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Synthetic study of the emergence of primary copper sulphide metallurgy

Céline Tomczyk, Patrice Brun, Christophe Petit

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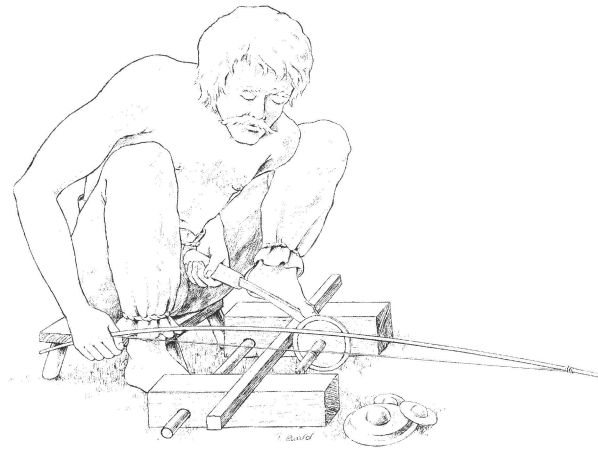
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Proceedings of the 5th International
Conference " Archaeometallurgy in Europe "

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Preface

The International Conference „Archaeometallurgy in Europe”, held at Miskolc in Hungary from the 19th to the 21st of June 2019 is by now a well-known and fully established international scientific meeting, at which scholars with different backgrounds can present their research on ancient metal finds, metal analysis, ancient mining, the reconstruction of various kinds of production processes, ancient technologies and every topic that belongs to metals and their transformation from ore to objects.

Our meeting at Miskolc was the fifth of a series that begun in Milan in 2003, followed in 2007 by the conference in Aquileia, both in Italy. The third was held at Bochum, in Germany, in 2011 and the fourth at Madrid, Spain, in 2015. The special aim of our 2019 conference was that of emphasizing and strengthening the interdisciplinary character and the various activities in the field of archaeometallurgy and widening the focus towards Eastern Europe.

The papers we present in this volume use scientifically collected data that allow the re-examination of aspects of archaeology and offer a view of antiquity based on materials science, supplemented by archaeological, literary and stylistic evidence, i.e. the methods by which human activities have been reconstructed in the past.

The presentation of research, availability of information, discussion and confrontation is an important side of this conference. Publishing new data and research in this frame - although in some cases only in short form - is important. The volumes of the conference „Archaeometallurgy in Europe” have been planned as a window on the world of archaeometallurgy, as general information for students, scholars and in general for anyone interested in these topics and, finally, as a tangible historical memory of the kind of studies carried out at this time. We all know that

research can be dated, just like the ancient objects we are studying. For these reasons and more, even though we received a good number of submissions, it is a pity that some interesting papers presented at Miskolc were not delivered for publication in this volume. Apparently, as it transpired at the conference, some of the authors decided to publish in a journal with impact factor. Nevertheless, a shorter or different version could have been submitted for publication in this volume as well, in particular as we know that the collection of papers, the peer-reviewing, corrections and the printing process normally take a couple of years. These volumes play an important role for our scholarly community, because they also represent an occasion for valuable corrections and discussion on weak points during the peer-reviewing stage, which is always carried out by two specialists in the field of the topic, while most journals with impact factor simply use their own reviewers, who do not know a thing about ancient metallurgy. The result is that the papers published in some journals are often less than mediocre.

We hope that the next volumes of this series will collect a larger number of papers presented at the conference, and we will be able to demonstrate once again that the frame within which archaeology can be studied is - and will be in the future - greatly enhanced by archaeometallurgical research.

We are very grateful to all reviewers and especially to the English native speakers who took the time to check the language of the papers in this volume.

To all of you a heartfelt thank you!

The editors

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At the meeting of the Standing Committee that took place during the conference, Béla TÖRÖK (Hungary), Jiří HOŠEK (Czech Republic) and Miljana RADIVOJEVIĆ (UK) were nominated for membership of the Standing Committee and accepted, and an Advisory Committee without voting right was established.

