

# Chemical Speciation of Gold in Arsenopyrites by *micro*-X-ray Analysis

R.A. Gordon, E.D. Crozier, L.J. Cabri\*, M. Newville†, S. Sutton†, D.T. Jiang and G. McMahon‡  
Simon Fraser University, Burnaby, BC, Canada V5A 1S6

\*Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, ON K1A 0G1

†Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL, USA 60637

‡Canada Centre for Mineral and Energy Technology, 568 Booth Street, Ottawa, ON K1A 0G1

## Introduction

The question of the chemical form of “invisible” gold in sulphide and sulpharsenide minerals has attracted much interest in the last 10 years [1,2]. The term “invisible” arises when conventional microscopy cannot distinguish between gold chemically bound in the mineral and submicroscopic inclusions. The ore genesis and metallurgical implications for the presence of invisible gold in minerals such as arsenopyrite (FeAsS) are potentially very significant [3], and experimental techniques to determine the gold valence are of current interest [4]. Experimental evidence, however, remains controversial because of low gold concentrations, near the resolution limits for conventional laboratory techniques, and non-uniform gold distribution. Using  $^{197}\text{Au}$  Mössbauer [5] and X-ray absorption near edge structure (XANES) [6] spectroscopies, both elemental and chemically-bound gold have been observed in bulk samples containing gold-bearing minerals, but these techniques lack the spatial selectivity to determine if the gold is present chemically bound in the arsenopyrite, as small inclusions or contained within some second mineral phase. Here, we demonstrate the use of focused synchrotron radiation for understanding the problem of “invisible” gold through microXANES studies.

Three samples of gold-bearing arsenopyrites were examined at the PNC-CAT and GSE-CARS undulator beamlines [7, 8], Sectors 20 and 13, respectively, at the Advanced Photon Source, Argonne National Laboratory. One sample, containing multiple arsenopyrite grains from the Olympiada deposit (Siberia, Russia) was examined. The other two samples, single grains of arsenopyrite from the São Bento mine (Minas Gerais, Brazil)[9] and the Sheba mine (Transvaal, South Africa)[1], have been characterised by secondary ion mass spectrometry (SIMS) to have approximate gold concentrations 150ppm (São Bento) and 1,182ppm (Sheba) by weight, with the expectation that the gold is chemically bound in the arsenopyrite. We illustrate the use of synchrotron X-rays with the Sheba sample.

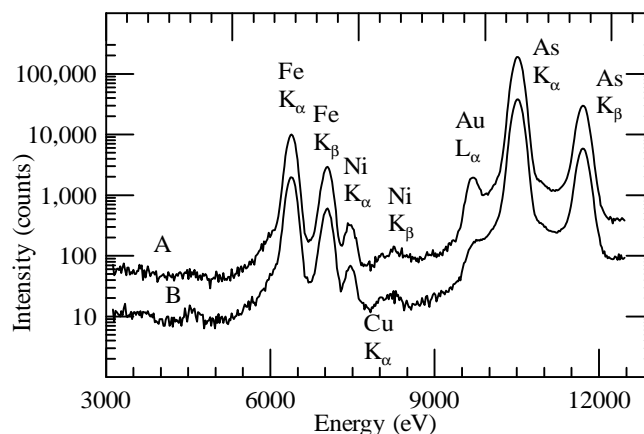
## Experimental

Monochromatic X-rays were focused with a penetration depth  $\sim 5\mu\text{m}$  ( $3\mu\text{m} \times 3\mu\text{m}$  spot, PNC;  $10\mu\text{m} \times 10\mu\text{m}$  spot, CARS) on the grains using Kirkpatrick-Baez mirror pairs. The samples were mounted on an XY translation stage to allow the focused beam to be positioned on any part of the sample. Fluorescent X-rays were detected

using a multi-element germanium detector at the PNC-CAT beamline and using an Oxford WDX-600 wavelength dispersive spectrometer at the GSE-CARS beamline. The germanium detector has the advantage of collecting the full fluorescence energy spectrum and allowing multiple energy regions to be monitored during a scan, but has a worse energy resolution (200eV vs 20eV) than the spectrometer.

## Results and Discussion

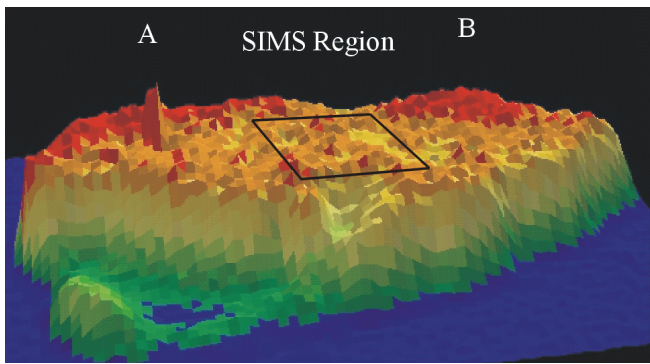
Figures 1-3 illustrate the challenge in determining the chemical form of “invisible” gold with X-rays. The K absorption edge of arsenic is 51eV *below* that of the gold  $L_3$  edge. Incident X-ray energies above the Au  $L_3$  edge also produce fluorescence from arsenic, or other elements (Fe, Ni, Cu) with lower absorption edge energies, as shown in the energy spectra of Fig. 1. At 10,543 eV, the arsenic  $K\alpha$



**Figure 1.** Fluorescence X-ray spectrum for two regions of the Sheba grain. The lower curve was displaced from the upper by dividing by 5.

fluorescence is centred 842eV above the gold  $L\alpha$  fluorescence (9,711 eV) but tails into the gold region of the spectrum, giving a background to the gold signal.

