the fracture surface (Fig. 10). Whatever the thickness of the slag, a prismatic morphology is observed consistently for the first 4–6 mm of the section below the top surface. This feature has been interpreted as resulting from water quenching as part of an optimization of the production rate. The morphological texture of olivines and spinel do not testify to such rapid cooling, even near to the upper surface. Consequently, it is assumed that the quenching has been carried out after the formation of these crystals. Despite a high variability of the olivine morphology in the Saint-Véran slags, a cooling rate of $\sim 50^\circ\text{C}/\text{hour}$ may be a good approximation (Burger, 2008). Considering a 1200–1050°C solidification interval, the water quenching would have been performed some 3 h after the end of heating.

4. Three archaeological issues for copper smelting: cases studies

4.1. The appraisal of copper smelting: sulfides or oxides?

It has long been assumed that the first type of copper ores to have been smelted were oxides and carbonates, with sulfides being exploited much later. In other words, it has been stated that the appraisal of copper metallurgy was totally driven by a particular geological determinism: therefore metallurgy began where oxides and carbonates were to be found. Yet, an overview of Chalcolithic smelting evidence (Bourgarit, 2007) has proven that a number of extractive metallurgies started with sulfides, although the mineralogical evidence for sulfide smelting may not be straightforward in a copper slag (see in Section 4.3 the discussion on melting crucibles). Another argument against early copper sulfide smelting was that sulfides are far more complex to smelt than oxides. In copper sulfides, people meant mainly iron-bearing sulfides such as chalcopyrite CuFeS_2 : there would be a double difficulty in separating copper from both Fe and S. Yet, the question was biased. First, Chalcolithic processes were not necessarily looking for productivity and thus for efficient separation. Remember the aforementioned ‘non-slugging’ early processes where the slags had to be crushed in order to recover the entrapped copper prills. Such an immature process obviously satisfied the small demand for copper at the beginning of copper metallurgy (Carozza and Mille, 2007). Second, Fe and S are actually promoting the recovery of Cu. On the one hand, the large affinity of Fe for Si facilitates the separation of Cu from its siliceous gangue by forming olivines and/or pyroxenes (equation 1). Therefore of course, proper thermodynamic conditions must be met. This was already the case during Chalcolithic periods, as evidenced by the presence of olivine and/or pyroxenes in the very first slags recovered so far. On the other hand, the large affinity of S for Cu has proven to promote the separation of Cu from the slag by gravity. The neo-formed copper sulfide droplets such as covellite (CuS) and chalcocite (Cu_2S) do indeed exhibit relatively low melting point and viscosity, together with high density (Hauptmann, 2003). Here again, mineralogical studies have revealed sulfidic phases in a number of Chalcolithic slags (see Krismer *et al.*, 2013 for the formation conditions of Cu_2S), thus demonstrating that copper sulfide ores were being smelted from an early period.

4.2. Multistep processes for copper sulfide smelting: from Late Bronze Age to Chalcolithic

We have seen in Section 3.2 how difficult it is to bring sufficient O into the system to remove S. Several models have been proposed so far to explain how chalcopyrite used to be desulfurized, and more generally how it was smelted. Models are based on archaeological and slag mineralogy investigations, as well as experimental simulations. Here are a few examples, starting from the more recent ones.

4.2.1. Chalcopyrite smelting during the Late Bronze Age in the Alps

During the Late Bronze Age in the Eastern Alps, *i.e.* >1000 years after the first attempts to smelt copper in this region, quite complex processes have been assumed (Metten, 2003) at sites producing massive quantities of metallic copper (or copper sulfides) out of chalcopyrite. Here, archaeologists have revealed systematically a complex set up of reactors including batteries of furnaces and possibly roasting beds (Cierny *et al.*, 2004; Goldenberg, 2004; Weisgerber, 2004). Roasting beds are large banks of open fire on which the ore is displayed in order to oxidize it in air at relatively low temperatures (500–700°C is an optimum, see Davenport *et al.*, 2002; Lossin, 2003). The roasting process has produced no waste in the archaeological record so far, thus no mineralogical study could be carried out on this first step. Note that the very existence of a roasting bed is still a matter of debate (Doonan *et al.*, 1996; Metten, 2003). The archaeological record encompasses different types of slags obviously stemming from the high-temperature furnaces. Mineralogical studies have helped understand why (see also the mineralogical study of a furnace by Moesta in Moesta and Schlick, 1990). The first thorough study of the three types of slag recovered at Acqua Fredda, Austrian Alps, namely coarse cake-like slags, thin plate slags and sand slag, has shown that all types are chemically and mineralogically very similar (Metten, 2003). Metten has thus proposed a one-step process, although a preliminary roasting operation and a second smelting step are not entirely excluded.

