Archaeometallurgy: the contribution of mineralogy
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Abstract

Modern mineralogy is a discipline that is intrinsically suited to face archaeometric problems, especially in the field of archaeometallurgy, which requires contributions from areas as diverse as geochemistry, petrology, materials science, metallurgy, archaeology, engineering, and many more. Arguably, it is show that mineralogy may provide the necessary frame to put into use the information derived from different sources, and combine it into a unifying interpretation. According to the mainstream of the metal production cycle, the most significant areas of investigation in archaeometallurgy are: (1) the characterization and identification of ore sources (the mining stage); (2) the reconstruction of the smelting technologies for reduction of the metal (the smelting stage); (3) the interpretation of the metallurgical manufacturing processes in the production of the artefacts (the metallurgical stage); (4) the reconstruction of the use and diffusion of the metal objects (the physical lifetime of the object) and the incorporation in the archaeological record and their preservation (the afterlife stage). Examples will be discussed of the contribution of mineralogy to all steps of the archaeometallurgical cycle.

Resumen

La mineralogía moderna es una disciplina intrínsecamente adecuada para abordar los problemas arqueométricos, especialmente en el campo de la arqueometalurgía, donde se requieren aportes de áreas tan diversas como la geoquímica, petrología, ciencia de los materiales, arqueología, ingeniería y otras. Podríamos decir que la mineralogía puede proporcionar los fundamentos necesarios para usar la información obtenida de diferentes fuentes y combinarla para ofrecer una interpretación unificada. De acuerdo con la línea central del ciclo de producción de los metales, las áreas más destacadas en la investigación arqueometalúrgica son: (1) la caracterización e identificación de las materias primas (la fase de minería); (2) la reconstrucción de las tecnologías de fusión con reducción del metal (la fase de fundición); (3) la interpretación de los procesos de manufactura metálica en la fabricación de artefactos (la fase metálica); (4) la reconstrucción del uso y difusión de los objetos metálicos (el tiempo de vida físico del objeto) y su incorporación al registro arqueológico y su conservación (la fase postviva). Se discuten aquí distintos ejemplos de la contribución de la mineralogía a todas las fases del ciclo arqueometalúrgico.

Key-words: Mineralogy, Metals, Archaeometallurgy, Archaeometry, Ore Minerals, Metallography, Texture, Provenancing, Geochemical Tracers.

1. Introduction

For a long time mineralogy as a discipline has been confined to the application of optical mineralogy and X-ray diffraction to the characterization of natural minerals, mainly within academic curricula in the Earth Sciences. In the last decades however modern mineralogy has contributed to many technical developments in collaborations with physics and chemistry, and now it is a mature discipline that is naturally suited to serve as a bridge and interface between the traditional Earth Science areas (petrology, geochemistry, structural geology, sedimentology, etc.) and the more materials science-oriented areas (physics, chemistry, engineering, metallurgy, etc.).

It is argued that mineralogy today may contribute deeply to cultural heritage studies in terms
of thorough knowledge of materials and optimization of investigation techniques (Artioli 2010a, Artioli and Angelini 2011). Being a truly interdisciplinary science, mineralogy therefore may well form a strong foundation for scientists working with cultural heritage materials, especially in the area of archeometallurgy.

As a matter of fact mineralogy naturally deals with complex mineral systems most often composed of a large number of chemical elements and several crystal-chemical phases, it has solid roots on crystallography and the atomic structure of matter, and it is technically and conceptually equipped to face the methodological and experimental challenges involved in the technical analysis of complex materials, and in the interpretation of the processes acting upon them (Fig. 1). Therefore mineralogy may well be the discipline possessing an adequate balance of the interdisciplinary knowledge required to face archeometallurgical problems (Artioli 2010b: pp 305-348).

2. Archeometallurgy

Pure and alloyed metals played a major role in the technological evolution of mankind (Fig. 2). It is indeed not surprising that post-Neolithic archeological periods are mostly defined on the basis of the metal technology: Copper Age (i.e. Chalcolithic, Eneolithic), Bronze Age, and Iron Age. To these we may well add the Steel Age, dominating technology and production after the industrial revolution. We are now in a period of extensive recycling and use of advanced alloy composites (Ashby 1987 & 2001).