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Synthetic study of the emergence of primary copper sulphide metallurgy

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Abstract

The extraction of copper from sulphides involves an oxidation phase to separate the copper from the iron contained in the chalcopyrite. It thus differs from the metallurgical processes used until then, which were limited to a single reduction. For this reason, the appearance of sulphide roasting is often described as an innovation in the field of copper production in prehistoric times.

This study therefore proposes to study the appearance and spread of the smelting of primary copper sulphides. The database created for this research work is the result of a bibliographic data collection exercise that includes both mines and smelting sites for which the type of ore mined is known. Sites related to the extraction and smelting of copper carbonates, co-smelting cases but also fahlores are grouped in a separate class as they can be processed by simple reduction.

A spatial and chronological scheme (between 3500 and 800 BCE) has been proposed, highlighting the places and dates of appearance of copper sulphide metallurgy but also the uneven distribution of its use occurring at the beginning of the third millennium BCE.

Synthetic study of the emergence of primary copper sulphide metallurgy

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Christophe Petit

Introduction

Copper smelting is regularly described as undergoing two phases of technical innovation between the Neolithic and later Bronze Ages:

Reductive fusion

The reduction is carried out using charcoal which, placed at the top of the crushed minerals in the right kind of furnace, produces a reducing atmosphere. The carbon monoxide (CO) from the burning charcoal then reacts with the copper ores. The result is a gaseous departure of the oxygen (O), carbon (C) and hydrogen (H) contained in the latter (Pickles and Peltenburg 1998; Ryndina et al. 1999; Bourgarit and Mille 2001). Copper (Cu) is obtained at the end of the process. This reductive smelting does not require high temperatures: copper can thus be produced from malachite from 700°C.

Reducing fusion enables copper to be extracted from almost all copper minerals:

- Oxidized and carbonated (weathered) copper minerals such as malachite or azurite: an unalloyed copper is then produced;
- Fahlore alone: a natural alloy of Cu-As or Cu-Sb is obtained, depending on the type of fahlore used (tetrahedrite-tennantite series);

- Co-smelting enables a mixture of copper carbonates and copper sulphides to be processed: the oxygen present in the carbonates then oxidises the sulphides present (Rostoker et al. 1989; Bourgarit and Mille 2001). This also results in the production of unalloyed copper.

Appearance of oxidation (roasting) in addition to reductive fusion

The extraction of copper from copper sulphides is often described as more complex. It requires an additional step: a preliminary roasting of the ore concentrate (in the open air and therefore in an oxidizing atmosphere), in order to oxidize the copper sulphides. The sulphur (S) contained in chalcopyrite reacts with the oxygen of the atmosphere. This departure is in the form of sulphur dioxide (SO₂) gas. A mixture of cuprous (copper) oxide (CuO) and ferrous (iron) oxide (FeO) is obtained at the end of the process. Roasting requires high smelting temperatures: to extract copper from the copper/iron sulphide ore chalcopyrite (CuFeS₂) it is necessary to reach 1000 °C (Pickles and Peltenburg 1998; Ryndina et al. 1999; Bourgarit and Mille 2001). Such areas of sulphide roasting (dating from the Bronze Age) have been found in the Austrian Tyrol (Hanning

2012; Tropper et al. 2017; Schibler et al. 2011), in Italy (Ambert 1998; Chiarantini et al. 2018; Bellintani et al. 2009) and in Cyprus (Knapp et al. 2001).

This first requires roasting which is then followed by smelting, a fusion under reducing atmosphere, which however differs greatly from the above-mentioned reducing fusion due to the presence of ferrous oxide (FeO) and the need to add a flux, often quartz or silica (SiO₂), to bind the iron present to silica (the influence of gangue composition will not be discussed here, although it is important in this smelting process).

Copper (Cu) is obtained at the end of the process. Iron (Fe) is trapped, bound to silica in a slag. The reduction is thus different and its main advantage is that it can manage the iron present in chalcopyrite sulphide ores (iron is absent from copper oxides and carbonates and not very abundant in fahlores). Getting rid of iron is then, perhaps, the biggest marker of innovation, rather than the roasting itself.

