

## Arsenic evolution as a tool for understanding formation of pyritic gold ores

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The work by Xing et al. (2019) presents results of thermo-dynamic modeling of formation of As-bearing pyritic gold ores. The study combined the results of the first-principle quantum mechanical techniques (Reich and Becker, 2006) with mineral equilibria modeling of hydrothermal processes. While the overall approach of the study is very promising, some of the predictions are inconsistent with observations in natural samples and experimental data.

A key prediction of the Xing et al. model is that pyrite coexisting with arsenopyrite must contain 5–6 wt% As. However, arsenopyrite is commonly found coexisting with pyrite with much lower As content (e.g., Li et al., 2018). The coexistence of arsenopyrite with pyrite containing <5 wt% As cannot be explained by the diagrams of Xing et al. and Reich and Becker (2006). However, these associations can be explained by the metastability of arsenian pyrite (Ballantyne and Moore, 1988; Fleet and Mumin, 1997).

Xing et al. conclude that As content in pyrite should gradually increase until arsenopyrite is precipitated. However, pyrite in gold deposits commonly has fine-scale oscillatory and sector zoning in As content (e.g., Wu et al., 2019) rather than systematically increasing As content from the core to the rim. The replacement textures of high-As pyrite by the aggregates of low-As pyrite and arsenopyrite (Mumin et al., 1994; Li et al., 2018) similar to Xing et al.'s figure 3C were interpreted by the decomposition of metastable arsenian pyrite (Mumin et al., 1994). Therefore, these textures cannot be used as an evidence of “upgrading” of As content in pyrite.

Xing et al. estimated that direct precipitation of As-rich pyrite from a hydrothermal fluid requires fluids that are extremely enriched in As. However, Kusebauch et al. (2018) directly synthesized pyrite with 1–8 wt% As starting from solutions with 10–100 ppm As, and fluids saturated in arsenopyrite have <100 ppm As (Pokrovski et al., 2002). Fluids with <100 ppm As could be readily produced by the metamorphism of typical sedimentary pyrite containing 300–1100 ppm As (Gregory et al., 2015), hence “upgrading” is not necessary.

Additionally, the phase diagram by Xing et al. presented in their figures 2C and 2D does not reproduce well the temperature constraints on the stability of pyrite and arsenopyrite assemblages. The highest stability temperature of the association pyrite-arsenopyrite is 491 °C at 1 bar (100 kPa) (Kretschmar and Scott, 1976), which increases by 14 °C per kbar with pressure (Sharp et al., 1985). The calculations of Xing et al. estimated the highest temperature of the assemblage pyrite-arsenopyrite at ~580 °C and 2 kbar (200 kPa), ~60 °C higher than experimental estimates.

Inconsistencies of the Xing et al. model with both natural samples and experimental data suggest that further studies are needed for a better understanding of phase relations involving arsenian pyrite.

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