Archeometallurgy deals with all aspects of metal production, distribution and usage in the history of mankind (Fig. 3, Rehren and Pernicka 2008). To date the vast majority of archeometallurgical investigations deal with the early part of the use of metals (i.e. up to the 2nd millennium BC), which include the technological use of a limited numbers of metallic elements (Cu, Pb, Au, Sn, Fe) and their alloys: mostly copper-based binary and ternary alloys (bronzes and brass: Cu-Sb, Cu-As, Cu-Sn, Cu-Zn, Cu-Sn-Pb, Cu-Sn-Zn), silver-based alloys (Ag-Cu, Ag-Au), and pewter (Sn-Pb) (Table 3.14 in Artioli 2010 summarizes the approximate time and place of introduction of the different metals and alloys in the past).

However, the archeometallurgical aspects concerning the introduction of Fe and its alloys (steel: Fe-C, Fe-C-P, etc.) and the subsequent use of all other known metals are equally fascinating. The recent paper by Bourgarit and Plateau (2007) dealing with
the early use of Al and the possibility to distinguish the later electrolytic production from the early chemical reduction is a nice examples of the problems and techniques involved in modern archaeometallurgical analysis.

A shortlist of reference textbooks and monographs is listed at the end of the paper as an introductory aid to archaeometallurgy.

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Fig. 2. Relative importance of the use of materials through the prehistory and history of mankind following Ashby (1987, 2005).

Fig. 3. The archaeometallurgical cycle (from Rehren and Pernicka 2008).
3. The contribution of mineralogy to archeometallurgy

Based on the schematic diagram shown in Fig. 3, we may distinguish several steps in the production and life cycle of metallic objects. The examples below are intended to show the contribution of mineralogy to the characterization and to the archeometallurgical interpretation of the materials pertaining to some of the major stages of the cycle.

3.1. The mining stage: ore extraction and provenancing

Our knowledge on mining and ore treatment in historical times has the support of written sources, oral accounts, toponyms and family names, and even direct evidence of galleries, mine surveys and maps, treatment plants, written records of production and trades, and the like. However, the more we venture into the past the more the evidence is confused and fragmentary.

When we deal with prehistory, there are no direct sources of information, and the material evidence is scarce and very often contaminated or altered by successive exploitation in late periods. Therefore the investigation of prehistoric archeometallurgy is a fascinating and challenging task, aimed to reconstruct the links between ore deposits, mining activities, ore treatment, and metallurgical sites.

One of the major problems is that the available pieces of archaeological evidence (prehistoric mines, roasting and smelting sites, technical ceramics, smelting slags, furnaces, crucibles, raw metal ingots) are almost never found in the same site: there are lots of pieces in the puzzle, though there is hardly a complete image. In the most general case it is virtually impossible to complete all aspects of the investigation for an individual site or area, simply because of time, cost, and record biases.

Only a few extensive long-term projects come close to delineating all the major features of the metallurgical chain in a geographical area, from the mine survey to the production and diffusion of metal. These are the cases of the prehistoric copper extraction in the Arabah (Timna and Faynan) region in the Near East where, over thirty years, long projects have investigated and detailed out all available evidence at different levels (Rothenberg and Merkel 1995, Rothenberg 1999, Weisgerber 2003, Hauptmann 2007), reaching a sound and complete interpretation of the regional archeometallurgy.

A recent long term project is the HiMAT one (www.uibk.ac.at/himat/), aimed to investigate the history of mining activities in the Tyrol and adjacent areas, with impact on environment and human societies (Tropper and Vavtar 2009, Schibler et al. 2011).

In general, the main questions involved in the investigation of prehistoric metal extraction sites are:

1. what metal was extracted and what was the nature of the mineral charge?
2. can we trace the provenance of the smelted or treated ore minerals?
3. when did the extraction activity started and how long did it last? and
4. what was the technology for metal extraction from the ores?

The answers often require investigations at very different scales: from the submicron scale of segregations and impurities in metals and slags, to the large geographic scale of the regional distribution of ore deposits and metal objects.

As an example, many of these questions concerning the rise and development of copper mining and metallurgy in the Alpine area from the end of the Neolithic (approx. in the 5th millennium BC) to the end of the Bronze Age (approx. the beginning of the 1st millennium BC) are still unanswered.

Our knowledge before the Iron Age is very fragmentary and we are confronted for example with mines showing early exploitation but little or no evidence of reduction slags (i.e. Libiola and Monte Loreto, Ligurian Alps, Italy: Maggi and Pearce 1998; Saint Véran, Queyras, France: Bourgarit et al. 2008, 2010), or with several smelting sites where a substantial amount of slags have been
found, but they show no straightforward connection with the ore deposits (i.e. Luserna, Trentino: Nicolis et al. 2007; Renon, Alto Adige).

