

## X-ray spectroscopy study of the chemical state of “invisible” Au in synthetic minerals in the Fe-As-S system

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### ABSTRACT

Minerals of the Fe-As-S system are the main components of Au ores in many hydrothermal deposits, including Carlin-type Au deposits, volcanogenic massive sulfide deposits, epithermal, mesothermal, sedimentary-hosted systems, and Archean Au lodes. The “invisible” (or refractory) form of Au is present in all types of hydrothermal ores and often predominates. Knowledge of the chemical state of “invisible” Au (local atomic environment/structural position, electronic structure, and oxidation state) is crucial for understanding the conditions of ore formation and necessary for the physical-chemical modeling of hydrothermal Au mineralization. In addition, it will help to improve the technologies of ore processing and Au extraction. Here we report an investigation of the chemical state of “invisible” Au in synthetic analogs of natural minerals (As-free pyrite FeS<sub>2</sub>, arsenopyrite FeAsS, and löllingite FeAs<sub>2</sub>). The compounds were synthesized by means of hydrothermal (pyrite) and salt flux techniques (in each case) and studied by X-ray absorption fine structure (XAFS) spectroscopy in a high-energy resolution fluorescence detection (HERFD) mode in combination with first-principles quantum chemical calculations. The content of “invisible” Au in the synthesized löllingite (800 ± 300 ppm) was much higher than that in arsenopyrite (23 ± 14 ppm). The lowest Au content was observed in zonal pyrite crystals synthesized in a salt flux. High “invisible” Au contents were observed in hydrothermal pyrite (40–90 ppm), which implies that this mineral can efficiently scavenge Au even in As-free systems. The Au content of the hydrothermal pyrite is independent of sulfur fugacity and probably corresponds to the maximum Au solubility at the experimental *P-T* parameters (450 °C, 1 kbar). It is shown that Au replaces Fe in the structures of löllingite, arsenopyrite, and hydrothermal pyrite. The Au-ligand distance increases by 0.14 Å (pyrite), 0.16 Å (löllingite), and 0.23 Å (As), 0.13 Å (S) (arsenopyrite) relative to the Fe-ligand distance in pure compounds. Distortions of the atomic structures are localized around Au atoms and disappear at *R* > ~4 Å. Chemically bound Au occurs only in hydrothermal pyrite, whereas pyrite synthesized without hydrothermal fluid contains only Au<sup>0</sup>. The heating (metamorphism) of hydrothermal pyrite results in the decomposition of chemically bound Au and formation of Au<sup>0</sup> nuggets, which coarsen with increasing temperature. Depending on the chemical composition of the host mineral, Au can play a role of either a cation or an anion: the Bader atomic partial charge of Au decreases in the order pyrite (+0.4 e) > arsenopyrite (0) > löllingite (–0.4 e). Our results suggest that other noble metals (platinum group elements, Ag) can form a chemically bound refractory admixture in base metal sulfides/chalcogenides. The content of chemically bound noble metals can vary depending on the composition of the host mineral and ore history.

**Keywords:** Invisible gold, pyrite, arsenopyrite, löllingite, synthetic minerals, X-ray absorption spectroscopy, atomic charges