Another very interesting investigation on coeval slags derived mainly from Luzerna, Trentino, has distinguished between three slightly different types, namely coarse (Fig. 1), massive and flat (Addis *et al.*, 2016). The distinction is based on a number of criteria including density, bulk chemistry, amount and composition of sulfide inclusions and relative amounts of fayalite/magnetite/pyroxene/quartz. These types are associated by the author with three distinct, successive, high-temperature metallurgical steps where chalcopyrite is transformed progressively into copper-sulfide (matte) growing in purity. Each step has various durations (see Section 3.3).

4.2.2. Early Bronze Age and Chalcolithic bornite and fahlore smelting

Such a multi-step process may be confirmed by another example of copper-sulfide smelting. The Early Bronze Age mining and metallurgical district of Saint-Véran, French Hautes-Alpes, provides the earliest evidence so far in Europe of primary copper mass production. A production of some seven tons of copper per year has been estimated (Rostan *et al.*, 2002) dated from the beginning of the 2nd millennium BC, *i.e.*

at least half a millennium before the two aforementioned sites. As for the Late Bronze Age sites, productivity was certainly a main concern. It has been shown that the mining and smelting rates were comparable (Bourgarit *et al.*, 2008, 2010). In order to promote efficient and rapid recovery of the copper compounds, slag viscosity was maintained below a critical level by controlling the amount of magnetite (Fig. 7). Also, as mentioned in the previous section, water quenching has been inferred as shown by the prismatic morphology below the top surface of the flat slags (Fig. 10). Interestingly, no roasting beds have been recovered so far at Saint-Véran, and only one type of slag has been exhumed at the two metallurgical sites excavated, namely the flat-type (Fig. 1). Does this mean that smelting was performed by a single-step process? Unlike the two aforementioned Late Bronze Age sites, the exploited ore is not chalcopyrite CuFeS_2 but bornite Cu_5FeS_4 . Much smaller amounts of S and Fe have to be removed. Hence, the starting product at Saint-Véran would be more or less the starting product of the third step at Luzerna, thus leading to similar flat slags.

Yet, early copper sulfide smelting does not systematically yield such homogenous ideal slags. More primitive types have been recovered in Chalcolithic southern France (Bourgarit and Mille, 2004) as well as during Early Bronze Age in northern Tyrol, Austria (Goldenberg, 1998; Martinek and Sydow, 2004; Goldenberg and Rieser, 2004; Höppner *et al.*, 2005). There, fahlores, *i.e.* solid solutions of tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ have been exploited. How? Several hypotheses have been

