Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.33479

Fluid pH Switches the Atomic-Scale Coupling of Gold and Arsenic in Hydrothermal Pyrite

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The correlation between arsenic and gold in pyrite is a critical yet enigmatic geochemical vector in gold exploration, as natural deposits exhibit coupled, decoupled, and complex heterogeneous relationships without a clear mechanistic basis. We hypothesize that fluid chemistry, specifically pH and sulfur speciation, orchestrates arsenic incorporation mechanisms, thereby programming the pyrite lattice for gold uptake. To test this, we synthesized pyrite via siderite replacement through controlled hydrothermal experimentation at 350 °C, systematically varying fluid pH (acidic, neutral, unbuffered), arsenic concentration, and sulfur source (native S^0- vs. thioacetamide-derived H_2S) (Eqns. 1 and 2). This design isolates the key fluid variables hypothesized to govern element coupling. The run products were analyzed using EPMA, NanoSIMS, and synchrotron XANES spectroscopy to resolve both geochemical distributions and arsenic oxidation state. We find that starting fluid pH acts as the primary switch: acidic conditions universally decouple Au and As, while neutral to unbuffered conditions promote coupling. Sulfur speciation dictates the reaction pathway, where S^0 leads to crystalline pyrite growth, whereas thioacetamide drives rapid growth via pyrrhotite intermediates, enhancing trace-element uptake. The XANES analysis directly demonstrates that the arsenic incorporation mechanism, either as As(-I) substituting for sulfur or As(II) substituting for iron is governed by these fluid parameters. The As(-I) pathway creates the necessary lattice defects for Au^+ incorporation, enabling the coupling observed under favorable pH conditions. By experimentally reproducing the full natural range of Au-As systematics, we demonstrate that decoupling is a positive indicator of acidic fluid influx or rapid disequilibrium crystallization. This work provides an experimental framework to decode pyrite geochemistry, transforming it into a dynamic record of hydrothermal fluid evolution and ore-forming processes.

Equations of sulfidation:

Thioacetamide decomposition at elevated temperature (>100 °C) produces $H_2S_{(aq)}$ according to the reaction:

$$CH_3CNH_2S_{(s)} + 2H_2O_{(l)} \rightarrow CH_2COOH_{(aq)} + NH_{3(aq)} + H_2S_{(aq)} \quad [1]$$

Sulfidation pathway from native sulfur is distinct from the direct release of H_2S bythioacetamide as seen in the reaction:

$$4S^\circ_{(s)} + 4H_2O_{(l)} \rightleftharpoons 3H_2S_{(aq)} + SO_2{}^{2-}{}_{(aq)} + 2H^+_{(aq)} \quad [2]$$