This operation occurs in two phases: oxidation and then reduction, which then enables the exploitation of simple primary copper sulphides and especially chalcopyrite. It also makes it possible to extract arsenic and antimony from fahlores which escape (as sulphurs do) in gaseous form during roasting. Copper-bound arsenic rates can then be gradually reduced by carrying out several successive oxidation phases. The silica can be added voluntarily or it can come from the gangue containing copper minerals. A 'purified' copper is then obtained, differing from the natural alloy produced in the case of a single reduction (McKerrell and Tylecote 1972).

However, while the appearance of the first (relatively simple) copper metallurgies is regularly studied, the appearance of this coupling of roasting and reduction with iron loss has never been much investigated or published. Moreover, few studies try to date this innovation: Bourgarit and Mille (2001) is one of the few to do so and places its start in the Middle Bronze, i.e. from the middle of the second millennium BCE. This work therefore aims to study the appearance and general adoption of this two-stage oxidation-reduction process between 3500 and 800 BCE in Europe and the Middle East (a time scale chosen to cover the appearance and use of this smelting

technology). It represents a bibliographic inventory that is intended to be as exhaustive as possible and includes both smelting sites and mines that have been the subject of scientific publications.

Methodology

A first step in this work consisted therefore in the creation of a database of copper mines and smelting sites for which the type of exploited copper ore is known. The workshops listed only concern the smelting of copper ore. The presence, on an archaeological site, of ceramics and other copper processing equipment (such as crucibles, furnaces or tuyères) alone is not sufficient to define the type of workshop and differentiate between primary smelting and secondary processing metal workshops as they can be used to remelt an ingot in bronze workshops (for casting, alloying and suchlike). Thus, in this database, we have only retained workshops where fragments have been found of: unprocessed ore and/or partially roasted ore and/or where reduction slag has been analysed (and the type of ore used identified). For these are characteristic elements of the presence of smelting sites (pyrometallurgical workshops). 170 mines and 157 smelting sites have been identified in the literature, among which 83 sites with evidence only of simple copper sulphides have been isolated (other types of copper minerals being absent or present only at trace levels). Chalcopyrite (CuFeS₂) is by far the most common mineral (Saint Véran (France) is a special case because bornite (Cu₅FeS₄) was exploited (Carozza et al. 2008). This study excludes sites with both simple sulphides and copper carbonates because they can be smelted by co-smelting in a single reduction process. Nor have sites of extraction and metallurgical treatment of fahlores been taken into account because, as mentioned above, although they can be roasted, they can also be smelted just by reduction.

It is important to stress that this corpus gives only a partial view of the sites that were actually in operation: some regions have been little studied (such as French Brittany) and others show signs of exploitation without any mines having been found (for instance Sardinia where mining is supposed by lead isotope tracing).