One further paradox is that there was abundant metal circulating since at least the 4th millennium BC, as exemplified by the Iceman copper axe (approx. 3200 BC: Fleckinger 2007) and a number of coeval artefacts, but there is no clear evidence of large scale mining or smelting until half a millennium later. The only earlier recognized smelting sites are small scale metallurgical activities confined to the Brixlegg site, in Tyrol (Höppner et al. 2005) and Belovode, Serbia (Radićovec et al. 2010). Several sites with Chalcolithic slags are known in the Eastern Alps (Artioli et al. 2007) although they mostly date to the mid 3rd century BC or later. They apparently indicate a sizeable mass copper production only towards the latter part of the Alpine Copper Age.

In the last few years a long-term project focused on prehistoric Alpine copper metallurgy (AAcP, Alpine Archaecopper Project: http://www.geoscienze.unipd.it/aacp/welcome.html) was launched in order to investigate in detail the relationship between ores, slags, and metal in the area. The core of the project is the development of an extensive database of Alpine copper mines containing mineralogical, petrological, chemical, isotopic, and genetic information on the ore deposits (Artioli et al. 2008a).

Solid minerogenetic interpretation of the deposits (Nimis et al. 2012) and advanced statistical analysis of the ore chemical and isotopic data is the basis to understand the applicability of the measured geochemical tracers (Pb and Cu isotopic ratios, nearly 60 minor and trace elements, including REE elements) to metallurgical processes, including slagging and reduction smelting. The discriminant analysis developed on the copper ore database was tested on the well-characterized area of Agordo, Alpi Bellunesi, Veneto, whose Valle Imperina copper mine was the principal source of copper for the Republic of Venice. The results of the Agordo case study indicate that the developed discriminant models can be applied to the smelting slags and to the unalloyed raw copper extracted from the ores (Artioli et al. 2008b).

Application of the tracing models to the manufactured objects requires a careful chemical and metallographic examination of the metal, in order to understand the nature of the alloy, the presence of remnants of the original charge as inclusions and segregations, and possible biases due to alteration or contamination. It may indeed be dangerous to pursue separately the investigation of the ores, of the slags, and of the metal objects: strict synergy is needed to understand the complexity of the metallurgical cycle.

Recent applications of the models based on the database of geochemical tracers have met some success in

- firmly locating in the Monte Fondoli area (Pfunderer Bergwerk, Chiusa, Alto Adige) the source of the copper ores used for all known Chalcolithic smelting slags in the Brixen area (Millan, Gudon, Circonvallazione Ovest: Angelini et al. 2012), and
- identifying the source of the ores used for the production of the Late Bronze Age objects found in the Monte Cavanero hoard (Chiusa di Pesio, Cuneo, Western Alps: Artioli et al. 2009).

These examples highlight the patient work of the mineralogist in provenancing studies, that is to critically filter the geological, geochemical, mineralogical, and archaeological information into a consistent and unifying interpretation. Key issues to be discussed are:

1. the development, consistency, and data-retrieval protocols of geochemical and isotopic databases;
2. the availability of chemical and isotopic databases for different ore deposits; and
3. the mineralogical, geochemical and statistical significance of the chemical and isotopic tracers used for provenance discrimination.
3.2. The smelting stage: metal production

Our knowledge concerning the ancient extraction processes of metals from the ores is more and more fragmentary as we go back in time, in analogy to our knowledge about mining operations. For recent times, starting from the fundamental 16th century volumes of Vannoccio Biringuccio (De la pirotechnia, published in 1540) and Georg Agricola (De re metallica, published in 1556) (Fig. 4), we have ample documentation, though sometimes the details are difficult to interpret and reproduce.

However for earlier times there are no direct accounts of the metallurgical operations, so that we have to rely on the archaeometric analysis and the archaeological reconstructions of the objects found in archaeometallurgical sites (see table 2.1 of Hauptmann 2007). The scarce evidence is based on: stratigraphy of the sites, furnaces, crucibles and other technical ceramics, ore fragments and smelting slags. Generally most of these evidences are sparse and removed from the mining sites.

A discussion of the logistic rationale for the location of the metallurgical smelting sites with respect to the ore mines is out of place here, it is sufficient to say that only in a few places there is a clear and recognized connection between mining and metallurgical activities: for example in the cited Faynan area (Hauptmann 2007) or at Cabrières, France where a small metallurgical village has been excavated close to a known mining area (Ambert and Vaquer 2005).

