**Abstract**

The present Ph.D. project attempts to clarify the metallurgical knowledge achieved at the end of the Bronze Age in Northern Italy starting with the study of the Trentino area slags. In archaeology, this area is well known for its protohistoric copper smelting sites dated to Late Bronze Age, such as Luserna, Transacqua and Segonzano. During the second year of activity, the huge amount of Luserna and Transacqua slags was investigated in order to understand: 1) the technological development of the smelting processes performed, 2) the possible use of different working-steps in the metal production process and the copper extraction efficiency, 3) the ore source of the smelted minerals. Therefore a multi-analytical approach has been applied and besides the minero-petrographic analyses, the research has involved lead isotopes analyses and metallurgical smelting experiments. These experiments were carried out in order to directly explore the roasting and the slagging processes, which are fundamental steps of the whole smelting process.

**Introduction**

Some of the most significant protohistoric copper smelting sites are located in the Trentino Area, such as Luserna, Segonzano and Transacqua, dated to the Alpine Final Bronze Age (Bellintani et al., 2009). In these sites, copper smelting slags, produced mainly by using a chalcopyrite charge, constitute a clear indicator that a pyrometallurgical process took place (Bachmann, 1982). In order to find out what level of metallurgical knowledge was achieved at the end of the Bronze Age in this area, it is important to understand how the slags were produced.

In the Luserna, Segonzano and Transacqua sites, the huge amount of slags found shows different morphologies, and the starting point of this research is to investigate whether these differences are linked to the variation of physical and chemical parameters in the one slag formation stage (low level of metallurgical knowledge and control) or are related to the presence of different working-steps in the metal production (high technological advancement and control of the processes).

Another debated subject is the use of an ore pre-treatment process, such as the roasting operation, carried out to remove sulphur from the ore, burning great heaps of sulphidic ores with brushwood in open air roasting beds (Cradock, 1995). In the Luserna archaeological sites, roasting bed structures have been likely identified, but it is necessary to verify and interpret the role of this specific treatment within the Luserna, Transacqua and Segonzano metallurgical processes.

In addition to these unanswered questions, there is also a lack of correlation between mine, smelting sites, and the metal obtained. In this area, ancient mines have not been clearly identified and metals findings are not available.

The purpose of this study is; 1) to understand the technological level of the processes performed on the three site 2) to reconstruct the chaîne opératoire of the slags/metal production in each sites and compare between them 3) to identify the provenance of the smelted minerals.

Firstly, we focus on analysing the smelting slags from Luserna, Segonzano and Transacqua by using a multianalytic approach in order to characterize the slags from a mineralogical, physical and chemical point of view. The purpose of this investigation is to define homogenous minero-petrographical and archaeometallurgical slags classes, linked to the working-steps in the smelting processes. Secondly, copper smelting experiments were performed in order to understand the different working-steps in the slagging processes paying attention to the intermediate product –for instance reacted sulphides (matte) –
formed during the smelting processes. Finally, we carried out lead isotopes analyses on the archaeological slags for the ore provenance using the geochemical database of Alpine copper mineralisations developed by Artioli et al. (2008), and on the smelting experiments materials in order to evaluate the contribution of the charge component in the lead ratio analysis of the products.

**Materials and Methods**

**Slags characterization:**
Concerning the slags analyses, the data of the densities measured on over 200 slags samples of Luserna, Transacqua and Segonzano were statistically treated using descriptive methods and inferential procedures (one-way ANOVA, Kruskal–Wallis, one-way analysis of variance, etc.) by Statgraphics Centurion software version 16. Then the slags were classified into morphological types in agreement with the macroscopic observations and the statistical analysis of the density. On the basis of the latter, the most representative slags of each types were analysed by X-ray powder diffraction (XRPD) and optical microscopy (OM-RL and OM-TL), to correlate macroscopic and microscopic parameters.

