EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

ESRF	**Experiment title:** Reconstruction of the first copper smelting processes in Western Europe by XRD and XANES of slags	**Experiment number:** EC 83
Beamline: ID21	**Date of experiment:** from: 27/11/06 to: 01/12/06	**Date of report:** 27/02/07
Shifts: 9	**Local contact(s):** Marine Cotte	*Received at ESRF:*

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Report:

The overall aim of the present interdisciplinary research program is to **reconstruct the first copper smelting processes in Western Europe** (from the early 3rd millenium BC to the beginning of the 1st millennium BC), that is, mainly, to determine the working conditions of the multi-stage processes: temperature, redox, kinetics. The main investigating tools are the structural and chemical characterisations of the almost only archaeological remains: the metallurgical waste, namely the slags.

Protohistoric copper slags are heterogeneous polymetallic silicate glass with relatively high iron contents (30-60 %wt). The aim of the experiments was to determine the Fe^{2+} /Fe^{3+} ratio in archaeological copper smelting slags, as a chemical probe of the redox condition prevailing during the pyrometallurgical step.

Previous structural and elemental analysis have revealed that iron is present in a large variety of submicrometric to millimetric crystallites, frequently distributed on an erratic manner: sulphides ($CuFeS_2$, FeS, Cu_2S, etc.), oxides (Fe_3O_4, $CuFeO_2$), and iron-containing silicates (olivines $(Fe,Mg)_2SiO_4$, clino-pyroxens $(Fe,Mg)CaSi_2O_8$) possibly exhibiting chemical zoning. Consequently, in addition to global Fe^{2+} /Fe^{3+} ratio quantification (^{57}Fe Mössbauer), a spatially selective determination of Fe^{2+} /Fe^{3+} ratio in polished slags may provide information on each pyrometallurgical stage. Given the complexity of slag microstructure, a microbeam XANES analysis on slags polished bulk section first had to be developed and optimized.

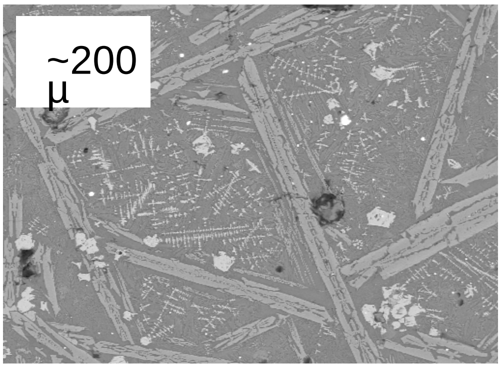
Experimental method:

Fe K-edge X-Ray absorption near edge structure (Xanes) spectra were collected on 7 polished section slags in fluorescence mode. The 7 archaeological slags refer to 3 different chronocultural contexts: Chalcolithic period in Italian Alps (~2500 BC), Early Bronze Age in French Alps (~2000 BC), and Late Bronze Age in Italian Alps (~1000 BC).

The beam was focused down to 1x1µm^2 in order to investigate the crystallites one by one. Present work focused on fayalites. The crystallites were first identified thanks to elemental cartography on major elements Fe and Ca. The fayalites bigger than 10µm were selected.
Main focus has been on the pre-edge region, therefore the spectra were collected in two steps. First a rapid scanning from ~20eV below to ~100 eV above the Fe K-edge (7080-7240eV) with 0,2 eV steps : 2 scans at 0.5s/step were summed up. Secondly, for the pre-edge region (7100-7119eV), 13 scans at 3s/step were summed up. 23 spectra have been collected.

Results

Whereas LBA and Chalcolithic slags exhibit the usual Fe^{2+} - bearing fayalite (in octahedral sites), pre-edge regions (Fig.2) clearly show a Fe^{3+} contribution in the fayalite of the EBA slags. Such distorted olivine structure has already been reported by mineralogists as laihunite (Fe^{+2} Fe_2 $^{+3}$ $(SiO4)_2$), it is described as a substitution of two Fe^{2+} atoms and one vacancy by three Fe^{3+}. Although substitution is never complete in the EBA metallurgical slags, the fayalite-laihunite solide solution clearly testifies for more oxidizing conditions during fayalite formation. Thus, surprisingly, our first results discard any monotone **chronological Chalcolithic-EBA-LBA evolution** of the oxidising conditions. One possible explanation might be the nature of the ore being smelted, a pure $CuFeS_2$ in Italy and a mixture of Cu_4FeS_5 + Fe_2O_3 in France. Laboratory experiments indeed have demonstrated the prominent role of the O:S ratio in the ore on the oxidising conditions in the melt.



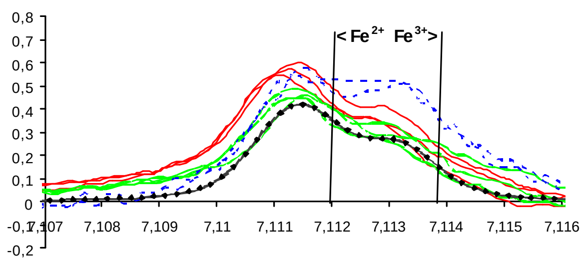


Fig. 1

Fig 1: microstructure of St-Veran slag by SEM (backscattered e$^-$)

The glassy matrix contains:

- ~ 600µm –long needles of fayalite
- ~ 50µm-diameter grains of magnetite
- ~ 100µm-long crystallisation of augite

Fig 2: Fayalite pre-edge

Chalcolithic Period – $CuFeS_2$
Early Bronze Age Bronze Age – Cu_5FeS_4
Late Bronze Age – $CuFeS_2$
6-coordonated Fe^{2+} fayalite

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Communications:

International conference of archeometry GMPCA - 18-21 avril 2007 – Aix-en-provence
2nd International Conference – « Archaeometallurgy in Europe » -17-21 June 2007 – Aquilea (Italy)