EXPERIMENTAL ARCHAEOMETALLURGY: towards the understanding of the Late Bronze Age Cu extraction process in the Eastern Alps

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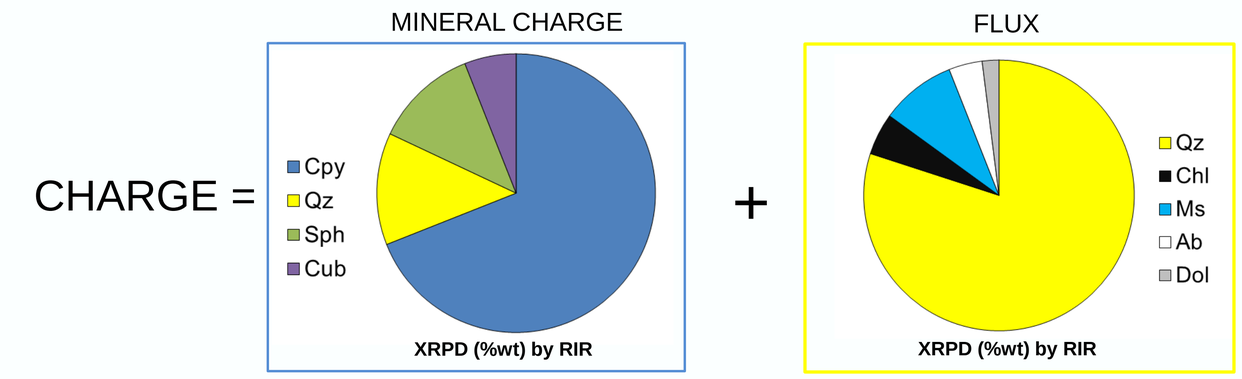
1. Introduction

The Italian Late Bronze Age was a period characterized by the presence of countless copper extraction sites, especially in the Eastern Alps, in which a significant amount of slags has been discovered. The detailed investigation of several copper slags found in these sites suggest that the smelting process was performed in at least three standardised steps related to different levels of copper extraction efficiency (Addis et al., 2012). In order to verify directly the high-temperature working steps assumed on the basis of the analyses of the archaeometallurgical slags, two seasons of copper smelting experiments were performed in the Summer of 2010 and 2011. The first session of experiments principally aimed to explore the effect of different roasting cycles on the process. The second experimental session was devoted to produce a highly copper-enriched matte from the optimized charge, and to understand the latter steps of the process including the final copper extraction.

2. Experiments Season 2010 ➡ the effect of the Roasting

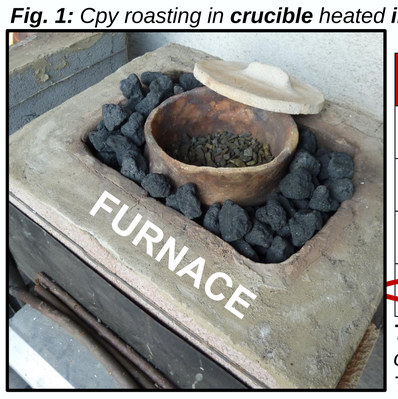
A) Selection of the Starting Materials:

Three types of commercial chalcopyrite were chosen with the aim of selecting the most appropriate charge to be used for the smelting. On these mineral charges the X-ray powder diffraction analysis were performed . The pie charts shown below display the phase compositions of the chosen chalcopyrite-enriched charge (Cpy = 66 %wt) and of the quartz-enriched sand (Qz = 80 %wt). The values are calculated by quantitative X-ray powder diffraction analysis using the RIR method.



B) Roasting: The mineral charge chosen was roasted with different equipment (wood piles and furnace) and the treatment was repeated several times (cycles of roasting). A number of three cycles of roasting is required; 1) to partially remove the sulphur as sulphur dioxide 2) to convert much of the iron sulphides to oxides which could then be removed by slagging 3) to form secondary copper sulphides.

