



Experiment title: Micromapping and speciation of copper and tin in archaeological tubular multilayered glass beads

**Experiment number:
ME-324**

Beamline: ID22	Date of experiment: from: 01.09.01 to: 04.09.01	Date of report: 08.02.02
Shifts: 9	Local contact(s): Drs. Sylvain Bohic and Andrea Somogyi	<i>Received at ESRF:</i>

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Report:

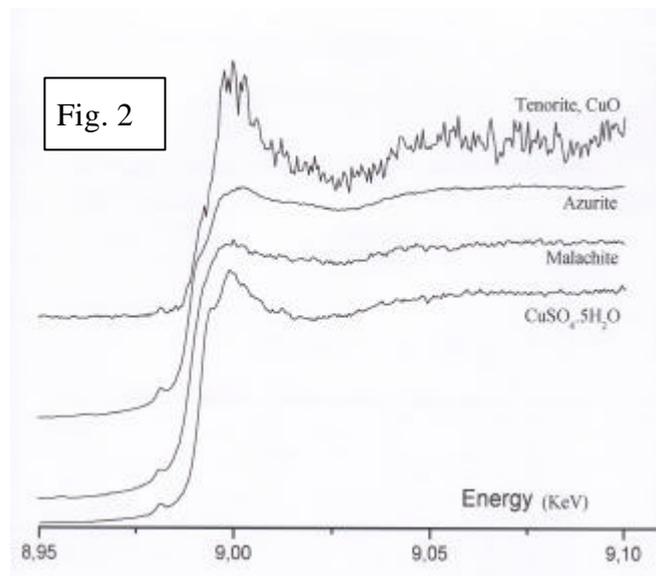
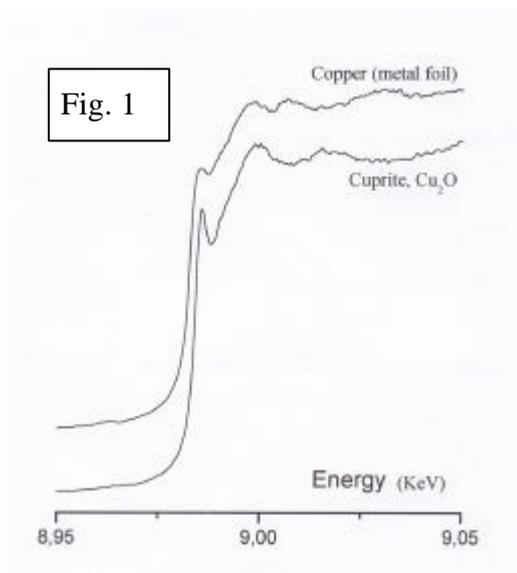
The experiment had a double purpose: first, to ascertain the *speciation* and the *coordination* assumed by *copper in ancient lead-rich glass beads* displaying *red, green, blue colourings*; second, to study the *topochemistry of tin vs. lead* across the consecutive blue and white layers in archaeological glass beads of Nueva-Cadiz type.

Studied tubular beads were 2-5cm long and had square or round cross-sections (area ~1cm²).

The Bragg-Fresnel optics of *ID22 microprobe* assured the focusing of the monochromatic beam to a suitable spot size (~0.05mm) on the bead, therefore allowing for a separate analysis of the several constituting layers - five or three, depending on the bead type.

The following minerals/compounds were used to model copper speciation in the formal valences (0, 1+, 2+) and different *binding*: a copper *metal foil*, Cu⁰; the blue compound CuSO₄.5H₂O (Cu²⁺ in octahedral coordination by four oxygen atoms from water molecules and two from sulphate ions); the oxide minerals *tenorite* (CuO, with Cu²⁺ in square coordination and O-atoms tetrahedrally surrounded by four copper atoms) and *cuprite* (Cu₂O, also a framework of [O^tCu₄] tetrahedra, now with Cu⁺ in linear coordination), and the natural carbonates *azurite*, Cu₃(OH)₂(CO₃)₂, and *malachite*, Cu₂(OH)₂(CO₃), both with Cu²⁺ in square coordination by two water molecules and two oxygen atoms from carbonate ions.

XANES spectra of **Cu K-edge** collected from the metal and Cu₂O are reproduced in fig. 1. Despite the poor quality of data from CuO (fig. 2), the *pre-edge peak* is common to all spectra from minerals and a model compound for Cu(2+) and *details at the ramp and post-edge* arising from different anionic environments are clearly perceptible. Spectra from *glass beads* (fig. 3) clearly support the suggestion of *metallic clusters as colouring agents in red*



layers [1]. The energy shift of the pre-peak in the glass compares well with Cu^0 in the metal and with $\text{Cu}(1+)$ linearly bonded to two oxygen atoms in cuprite, being therefore indicative of an atomic environment differing much from the ionic situations. *Ab initio* calculations using the FEFF8.10 code [2] are in progress to interpret and model Cu *K*-edge absorption spectra collected from red-, green- and blue-coloured ancient glass beads.

Topochemical mappings of *Sn* vs. *Pb* in white and blue layers of Nueva-Cadiz type glass beads are still being performed using the software “xplot”.

[1] I. NAKAI *et al.* (1999). Origin of the red color of satsuma copper-ruby glass as determined by EXAFS and optical absorption spectroscopy. *J. Amer. Ceramic Soc.* **82** 689-695.

[2] A. ANKUDINOV, B. RAVEL & J. REHER (2000). Manual of FEFF8.10 program. The FEFF Project. Dept. Phys., Univ. Washington, Seattle, USA, 62 p.