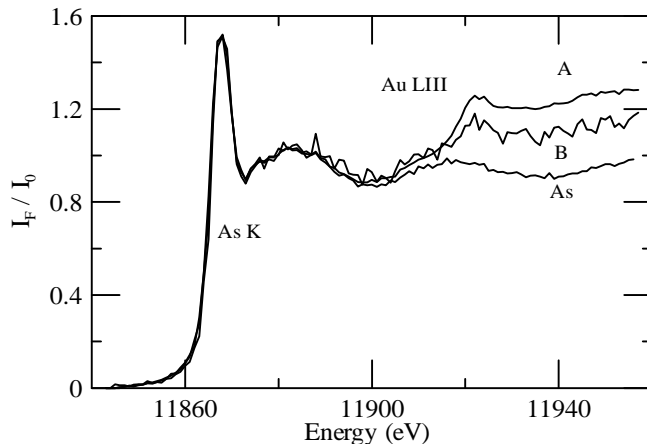
The gold signal (with background) as a function of position is shown in Fig. 2 for the Sheba arsenopyrite grain (size  $\sim 150\mu\text{m} \times 300\mu\text{m}$ ). The gold distribution is non-uniform in this grain with a larger gold signal along the northern edge of the grain and in a spike in the western half. The As fluorescence distribution (not shown) is similar, but more uniform, with only a 7% increase at the edge and no spike. The upper energy spectrum (A) shown in Fig. 1



**Figure 2.** Gold fluorescence map for the Sheba grain indicating the two regions (A, B) examined in Fig. 1, and the region examined by SIMS.

comes from the spike in the west and the lower spectrum (B) from the region in the northeast as indicated in Fig. 2.

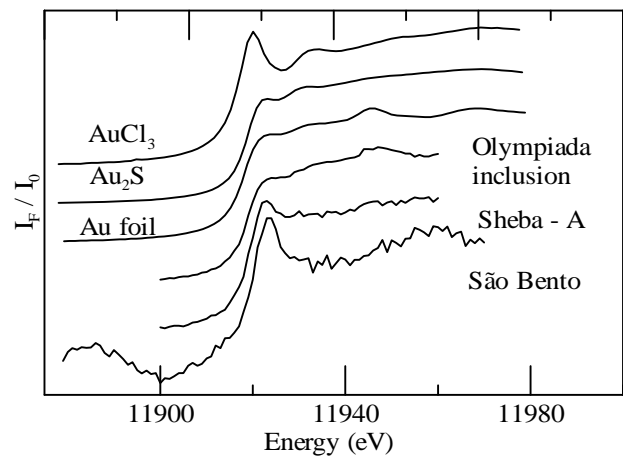
XANES spectra for these two regions are shown in Fig. 3, where a gold signal originating from absorption at the Au L<sub>3</sub>-edge (~11,919eV) is clearly discernible from the arsenic background arising from absorption at the arsenic K-edge (11,868 eV). The XANES for region A is an average of 28 scans while that for region B is just 1 scan (5s per point). The peak in the XANES evident just above the gold edge arises from an appreciable number of unfilled gold 5d-



**Figure 3.** XANES spectra for regions A and B of the Sheba grain compared with As XANES from a gold-deficient region of the Olympiada sample.

states and suggests chemically-bound gold. We also recognize that the strong peak at the arsenic K-edge indicates the presence of unfilled As 4p-states. Assignment of ionic valence for the chemically-bound elements is not straightforward since comparable electronegativities indicate the presence of significant covalent interactions.

In Fig. 4, we show data from the WDX-600 spectrometer for the three samples. Also shown are reference XANES spectra for Au foil, Au<sub>2</sub>S and AuCl<sub>3</sub> (in sealed ampoule) taken in transmission (foil) or fluorescence mode (sulphide, chloride) with ionisation chambers and represent Au<sup>0</sup>, Au<sup>+1</sup> and Au<sup>+3</sup> respectively. The Olympiada XANES data were taken from a single region 30 μm in diameter with high Au fluorescence signal in an arsenopyrite



**Figure 4.** Gold XANES spectra from the minear and reference samples with vertical displacement for clarity.

grain from the Olympiada sample and strongly resemble the spectrum for elemental gold. The edge positions of the Sheba and São Bento spectra are suggestive of Au<sup>+1</sup> but the peaks due to unoccupied d-states, again, indicate that an ionic description is not appropriate.

#### Acknowledgements

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