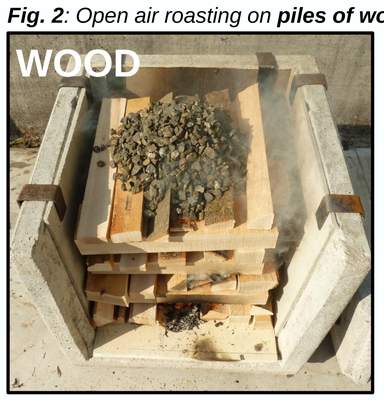
Fig. 1: *Cpy roasting in* ***crucible*** *heated* ***in a furnace.***



Cycles	$CuFeS_2$	SiO_2	$CuFe_2S_3$	Fe_2O_3	Fe_3O_4	Cu_2O	Cu_5FeS_4	$CuSO_4$	Cu_9S_5	$CuFeO_2$
0	66	13	6							
1	12	15		27	13	1		6	4	7
2	7	17		25	6	2	10	12	2	7
3	2	18	2	31	5	1	15	24	2	7

Tab. 1*: Weighted percentages of the most significant minerals constituted the mineral charge at the different roasting cycles repeated using the crucible – furnace equipment. The values are calculated by XRPD analysis using the RIR method.*

Fig. 2*: Open air roasting on* ***piles of wood****.*

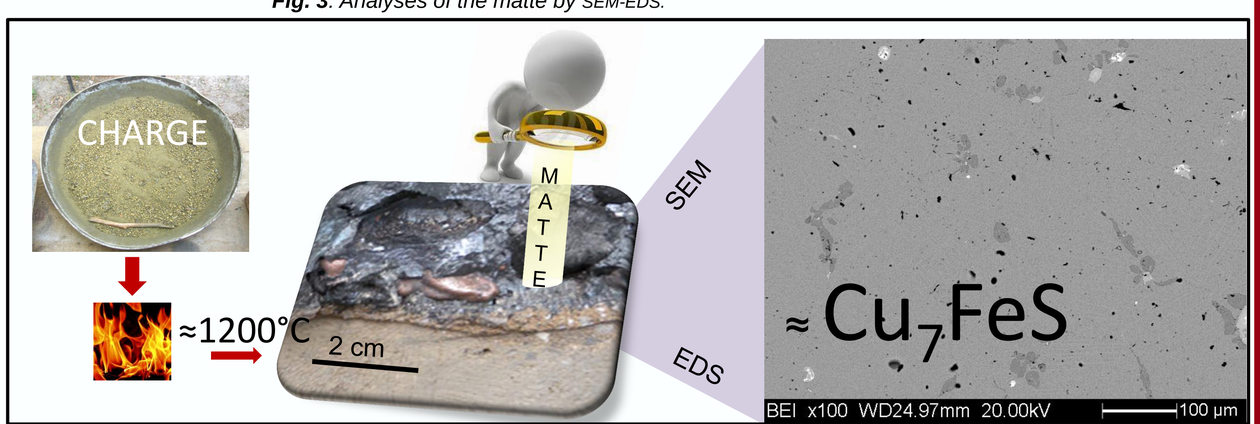


Cycles	$CuFeS_2$	SiO_2	$CuFe_2S_3$	FeS_2	Fe_2O_3	Fe_3O_4	Cu_2O	Cu_5FeS_4	Cu_9S_5
0	66	13	6	3					
1	35	13	19	1	16	5	1		
2	19	15	19	2	13	7	1	7	
3	20	14	22	2	20	9	2	10	3

Tab. 2*: Values (wt%) of the major minerals at the different roasting cycles repeated using the wood piles equipment.*

C) High temperature treatment: Ten heat-treatment experiments were carried out on the charge roasted three times with different methods. Only a few experiments provided copper and a Cu-enriched matte from copper-iron sulphides. The amount of Cu and matte produced is not directly proportional to the efficiency of the roasting process. However comparing the smelting products obtained from the roasted charge with the ones obtained from no-roasted charge, it is clear that the roasting plays an important role. The chemical composition of the matte, calculated by the energy dispersive X-ray spectrometer, was essential for the stoichiometric calculation of the quartz-flux to add at the mineral charge in the smelting experiments of the second season.