Results and discussion

From a spatial point of view

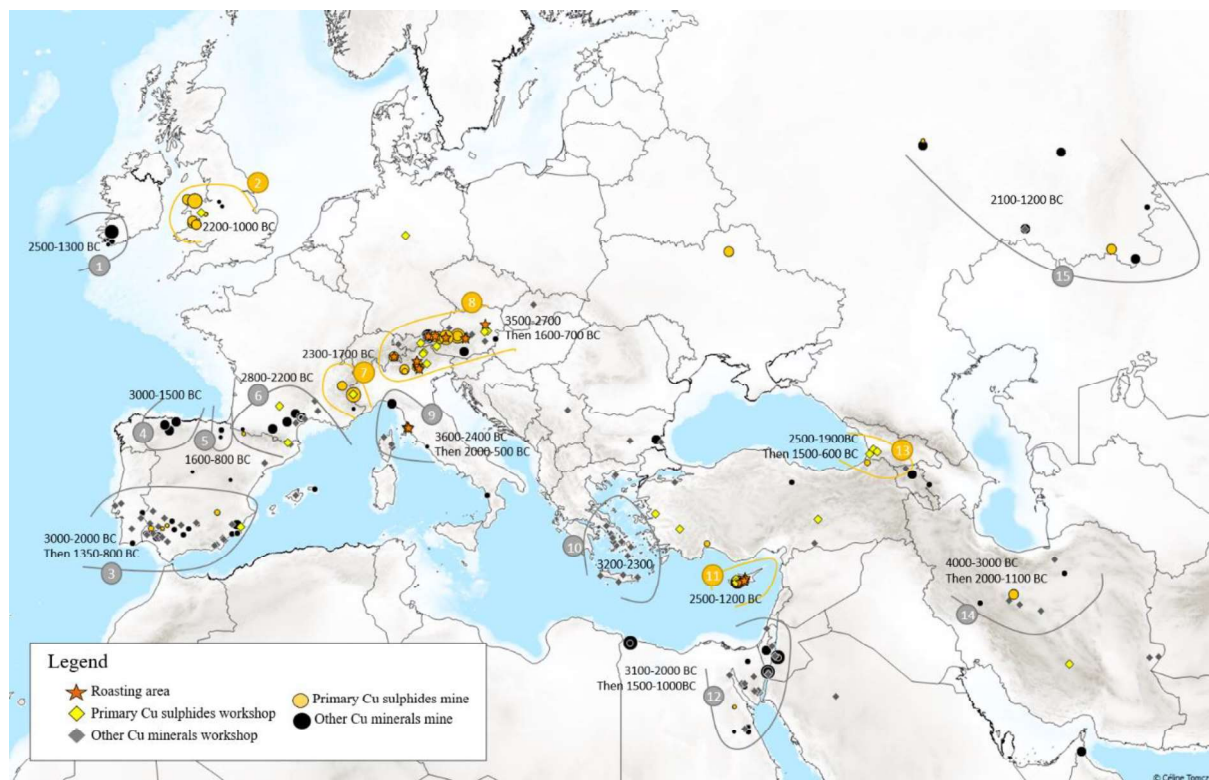


Fig. 1: Location of copper mines and pyrometallurgy (smelting) workshops and main operating periods of the major mining areas. The activity period indicated corresponds to the period of time most representative of the operating period: see the histograms below for a more detailed chronological breakdown.

Primary copper sulphide production is divided into large areas that fluctuate over time (Fig. 1). 15 production areas that are consistent in terms of age and type of minerals mined can be identified by this study. Mines and workshops that appeared isolated in date or place were not assigned to an area. This applies particularly to Turkey, where the division could be improved. It is difficult to integrate poorly dated sites into the database, although including them might highlight further areas.

Some areas saw renewed mining and have several operating periods between 3500 and 800 (in the case of zones 3, 8, 9, 12 and 14). The spatial distribution of mines and workshops seems to highlight five areas where the copper minerals mined and smelted are mainly primary copper sulphides. Of these areas, only the eastern Alps (zone 8) has many mines and smelting sites (together with roasting areas). In the Wales region (zone 2) and the Western Alps (zone 7) mainly mines have been found, while in Cyprus (zone 11) and southern Georgia (zone 13) mainly smelting sites have been found (this

is explained in Cyprus by the strong mining recovery).

It is interesting to note that there seems to be a shift in some production areas. This fact has been described (Carozza et al. 2015) for the south of France where production is thought to have migrated from the south of the Massif Central (zone 6) to the Western Alps (zone 7) and then to the Eastern Alps (zone 8).

B. From a chronological point of view

Histograms were drawn from the resulting database using a LibreOffice macro developed by Desachy (2016). If we examine the histogram compiling all the data (Fig. 2) we note that:

The first smelting workshops dedicated to copper sulphides appeared in the second half of the fourth millennium. The first copper sulphide mines excavated, on the other hand, date from the second half of the third millennium.

