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Role of impurities in the semiconducting properties of natural pyrite: Implications for the electrochemical accumulation of visible gold and formation of hydrothermal gold deposits

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Abstract

Pyrite (FeS_2), the most abundant sulfide mineral on Earth, typically contains a host of minor and trace elements, including As, Co, Ni, and Au. It is an important semiconductor with unique structural properties markedly influenced by elemental impurities. However, whether the change in semiconducting properties of natural pyrite is caused by the type and concentration of trace elements or by a non-stoichiometry-related doping mechanism remains uncertain. Moreover, the effect of semiconducting properties on the enrichment mechanism of Au has not been well addressed. Here, we investigate microscopic pyrite crystals from the Heilangou gold field (HGF) in the eastern Jiaodong Peninsula using field emission scanning electron microscopy (SEM), electron probe microanalysis (EPMA), in situ laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), potential-Seebeck microprobe (PSM), and thermoelectric measurements. The results demonstrate that pyrite grains show either p- or n-type conductivity depending on chemical compositions. Pyrite enriched in As, which typically substitutes for S in the crystal structure, tends to be p-type with a positive Seebeck coefficient, whereas pyrite crystals enriched in Co, Ni, Cu, and Zn, as well as those depleted in As, are typically n-type. Moreover, As shows the strongest influence on the semiconducting properties of natural pyrite crystals and a strong positive correlation with Au. We observed that visible Au grains are preferentially accumulated on individual domains of sulfides (e.g., As-rich pyrite) that act as cathodes, suggesting that electrical p-n junctions in sulfides drive electrochemical reactions with ore-forming fluids, resulting in the deposition of visible Au. The electrochemical precipitation mechanism of Au may account for the formation of other types of hydrothermal Au deposits.

Keywords: As-rich pyrite, electrochemical precipitation, semiconducting properties, impurities, Heilan'gou, Jiaodong Peninsula