Fig. 3*: Analyses of the matte by SEM-EDS.*



3. Experiments Season 2011 ➡ the Matting process

A) Smelting Experiments:

A number of seven smelting experiments were conducted: 4 using the mineral charge roasted with the furnace equipment and 3 roasted using the wood piles equipment. The combustion was feed with an artificial air source and carbon cakes. The smelting took place into fireclay crucibles sited on furnaces.

Fig. 4: *The furnace.*

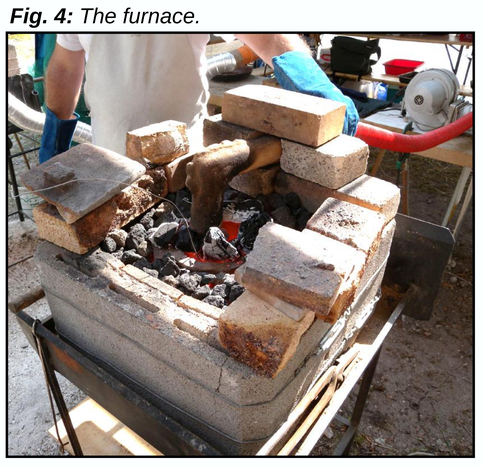
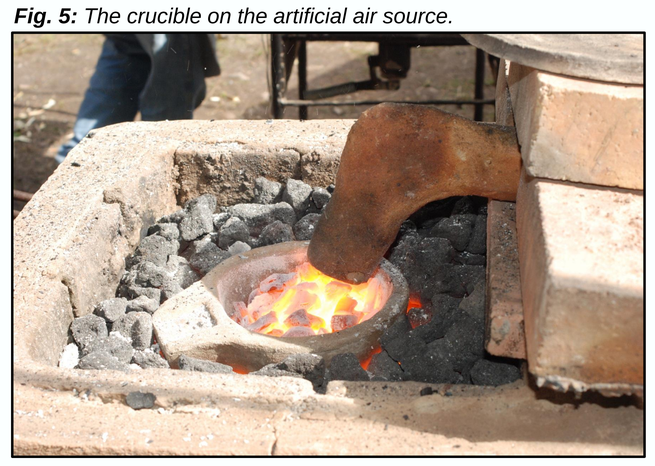


Fig. 5: *The crucible on the artificial air source.*



B) Matting Experiments:

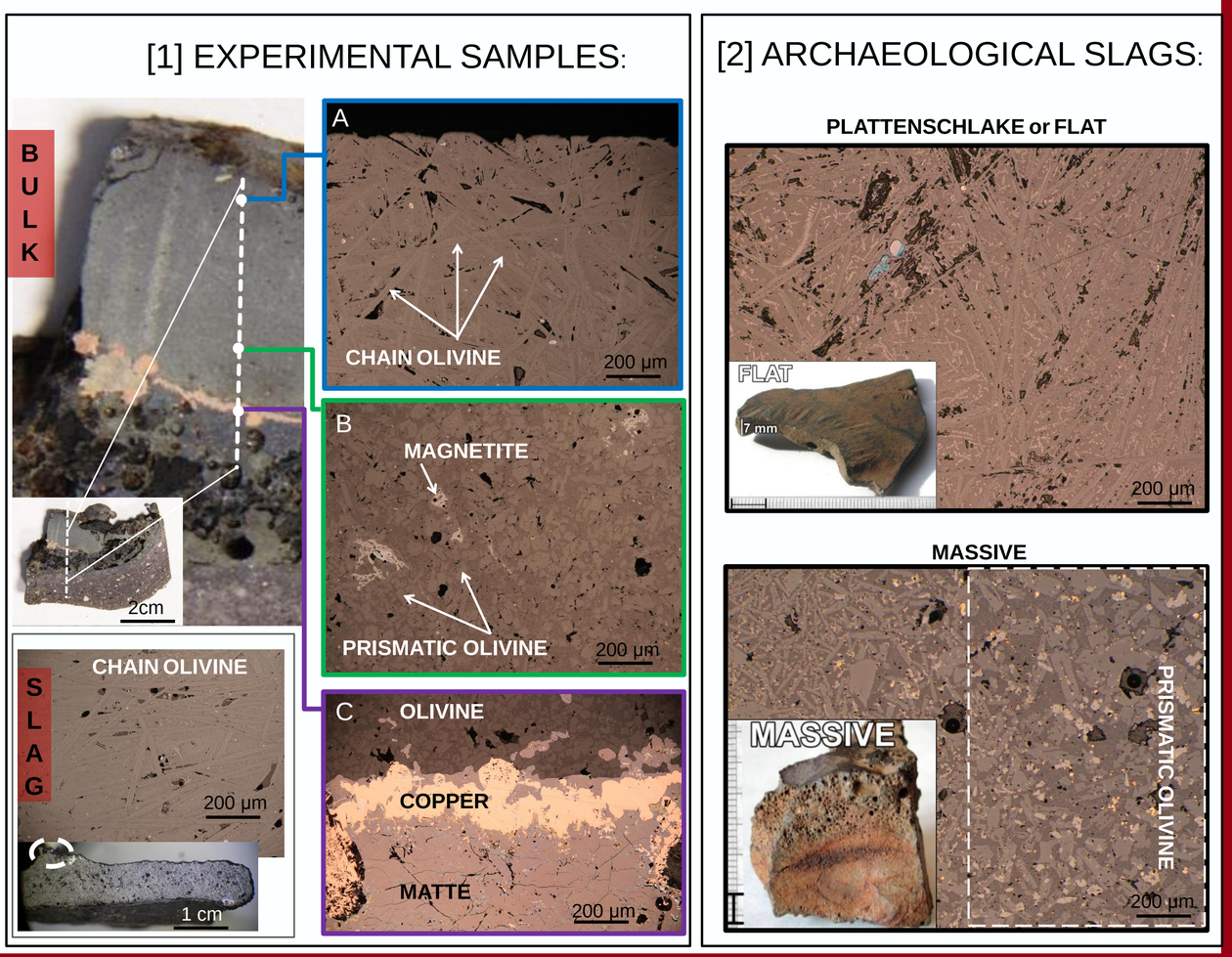
The highly copper-enriched matte produced in the smelting experiments was selected and used for the subsequent matte smelting experiments (matting). In this step copper was produced. In several cases Cu is present in the crucibles as a layer within the slag and the matte; indicating the incipient metal extraction.

C) Slagging process:

The microstructural morphologies and the phase compositions of the slags removed from the bulk during the experiments display high similarities with those present in the Late Bronze Age slags of the Alpine area. We can distinguish the Plattenschlake-like slags and tentatively identify the massive type of slags, both related to two different steps of the metal production.

Fig. 6: The box [1] *shows in the upper part the section of a crucible using in the smelting and the relative thin section. Three micrographs of different thin section parts are displayed. A) and B) show the typical slags morphologies and C) the interface made of copper between slag and matte. In the lower left area is shown the morphology of a slags produced during the slagging process.*

The box [2] *displays two common Late Bronze Age slags types: the massive slags and the flat slags.*



4. Conclusions

Based on the results of the experiments and in agreement with the observed features of the archaeological slags, a 3-step working process is proposed as the basic scheme for LBA copper extraction activity:

(1) roasting of the charge

(2) mass production of copper-enriched matte with slags formation

(3) re-processing of the matte for the extraction of copper, with multiple production of different slags.

5. References

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