

## Arsenic speciation in fluid inclusions using micro-beam X-ray absorption spectroscopy

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### ABSTRACT

Synchrotron radiation X-ray fluorescence (SR-XRF) was used to characterize As speciation within natural fluid inclusions from three deposits with different hydrogeochemical and geological settings. The studied samples represent different compositions of Au-bearing fluids: typical orogenic Au deposit (low-salinity, ~6 mol% CO<sub>2</sub> ± CH<sub>4</sub>; Brusson, Western Italian Alps); brines from a Proterozoic (Fe)-Cu-Au deposit (Starra, Queensland, Australia); and an As-rich magmatic fluid with a bulk composition similar to that typical of orogenic gold (Muiane pegmatite, Mozambique). Arsenic *K*-edge X-ray absorption spectra (XAS) were obtained from fluid inclusions at temperatures ranging from 25 to 200 °C, and compared with spectra of aqueous As(III) and As(V) solutions and minerals. X-ray absorption near edge structure (XANES) data show that initially the fluid inclusions from all three regions contain some As in reduced form [As(III) at Brusson and Muiane; As-sulfide or possibly As(0) at Starra]. However, this reduced As is readily oxidized under the beam to As(V). Therefore, extended X-ray absorption fine structure (EXAFS) spectra for the As(III) aqueous complex could be collected only on the sample from the Muiane pegmatite containing large fluid inclusions with high As concentrations (>>1000 ppm). Analysis of these EXAFS data shows that As(OH)<sub>3(aq)</sub> (coordination number of 3.0 ± 0.2 atoms, bond length of 1.76 ± 0.01 Å) is the dominant arsenic aqueous species in the Muiane fluid inclusions at 100 °C, in accordance with predictions based on studies conducted using autoclaves. The As(V) complex resulting from photooxidation in the Muiane inclusions was characterized at 200 °C; the As-O bond distance (1.711 ± 0.025 Å) corresponds to that found in the arsenate group in minerals, and to that measured for the (HASO<sub>4</sub>)<sup>2-</sup> complex at room temperature (1.700 ± 0.023 Å).

The extent of the XAS information that could be obtained for As in this study was limited by the rapid photooxidation that occurred in all inclusions, despite the relatively low photon flux density used (~4.4 × 10<sup>6</sup> photons/s/μm<sup>2</sup>). Photosensitivity was not observed in autoclave experiments and is the result of a complex interaction between redox-sensitive complexes in solution and the products of water radiolysis generated by the beam. Even under such challenging experimental conditions, the information gathered provides some precious information about As chemistry in ore-forming fluids.

**Keywords:** Fluid inclusion, X-ray absorption spectroscopy, arsenic speciation, hydrothermal gold deposits