

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

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Stepanov (2019) challenges our thermodynamic modeling on compositions of arsenian pyrite and arsenopyrite by arguing that there are inconsistencies between our theoretical predictions and data from natural samples and experiments. His comments serve to highlight two important aspects of our model: (1) it is necessary to understand equilibrium in order to recognise kinetic and far-from-equilibrium effects; and (2) reactions under hydrothermal conditions are complex, in particular compared to dry systems.

An important premise of our thermodynamic modeling is the equilibrium between fluid and minerals. In practice, the definition of equilibrium depends on scale (e.g., local versus global) and may vary in both time and space. At all scales, fluid-mineral/rock interaction proceeds toward equilibrium. Understanding the equilibrium is the first step in discussing kinetics, and equilibrium modeling often describes the overall evolution of a system accurately (e.g., deposit-scale), even when disequilibrium phenomena rule at the micro-scale. For example, it is difficult to form pyrite directly from acidic solutions for kinetic reasons: metastable marcasite is formed as a precursor of pyrite, but marcasite will transform to pyrite over time, reaching the equilibrium state (Qian et al., 2011).

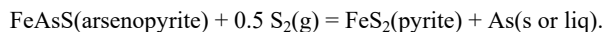
Stepanov inadvertently illustrates the importance of understanding equilibrium by noting that many arsenopyrites are found coexisting with pyrites that have an As content much lower than 5–6 wt%, which he believes is difficult to be explained by our modeling. Stepanov cites Li et al.'s (2018) study in support of this claim. However, the textural relationships between pyrite and arsenopyrite shown by Li et al. (2018) do not seem to reflect their equilibrium co-precipitation. In fact, many of such coexisting arsenopyrite and pyrite in natural hydrothermal mineralizing systems are formed by processes where (ultra-)local fluid compositions, fluid-mineral disequilibria, and crystal nucleation kinetics may control the composition of pyrite and arsenopyrite (e.g., Fougereuse et al., 2016; Wu et al., 2019), resulting in out-of-equilibrium compositions (Altree-Williams et al., 2016).

We also show that complex textures and mineral compositions can arise even at conditions of fluid-rock equilibrium in dynamic hydrothermal systems (e.g., our figure 3). Our upgrading model provides important information on how on-going or cyclical fluid-mineral interactions are able to enrich As in pyrite. In this manner, fluids with low As concentrations are able to form pyrite with high As contents. This indicates that low-As fluids, which are more common in nature, can indeed form As-rich pyritic ores.

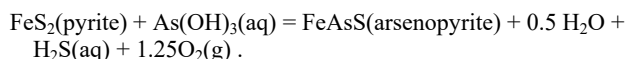
Stepanov challenges the accuracy of our model, suggesting that the model's predictions are inconsistent with the experimental studies of Pokrovski et al. (2002) and Kusebauch et al. (2018). However, the solubilities of As in solutions equilibrated with arsenopyrite predicted by our model are consistent with the study of Pokrovski et al. (2002) under the same temperature and redox conditions (i.e., 300–450 °C, arsenopyrite-pyrite-pyrrhotite-magnetite buffer; our figure 2). Our results are also consistent with the results from the experimental study of Kusebauch et al. (2018), with similar As partitioning coefficients under the same conditions (our figure DR3).

Finally, Stepanov argues that the replacement of pyrite+arsenopyrite by arsenopyrite+pyrrhotite at 491 °C in the phase diagram presented by Kretschmar and Scott (1976) is inconsistent with the phase relationships in our figure 2. The phase diagrams presented by Kretschmar and Scott (1976) or Sharp et al. (1985) are based on a dry Fe-As-S system (i.e., no

water phase). In these diagrams, sulfur [e.g., S₂(g)] and arsenic are buffered by Fe-As-sulfides ± As-S rich melt ± elemental arsenic according to Sharp et al.'s reaction (1985, their reaction 1):



However, our modeled system is a fluid-mediated Fe-As-S system, where pyrite and arsenopyrite coexistence is affected by $f_{\text{O}_2}(\text{g})$ and by the concentrations (activities) of the predominant As and S aqueous complexes (Sharp et al.'s, reaction 2):



Because As and S solubilities increase dramatically at high temperatures and under oxidizing conditions (our figures 2 and DR2), the partitioning of As, and thus the composition of pyrite and arsenopyrite and the relative stabilities of pyrite and pyrrhotite, are strongly dependent on the temperature and redox state in aqueous solutions. This has been highlighted by us as an important breakthrough of the study, compared to the studies of Kretschmar and Scott (1976) and Sharp et al. (1985).

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