Electronic Controls on Transition-metal Incorporation in Pyrite: Insights from *Ab initio* Simulations

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Why do economically significant impurities occur in pyrite?

- Pyrite is one of the most abundant sulfide minerals in the crust and can host a wide range of transition metals, including elements such as Co, Ni, Cu, Au, etc.
- As-Au coupling suggests that As may be crucial for promoting Au substitution.

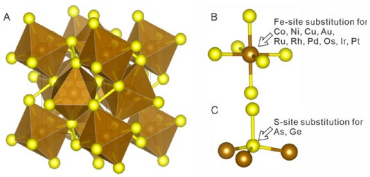

Fig. 1. (A) Crystal structural model of bulk pyrite; (B) Coordination octahedron in which Fe is substituted by Au; (C) Coordination tetrahedron in which S is substituted by As.

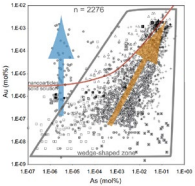

Fig. 2. Compilation of pyrite compositions in Au–As space (Deditius et al., 2014 GCA)

Joint substitutions promotes gold enrichment in pyrite

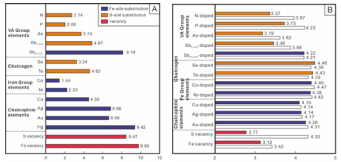

Fig. 3. Energetic responses of substitution.

- Joint substitutions better accommodate the induced stress, decrease energy barriers, and thereby facilitate gold incorporation.
- Among various trace elements, arsenic substitution for sulfur is the most favorable for gold incorporation, due to $[AuAs_nS_{6-n}]$.

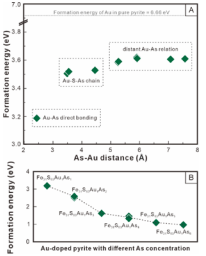

Fig. 4. Formation energy of Au within different types of As-doped model.

Note: 1 eV ≈ 96.485 kJ/mol

Electronic controls on transition-metal incorporation in pyrite: a physical framework

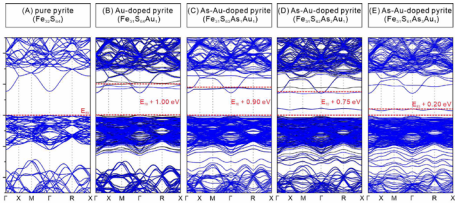

Fig. 5. Electronic band structure of Au with different As dopants

- We show that Au incorporation behaves as shallow donor, introducing excess electrons that shift the Fermi level toward the conduction-band, and increase the substitution energies.
- In contrast, coexisting As impurities introduce *p*-orbital holes that compensate the donor electrons and reshape the electronic structures.
- This electron–hole interplay suppresses conduction-band filling and stabilizes the defects.

(Reich et al., 2005 GCA)

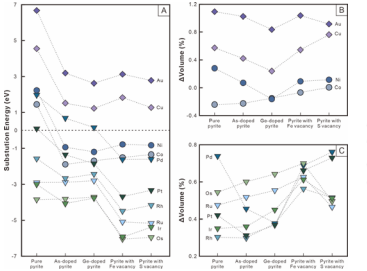

Fig. 6. Calculations of the energy of formation of various substitutions on the Fe site of various economically-important metals.

- Physicochemical parameters function as extrinsic controls on metal precipitation, whereas crystal-structural evolution constitutes the intrinsic control on elemental incorporation and preservation.

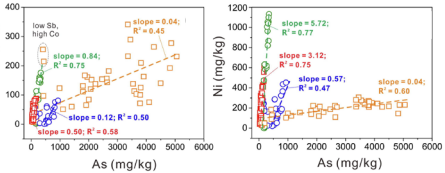

Fig. 7. Compilation of pyrite compositions in Co–As space and Ni –As space

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1. Large-scale gold incorporation in bulk pyrite mediated by arsenic (2026) ZY Gao, KF Qiu, R Caracas, et al. Geochimica et Cosmochimica Acta 421, 44-53.
2. The electronic origin of the incorporation of transitional metals in FeS_2 pyrite. ZY Gao, KF Qiu, R Caracas, et al. in prep.