In many instances furnaces and slag heaps are quite far from the ores, or even in areas totally deprived of ore minerals, especially for pre-Bronze Age activities (Hauptmann 2007, Artioli 2010). The reasons for the transportation of the ores are subject to debate: in the case of early Chalcolithic smelting the following of Neolithic trade patterns from sources to settlements have been postulated (Hauptmann 2007), whereas the Bronze Age smelting sites are close to the ores, though their geographical distribution may follow the requirements for large amount of fuel or other technical considerations.

Concerning the smelting technology, if furna-
ces and technical ceramics (crucibles, tuyeres, bellows, etc.) are available, they may greatly help in the technical reconstruction of the reduction process.

Mineralogical analysis of the ceramics and the furnace components may be important to the identification of the ores being treated, the temperatures of firing, and the parameters of the smelting operations, though most commonly these data are obtained by the detailed investigation of the smelting slags (Bachmann 1982). The mineralogical, textural, and chemical analysis of the slags yield information on the type of minerals in the charge, the smelting temperatures, the viscosity, the different steps of metal reduction, the efficiency of the process, the redox conditions, the cooling rates, etc. The information is commonly extracted by a combination of X-ray diffraction, optical microscopy, scanning electron microscopy, electron probe micro-analysis, and X-ray fluorescence spectroscopy (see Artioli 2010: box 3.k).

The great majority of the ancient smelting slags were derived from the processing of copper, iron, and lead ores, mostly sulphides. Tin, antimony, and zinc slags are also known; they are scarce but they can be rather important to pinpoint the source of alloying elements in bronzes and brass.

By far most of the slag studies in the literature involve copper smelting and iron smelting/smithing. The major difference between the two processes is that metallic copper (melting temperature 1080°C) can be produced through a fully molten state (i.e. the gangue and the slag are more viscous than the running matte and metal), whereas the molten state of metallic iron (melting temperature 1540°C) could not be reached before modern cast iron production, so that the pre-industrial technologies required squeezing the fluid slag out of the solid metal at high temperature by forging.

The chemical, mineralogical and textural characteristics of the different types of smelting slags can be found in the cited literature (Bachmann 1982, Hauptmann 2007, Artioli 2010, and references therein).

Here, it is important to remind that a neat change in copper smelting technology appears to take place at about the Chalcolithic-Bronze Age transition, as evidenced by the marked differences in the Chalcolithic slags (Bourgarit 2007) in terms of texture, heterogeneity, incompleteness of the melting process, absence of fluxing, low density, and low reducing conditions with respect to the later Bronze Age slags (Anguilano et al. 2002, Mette 2003). Fig. 5 shows typical microscopic textures of Chalcolithic copper smelting slags in the Alpine region.

One further note should be mentioned on the investigations of the smelting sites. Very frequently in the past during the archaeological excavations of the sites the metallurgical slags were not considered as important as the metals, technical ceramics, or other archaeological finds, thus producing loss of valuable knowledge.

Modern excavations now pay due attention to the distribution and quantification of the slags (even micro-slags, such as the ham-
merscales produced during iron smithing and forging, for example Angelini et al. 2011) in the archaeological record, so that this information can be fully used to interpret and reconstruct the metallurgical activities. Interaction between the archaeometallurgist and the archaeologist during excavation is fundamental.

3.3. The manufacturing stage: metallurgy and metallography

The physical properties of a metal object (i.e. hardness, ductility, etc.) are dependent on the size, shape, and orientation of the crystallites (i.e. the micro-texture) in the material. In turn, the metal texture is determined by its thermo-mechanical history, that is the temperature-time path (i.e. cooling rates, annealing temperatures) and the mechanical stress imposed during manufacturing. On one hand, modern metallurgical engineering is interested in designing and optimizing the production processes in order to meet specific physical properties, on the other hand archaeometallurgical investigations aim to measure the physical properties in order to reconstruct the ancient manufacturing processes of the objects. Both investigations rely in the measurement and quantification of the metal texture, which may be experimentally performed by optical metallography, electron backscattering diffraction, or crystallographic texture analysis (see details in Artioli 2010, box 3.l).