![Table showing slags characterization](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>Total Samples</th>
<th>Thin Section</th>
<th>XRPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUSERNA</td>
<td>92</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>TRANSACQUA</td>
<td>103</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>SEGONZANO</td>
<td>32</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

**Smelting Experiments:**
In July 2011 a one-week of smelting experiments session was conducted at Agordo (BL) in collaboration with the ARCA group: Gruppo Archeologico Agordino. These experiments followed those conducted in 2010 (Addis, 2010), with the aim to understanding the smelting process directly. Particularly in 2011 the experiments were carried out to explore the effect of different roasting cycles on the process. X-Ray powder diffraction analyses on the three chalcopyrite types used for the 2010 smelting experiments and on their roasting products at different cycles have allowed to identify the most appropriate chalcopyrite type for the 2011 experiments and the suitable number of roasting cycles needed; 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.

SEM-EDS analyses were performed on the matte forming during one of the eight smelting experiments in 2010, in which little prills of copper were obtained from four chalcopyrite roasting cycles plus quartz. The chemical composition of the matte was essential for the stoichiometric calculation of the quartz-flux to add at chalcopyrite in the smelting experiments of 2011.

**Lead Isotopes analyses :**
Concerning the lead isotopes analyses, a sampling strategy was developed to analyse and compare the Pb isotope ratios measured on silicates, on the copper prills, on the ore relics and on the reacted sulphides (matte). Several selected Luserna slags were sectioned and micro-sampled using the Micro-Drill device under the stereomicroscope, the powders obtained were weighed and analysed by XRPD. Then the powder samples were dissolved with nitrohydrochloric acid in the clean Geochronology laboratory at the University of Padova Geoscience Department and the subsequent Pb separation (Villa, 2009) and the MC-ICP-MS analyses have been carried out at the Institute of Geology in Bern University.

**Preliminary results on the Luserna and Transacqua smelting slags**
As regards the Luserna archaeological site, beyond 80 slag samples were classified into four morphological types, according to the literature: coarse/cake slags and flat/Plattenschlacke slags (Burger et al. 2007), as well as two new typological classes tentatively referred as flat-thick and massive.
Quartz, mostly present as a relict phase with typical rounded shape, is the most abundant mineral in the coarse slags (mean value = 72 wt%, by quantitative X-ray powder diffraction analysis using the RIR method). Fayalite, a newly formed phase crystallizing in the silicate matrix, is the second most abundant mineral (18 wt%), and it is present with different morphologies derived from the slag cooling history (Donaldson, 1976), ranging from euhedral to subhedral. Different amounts of partially reacted chalcopyrite are trapped within the major minerals in the coarse slags. Compared to the other types of slags, the sulphides present in the coarse slags are only partially reacted and the transformation into copper-rich sulphides (matte) occurred mainly in the grain fractures. Massive slags are characterized by higher amounts of fayalite and magnetite (55 wt% and 27 wt% respectively), whereas quartz is hardly detected by X-ray diffraction (2 wt%). The chalcopyrite relics present in these slags display advanced conversion into very copper-enriched sulphides and metallic copper. The latter is present in droplets, surrounded by recrystallized magnetite. The flat slag group is characterized by the highest amount of fayalite (mean 70 wt%) and the lowest amount of quartz (≈ 1 wt%). Optical microscopy investigation reveals the widespread occurrence of magnetite and matte, both finely dispersed within the fayalitic matrix. In addition to the typically observed chain morphology, the fayalite also displays prismatic habit, suggesting different cooling rates.
Concerning the flat-thick group, the characterisation of the mineral phases suggests that this group of slags do not form a homogeneous group, since it includes slags that can be defined either massive or flat based on the mineralogical and textural features.

The preliminary lead isotope ratios measured on the copper - chalcopyrite - matte of coarse slags were compared with the geochemical database of Alpine copper mineralisations model. A good correspondence is given with the three mining areas of the Calceranica, Vetriolo and Valle Imperina mineralisations, Valsugana district (Passardi, 2004). These three mines present the same minerogenetic deposit history and their lead isotope ratios values overlap. The current state of the research suggest that the copper source used in the Luserna site was supplied by these mines, probably from the Calceranica mine, located 10 km to the North of the Luserna smelting site.