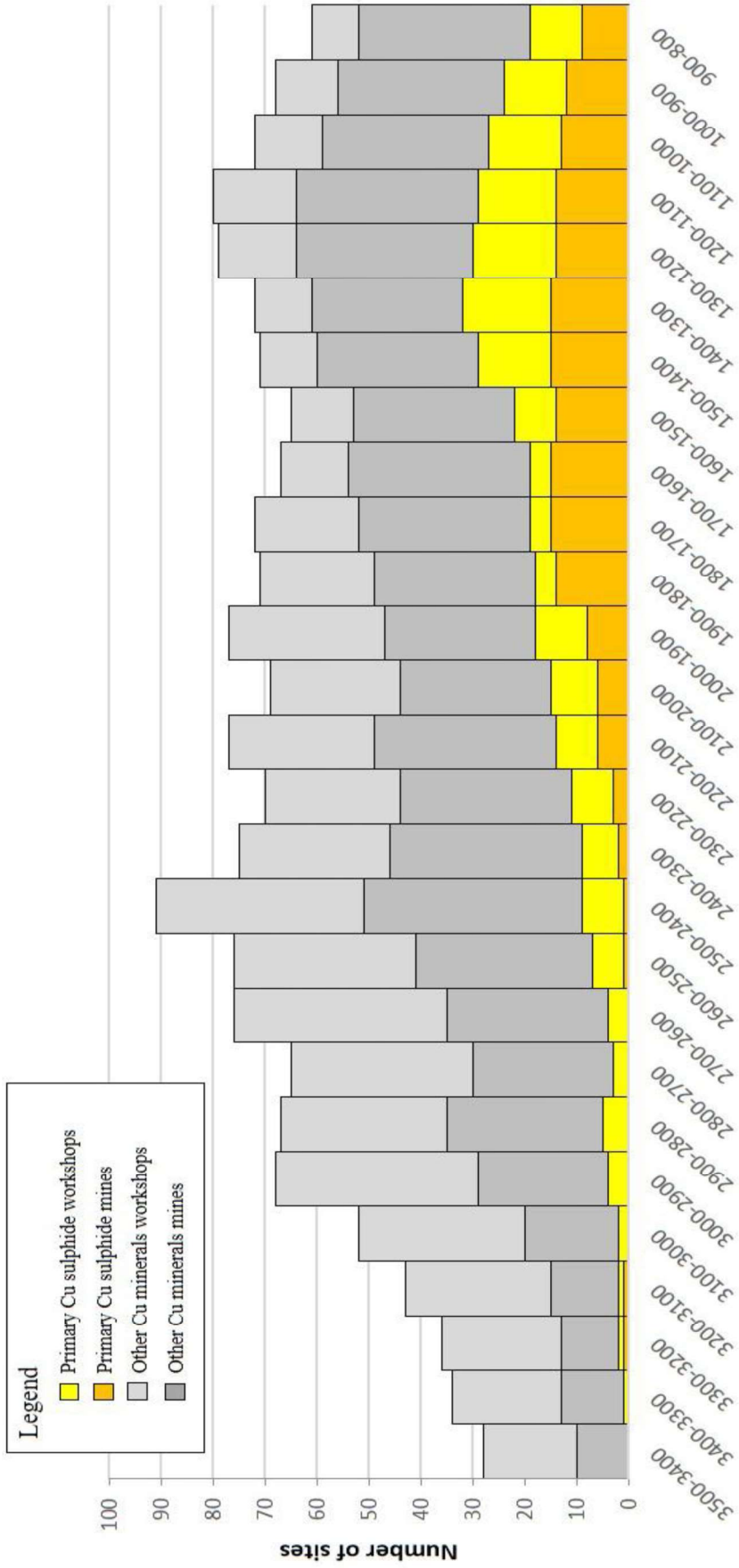


Fig. 2: Evolution of the number of mines and smelting sites (workshops) recorded between 3,500 and 800 BCE in Europe and the Middle East. The number of mines is not necessarily representative of production as the size of mines is generally important.