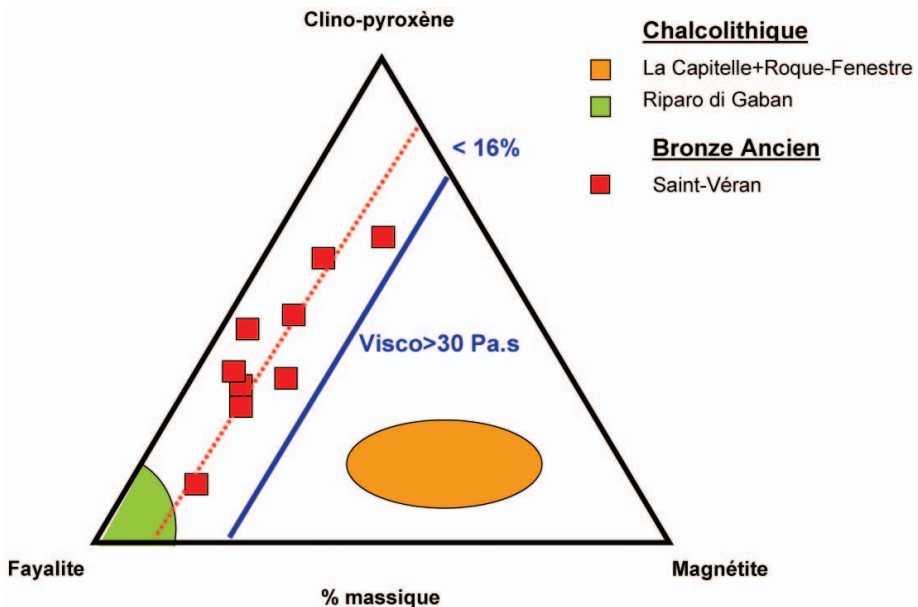


Figure 7. Relative amounts of fayalite, pyroxenes and magnetite in the Saint-Véran slags (red squares) as deduced by Rietveld refinement of powder diffraction diagrams. 16 wt.% of magnetite is the modern upper limit beyond which slags are considered too viscous. As a comparison, chalcolithic slags from La Capitelle and Roque Fenestre (orange area) are much too rich in magnetite, thus leading to high viscosity.

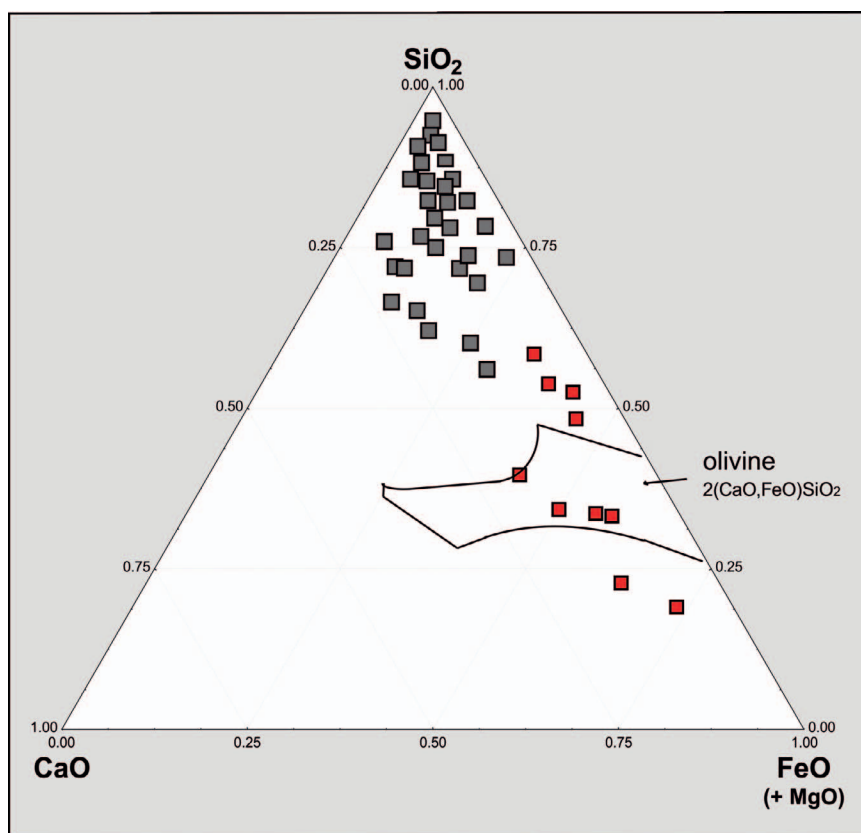


Figure 8. Bulk chemical composition (wt.%) of Chalcolithic slags from La Capitelle du Broum (grey squares) and Early Bronze Age (EBA) slags from Saint-Véran (red squares) plotted on the ternary diagram $\text{FeO(+MgO)}-\text{CaO}-\text{SiO}_2$ (analysis by proton-induced X-ray emission of pellets of homogenized powder). The line shows the fayalite liquidus domain (after Osborn and Muan, 1960) elemental composition. Most EBA slag compositions fit within the fayalite domain, whereas chalcolithic slags are much too rich in silica.

formulated, including a two-step process finishing with matte conversion (Bourgarit and Mille, 2005) as suggested by matte pieces in the archaeological record. The most crucial issue remains the removal of S. Therefore, both low-temperature roasting-like (Burger *et al.*, 2011) and high-temperature smelting steps (Burger *et al.*, 2010) have been carried out on chalcopryrite. Similar investigations have been performed on tennantite at high temperature (Bourgarit *et al.*, 2003). The main conclusion is that under pre-industrial working conditions – *i.e.* without massive O_2 input – such as those prevailing in the modern matte conversion processes (Davenport *et al.*, 2002), it is virtually impossible to de-sulfurize entirely the copper sulfide in a simple manner. There are three ways. First, dead-roasting is carried out for several days or even weeks, as testified by 16th and 18th Century texts (Agricola, 1556; Maréchal, 1985). The