Concerning the over 100 Transacqua smelting slags, the same groups identified on the bases of mineralogical and textural features in the Luserna slags were recognized: coarse slags, flat slags and massive slags. The coarse group of Transacqua have a lower amount of quartz (mean value = 60 wt%, by quantitative X-ray powder diffraction analysis using the RIR method) and an higher of fayalite (25 wt%) and of magnetite (6 wt%) than Luserna. From the textural point of view these slags seems more reacted, with small grains of chalcopyrite dispersed in the fayalitic matrix and small prills of copper. The fayalite is present with the chain morphology, that suggest a fast cooling rates.

From the point of view of mineralogy, the massive slags of Transacqua can be divided in two sub-groups called M1 and M2. M1 is mostly composed by quartz (50 wt%) followed by fayalite (31 wt%) and magnetite (9 wt%). The M2 group presents a higher content of fayalite (59 wt%) and magnetite (34 wt%),
while quartz is only 5 wt%. As for the texture of these two sub-groups, two representative images of $M_1$ (quartz in TL-OM) and $M_2$ (highly reacted sulphides in RL-OM) are above shown.

The analyses on the flat slags of Transacqua, indicate a strong similarity to the Luserna flat group. These slags display a very high amount of fayalite (81 wt%) present in different morphology possibly depending on the cooling rate.

The results of the physical, mineralogical and petrographic analyses on the Luserna and Transacqua slags lead to exclude the presence of one single metallurgical step of copper extraction. The different proportions of the unreacted minerals versus the newly formed phases and the abundance of metallic copper into the three different groups, indicate a smelting process performed in at least two steps (possibly three Luserna and four in Transacqua), related to different levels of matte enrichment, copper reduction and separation efficiency.

**Future improvements**

On the subject of the archaeometallurgical sites, the differences between the Luserna and Transacqua sites: 1) concerning the coarse group of slags, the transformation degree of the sulphides - more advanced in Transacqua and the amount of quartz - more abundant in Luserna 2) the presence of two sub-group of massive slags in Transacqua, compared to all homogeneous character of the massive slags in Luserna, may indicate different smelting processes. The full reconstruction of the metal chaîne opératoire of these two sites and the Segonzano site, for which observations in reflected and transmitted light microscope and the XRPD analyses are in progress, will be achieved in the next months and will allow to understand the technological level of the smelting processes performed on the Trentino area at the end of the Bronze Age.

SEM-EDS analyses will be carried out on the slags groups of the three sites, in particular they will focus 1) on the zoned olivine crystals observed under the optical microscope, 2) on the partially reacted chalcopyrite and on the highly reacted copper sulphides (matte) to control the copper enrichment produced within the different working-steps of the smelting process, 3) on principal amorphous phases 4) and on the phases that are below the XRPD detection limit.

The smelting experiments will play an important role in the interpretation of the working steps assumed on the basis of the archaeometric analyses. The project in the next months will be to characterize the products obtained in the 2011 season of experimental metallurgy, focusing on the slags and on the matte.

The lead isotopes analyses strategy applied to the Luserna coarse slags will be also performed on the coarse slags of the other sites, to verify 1) the ore provenance, 2) whether there was only one mining area supply for the three sites 3) whether the smelting sites used the same mining source during the period of the metallurgical activity.
References


Alpine Archaeocopper Project: http://www.geoscienze.unipd.it/aacp/welcome.html

BACHMANN, H. G. 1982. The identification of slag from archaeological sites. Occasional Publication No.6. Published by the Institute of Archaeology, 31-34 Gordon Square, London, WC1H 0PY.


SUMMARY LAST YEAR’S ACTIVITY

Courses, Schools and workshops:


D’ALPAOS, A.: “Matematica III” Dipartimento di Geoscienze, Università degli Studi di Padova.


XI School on Synchrotron Radiation: Fundamentals, Methods and Applications. Duino (TS), Italy, 5th-16th September 2011.

Communications:


Field and experimental activities:

Characterisation of the slags: photographic documentation, XRPD analyses (sampling, pulverization by means of the mortar and the micronizing mill), thin sections OM observations (sampling, sectioning), density measures.

Isotopes separation (clean laboratory) and ICP-MC-MS analyses at Institute of Geology in Bern University: 15th – 19th February 2011 and 1st – 3rd August 2011.

Archaeometallurgical copper smelting experiments performed at Agordo (BL): from 26th July till 29th July 2011. Sampling and cataloguing of the products.