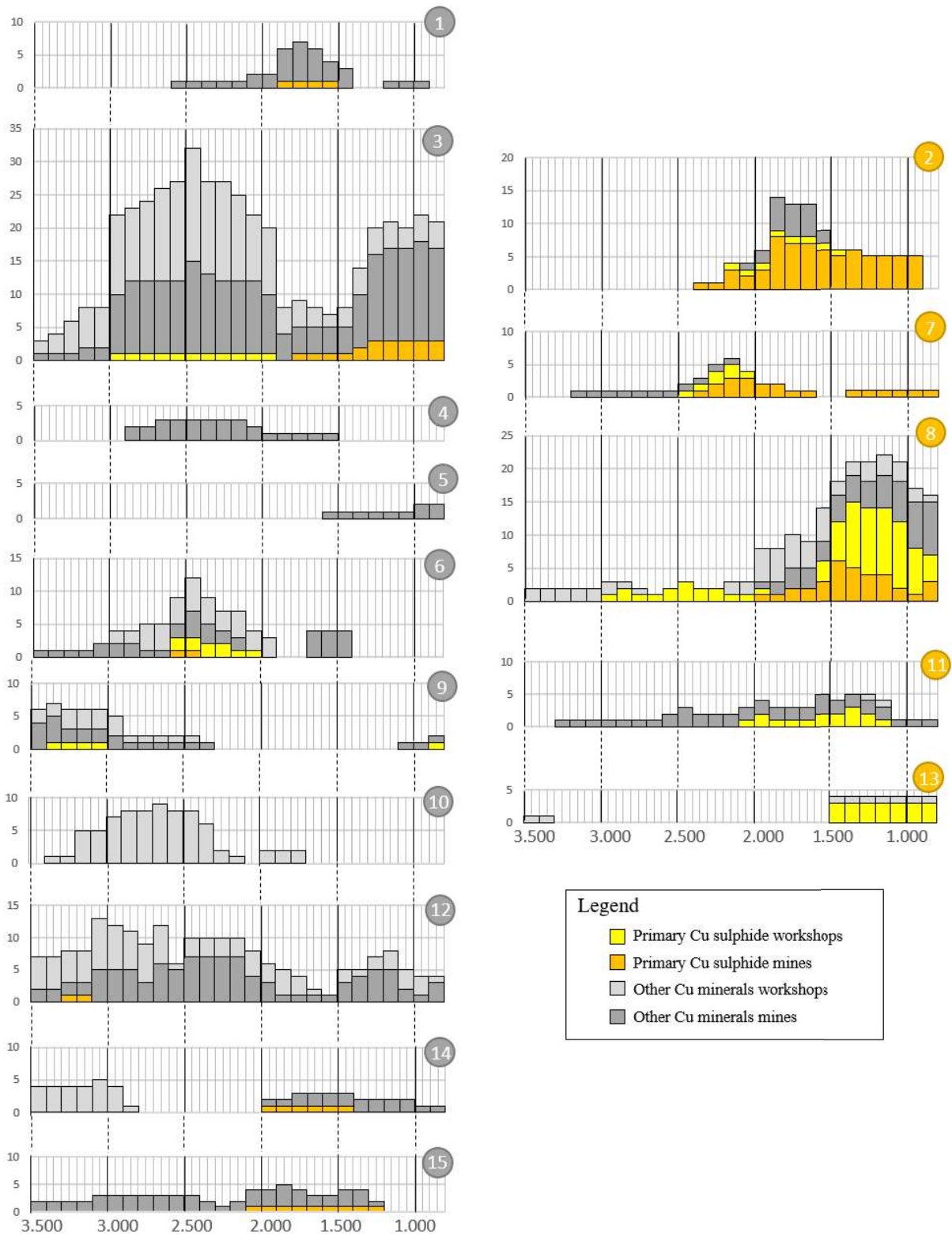


Fig. 3: Analysis by region: on the right are the regions where sulphide exploitations predominate, on the left those where few sulphide operations have been identified. Cyprus (zone 11) has been placed in the sulphide area because (although the mines known seem to indicate copper carbonates) the workshops excavated indicate that sulphides were exploited.

The number of mines and smelting sites associated with simple sulphides gradually increases between the beginning and the second half of the third millennium.

From the second half of the second millennium, sites related to simple copper sulphides constituted nearly half of the discovered exploitations.

An analysis by zones (Fig. 3) again highlights the presence of regions where sulphide exploitation was particularly important. However, while sites related to simple copper sulphide work were predominant in some areas, it appears that almost all areas had some simple copper sulphide operations. Only zones 4 and 5 and zone 10 (where only workshops smelting copper carbonates are described) show no evidence of copper sulphide mining (but this may be only because these have not yet been discovered). The relatively large number of workshops in zone 10 could indicate a real trend whilst the information for zones 4 and 5 is to be tempered by the low number of mines and smelting sites discovered.

