

## **Oxidation state of gold and arsenic in gold-bearing arsenian pyrite**

**GRIGORE SIMON,<sup>1,\*</sup> HUI HUANG,<sup>2</sup> JAMES E. PENNER-HAHN,<sup>2</sup> STEPHEN E. KESLER,<sup>1,†</sup> AND LI-SHUN KAO<sup>1</sup>**

<sup>1</sup>Department of Geological Sciences, University of Michigan, 2534 C.C. Little Building, Ann Arbor, Michigan 48109, U.S.A.

<sup>2</sup>Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, U.S.A.

### **ABSTRACT**

XANES measurements on gold-bearing arsenian pyrite from the Twin Creeks Carlin-type gold deposits show that gold is present as both Au<sup>0</sup> and Au<sup>I+</sup> and arsenic is present at As<sup>I-</sup>. Au<sup>0</sup> is attributed to sub-micrometer size inclusions of free gold, whereas Au<sup>I+</sup> is attributed to gold in the lattice of the arsenian pyrite. STEM observations suggest that As<sup>I-</sup> is probably concentrated in angstrom-scale, randomly distributed layers with a marcasite or arsenopyrite structure. Ionic gold (Au<sup>I+</sup>) could be concentrated in these layers as well, and is present in both twofold- and fourfold-coordinated forms, with fourfold-coordinated Au<sup>I+</sup> more abundant. Twofold-coordinated Au<sup>I+</sup> is similar to gold in Au<sub>2</sub>S in which it is linearly coordinated to two sulfur atoms. The nature of fourfold-coordinated Au<sup>I+</sup> is not well understood, although it might be present as an Au-As-S compound where gold is bonded in fourfold coordination to sulfur and arsenic atoms, or in vacancy positions on a cation site in the arsenian pyrite. Au<sup>I+</sup> was probably incorporated into arsenian pyrite by adsorption onto pyrite surfaces during crystal growth. The most likely compound in the case of twofold-coordinated Au<sup>I+</sup> was probably a tri-atomic surface complex such as S<sub>pyrite</sub>-Au<sup>I+</sup>-S<sub>bi-sulfide</sub>H or Au<sup>I+</sup>-S-Au<sup>I+</sup>. The correlation between gold and arsenic might be related to the role of arsenic in enhancing the adsorption of gold complexes of this type on pyrite surfaces, possibly through semiconductor effects.