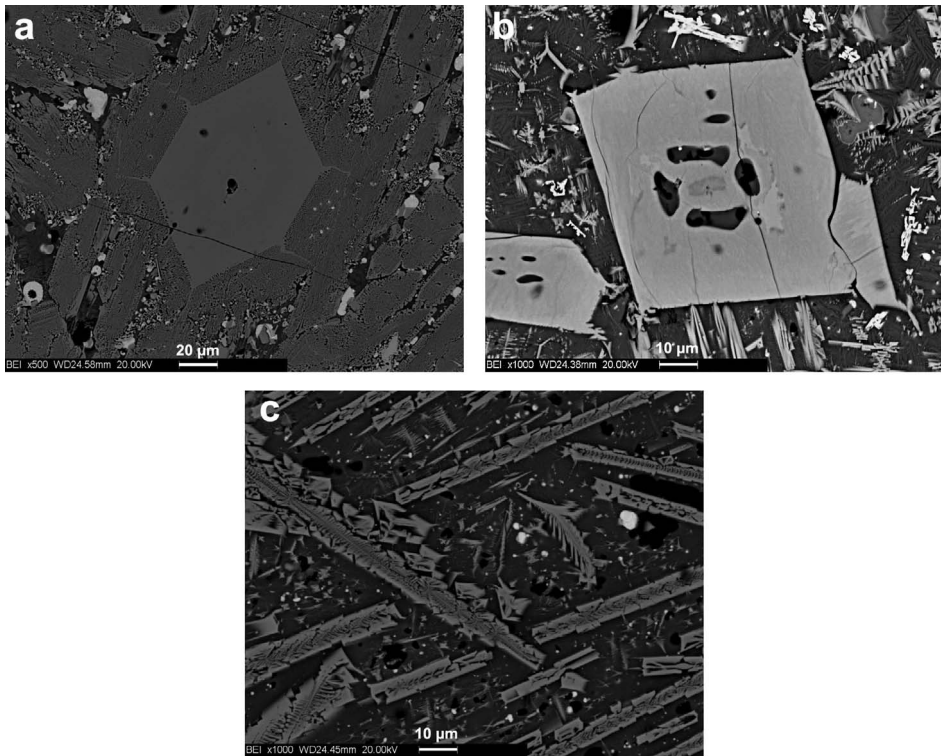


Figure 9. Different fayalite habits encountered at the Luzerna, Late Bronze Age Trentino smelting site, and corresponding cooling rates (after Addis *et al.*, 2016). (a) Prismatic olivine in coarse slags testifies to slow cooling rates (0.5°C/h), (b) Elongate hoppers in massive slags (40°C/h), and (c) chain olivine in flat slags indicate faster cooling rate (80–350°C/h).

resulting S-free ore is then smelted. Second, solid instead of gaseous oxygen is introduced in the system. This idea was raised first by Rostoker *et al.* (1989), confirmed by the present author's own experiments (Bourgarit *et al.*, 2003; Burger *et al.*, 2010) and by archaeological evidence (Bourgarit, 2007; Pelton *et al.*, 2015) showing that at a number of early sites mixed oxidic and sulfidic ores might have been smelted. Third, final product was not metallic copper. At all the sites dealing with chalcopyrite and bornite mentioned in this paragraph, the very nature of the final product is not known. Copper sulfide known as black copper might have been the primary product (Doonan, 1999). Where and how this black copper was converted has still to be found.

4.3. Smelting or melting?

As seen above, our understanding of copper-smelting processes and production modes has increased dramatically over recent decades, due mostly to thorough mineralogical and petrological studies and associated theoretical and experimental simulations. In such a scientific context, the apparently simple question of how to distinguish between



Figure 10. Side view of a slag fragment from Saint-Véran showing the typical prismatic layer 1–2 mm below the upper surface (total thickness ~10 mm)

melting and smelting should seem trivial. It is not. Smelting reactors at the beginning of copper metallurgy were rather rudimentary, being either mere holes in the ground or ceramic vessels (Craddock, 1999; Bourgarit, 2007). The type of metallurgy carried out in the latter has often been controversial (Tylecote, 1974). The ceramic materials used for both processes are indeed often the same, namely ordinary clay with no particular refractory properties. Moreover, smelting a copper ore may affect the ceramic vessel the same way melting of copper does. In other words, both processes may generate similar slaggy layers on the inner surface of the vessel.