In addition, the histograms by zones show that the first copper sulphide operations appeared in two unconnected zones as early as the middle of the fourth millennium. However, in these two zones (9 and 12), the evidence comes in each case from only one site: the San Carlo workshop (in Tuscany, zone 9) (Artioli et al. 2007) and the Um Balad mine (Eastern Desert Egypt, zone 12) whose context is more confusing because copper is considered here as a by-product of a gold mining operation (Castel et al. 1998).

Workshops smelting simple sulphide ores and dating back to about 3000 BCE have been discovered in the Iberian Peninsula: la Ceñuela (Murcia, zone 3: Bourgarit 2007; Lull et al. 2010); in the Western Alps: Acquaviva di Besenello (Trento, zone 8: Burger 2008; Dolfini 2014); but also in Turkey at Altuntepe (Oy 2017) and Arslantepe (Hauptmann et al. 2002). Furthermore, the dates highlighted in the general histogram are also found in the regional histograms. Copper sulphide sites have been reported in almost all zones (except zones 4, 5 and 10) from the beginning of the second millennium, around the beginning of the main European Bronze Age.

The phenomenon of an increase in the number of sulphide workshops and mines observed in the general histogram (during the first half of the second millennium) is modified by the zone histograms: zones 8 and 2 account for most of this increase. The histograms thus make it possible to highlight differences between areas in the number of sites found.

Discussion

Simple copper sulphides appear to be mined and smelted mainly in 'specialized' areas: their deposits are then targeted in areas where other types of copper minerals are found, as for copper carbonates in Cyprus or fahlores in the Eastern Alps (fahlores even seem preferably targeted in the Mitterberg mines before chalcopyrite became the main ore extracted (Pernicka et al. 2016).

More surprisingly, the presence of a small number of mines exploiting unweathered sulphide ores in all regions (with the exception, as previously mentioned, of the Aegean region) shows that, although the technology was mastered, it was not being generalized. Thus, some regions such as the southern Iberian Peninsula and the Levant continued to prefer extracting copper carbonates despite the presence of accessible sulphide-rich deposits. This fact seems to be more related to a choice of production than to a technological gap because sites related to sulphide work have been found showing that these areas had mastered the combination of roasting and reduction. The preferential selection of copper carbonates could partly be explained by the copper content of local supergenic deposits compared to primary simple sulphide deposits.

The working of simple sulphides seems to coincide well with the appearance of bronze in the different zones studied (the first appearance of such workings in Wales can be paralleled by the arrival of the first bronzes in the region). It is interesting to note that a link could be made between the appearance of the first bronzes and the gradual increase in simple sulphide exploitation: although more complex to extract (because it is linked to iron), copper from chalcopyrite is generally low in impurities (nevertheless studies have shown that Cyprus has chalcopyrite deposits of variable purity (Fasnacht 2002) and some copper carbonate

deposits can be low in impurities). It could therefore be a valuable resource for the production of very pure copper ingots that can be used to produce high quality bronzes. The significant increase in production from the second half of the second millennium coincides in Europe with the Middle Bronze and the beginnings of long-distance trade.

Conclusions

Although appearing in the second half of the fourth millennium BCE, copper sulphide metallurgy (and mining) sites only flourished at the beginning of the third millennium. The number of exploitations then gradually increased until it represented about half of the known exploitation sites in the middle of the second millennium, that is the Middle Bronze Age in Western Europe. The increase in the number of exploitations can be paralleled with the appearance of the first bronzes.

Copper production from simple sulphides was concentrated in five main geographical areas. Chalcopyrite deposits are present in the other production areas and the data seem to show that the technology to extract copper from them was mastered at least in some sites in the area. However, these regions did not exploit it and continued to extract copper carbonates or fahlores. Thus, even at their peak, sites related to copper sulphides represented only half of the mining and smelting sites recorded. It is important also to note that this study is based on a simple site count. It could therefore be relevant to take into account the size of the mines and workshops.

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