Reflected-light optical metallography (Scott 1991, Wang and Ottaway 2004), based on polishing and chemical etching of a small portion of the metal surface, is by far the most diffused, fast and cheap technique, though it is generally invasive and only yields 2D information of the crystalline arrangement (Fig. 6). It can be used as a micro-invasive technique only by careful micro-sampling of pertinent areas of the unaltered metal (Angelini et al. 2009).

Electron backscattering diffraction (EBSD) is
based on the point-by-point analysis of the orientation of the crystallite through interpretation of the Kikuchi lines (Schwartz et al. 2000); the 2D texture is obtained by mapping the domains with equal crystal orientation. It may be performed micro-invasively on submillimeter-sized samples, though the analysis and interpretation of polyphasic metals may be a complicated issue.

The non-homogeneous spatial distribution of crystallites in a metal sample implies a non-homogeneous distribution of Bragg intensity in the Debye diffraction rings. The measurement of the variation in intensity along the diffraction rings allows recalculation of the so-called orientation distribution function (ODF) of the crystallites, that is the function statistically describing the crystallographic orientation of the crystals in the samples with respect to the sample orientation (Kocks et al. 1998, Popa 2008). Orientation distributions are generally represented graphically by means of the pole figures in direct (i.e. the sample space) or inverse (i.e. the crystal space) space (Monaco and Artioli 2011). The measurement of the crystallographic textural features of the sample (CTA: crystallographic texture analysis) therefore is a powerful alternative to perform metallographic analysis in a totally non-invasive mode (Artioli 2007, Artioli 2010 pp 343-348).

It should also be reminded that for metals and average absorbing materials, texture analysis performed with X-rays gives only an appropriate description of the surface layer of the sample, whereas the same analysis performed with deeply penetrating neutrons may yield a more appropriate interpretation of the bulk. Fig. 7 shows an example of the pole figures resulting from the full CTA analysis of a prehistoric copper axe: the data allow complete interpretation of the thermo-mechanical
history and the interpretation of the metallurgical techniques employed to produce the object.

Further information on the manufacturing techniques and assemblage of composite objects may be obtained by routine and advances imaging techniques (i.e. 2D radiography and 3D tomographic reconstructions). Neutron imaging is especially useful for metals because of the penetrating power of neutron beams (Lehmann et al. 2005; Casali 2006). Fig. 8 (from Lehmann 2008) shows the comparison of high energy and neutron radiographies on a complex composite statue.

### 3.4. The life and death of metal objects

Surface analyses of archaeological metal finds and art objects are aimed to

- verify the presence of marks derived from the manufacturing process, polishing, and tool use (Fig. 9);
- analyse the composition of the surface layers to check for original patinas, protective layers, or chemical treatments; and
- assess the alteration and corrosion state of the metal for conservation purposes (Scott 2002, 2009).

A number of characterization techniques are used to investigate the external metal surfaces, through the corrosion layers, to the pristine metal: high magnification optical microscopy, scanning electron microscopy, X-ray diffraction depth profiling, X-ray and neutron imaging, X-ray fluorescence spectroscopy, proton induced X-ray emission, X-ray photoemission spectroscopy, and many more.

Fig. 10 shows the use of hard X-ray tomographic reconstruction techniques for the non-invasive visualization of the alteration layers in a strongly corroded Bronze Age copper ingot (Artioli et al. 2011).

The interpretation of the surface layers of the metal in terms of the original composition and the subsequent corrosion processes may be very difficult, particularly in presence of polymetallic alloys, original surface treatments and patinas, or complex soil-metal and atmosphere-metal interactions.

The archaeometrical problems involved in the characterization of metal surfaces are com-
plex and various (Giumlia-Mair 2005), they include the assessment of the corrosion processes, the identification of original patinas, the reconnaissance of redeposited phases, the identification of fake alteration layers in forgeries (Craddock 2007), and so on.

In principle many of these problems are related. Sometimes the identification of external contamination or diffusion phenomena related to corrosion is straightforward. In other cases the identification of the actual processes is much more difficult. For example, enrichment of Sn at the surface of bronze is a very common feature that can be produced by very different mechanisms: inverse segregation during casting, preferential dissolution of copper with respect to tin during corrosion, or explicit superficial tinning of the object (Tylecote 1985).

Simple chemical analysis is sometimes not sufficient to resolve the issue and careful analysis of the micro-textural features (such as the interstitial position and the morphology of the re-precipitated crystalline phases, presence of chemical coring, etc.) are needed.

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5. Selected introductory and reference volumes on archaeometallurgy