To distinguish between melting and smelting activity is a crucial issue for archaeologists, especially at the beginnings of metallurgy. Each activity indeed refers to very specific knowledge and possible particular social, economic and political status. Thorough mineralogical investigations of Neolithic crucibles from Switzerland (Maggetti *et al.*, 1990) have concluded that chalcopyrite had been smelted therein. Yet, simpler optical observations of the same crucibles (Rehren, 2009) have shown that, because of their location in the slag and their texture, the CuFeS_2 inclusions could not be remnant of a copper ore. Instead, these inclusions have been formed by biochemical reactions after deposition of the crucible in silty sediments, as confirmed by the presence of particular aggregates of pyrite crystals. Rehren (2009) concluded by stressing the “strength of optical methods, common sense and an open mind when considering the seemingly firm and indisputable results obtained by advanced scientific instruments”. In some instances, archaeological observations may even provide the unique decisive arguments. This was notably the case at another Neolithic settlement, in SW France, with the opposite conclusion (Carozza *et al.*, 1997; Carozza, 1998;

Bourgarit *et al.*, 2002). Here the slaggy material layering the common domestic ceramic-ware sherds was proved to stem from chalcopyrite smelting. But the proof was not brought by the mineralogical investigations. The unusual fragmentation of the vases, their relative thinness, and the systematic absence of ceramic reshaping – as usually seen on melting crucibles due to re-use (Queixalos *et al.*, 1987) – constituted the main arguments towards a smelting operation. The considerable fragmentation of slagged sherds has also been used elsewhere as an argument in support of smelting (Müller *et al.*, 2004), although in that case, the argument was supported by chemical evidence as well (*i.e.* the presence of gangue elements).

5. Conclusion

This review focuses on pre-industrial copper smelting. Yet other non-ferrous and ferrous metallurgies have been documented by using slag mineralogical investigations as well. The first studies of iron slags and related material started slightly before first copper slag studies (Morton and Wingrove, 1969, 1972). They led to a number of very interesting advances in our understanding of metal production modes, lineages and evolutions (Humphris and Rehren, 2013) which can be applied to any kind of metallurgy including copper extractive metallurgy. To date, much less attention has been paid to tin, lead and silver (Rehren *et al.*, 1999; Yener *et al.*, 2003; Ettler *et al.*, 2009; Chirikure *et al.*, 2010). Arsenic-rich compounds, speiss, aimed at the elaboration of copper-arsenic alloys has recently been discovered at Arisman, Central Iran, from the Early Bronze Age (Rehren *et al.*, 2012). The production process has been documented by the investigation of the associated slags (Boscher, 2016). Whatever the metallurgy, slags have long shown their importance for specialized research on ancient techniques. Archaeological collections are under construction in the British Isles (see National slag collection at <http://hist-met.org/resources/national-slag-collection.html>). Some museums – mainly German and Anglo Saxon – are keen to present these wastes together with more valuable/aesthetic representations of cultural heritage. Slags may even form an integral part contemporaneous artworks as seen notably in *Blackout* by Mike Kelley. The contribution of mineralogy and petrography to the study of ancient extractive metallurgies is not restricted to slag. Technical ceramics such as furnaces, vessels and tuyeres, provide invaluable materials for investigation also. Other ceramics related to metal melting and casting including melting crucibles, molds (Katona *et al.*, 2007) and cores (Castelle *et al.*, 2016) are also studied increasingly.

Back to ancient copper smelting, there is no doubting that mineralogical and petrographic slag studies represent a major archaeometallurgical approach. In the past two decades, these techniques have been combined increasingly closely with a number of other sciences, including the humanities, to deal successfully with what are often complex archaeological and/or historical problems. Although scientific investigations in the field are increasing both in terms of quantity and quality, a few directions for the future may be suggested. The mineralogical approach should be maintained at its current high level involving as much petrography as possible. Studies of slag and

metallurgical technical ceramics would benefit greatly from this. Modern metallurgical tools should be brought into play. There should be more collaboration with those working on ancient iron smelting. Finally, a more systematic but careful use of relevant anthropological concepts and tools may help to extract from the slags some fundamental answers regarding technological changes between human groups.

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