

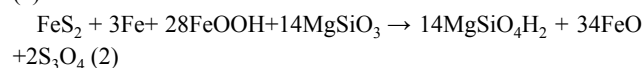
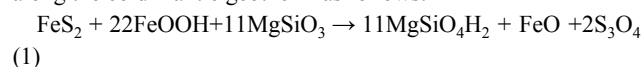
Thermodynamic of Pyrite in the Deep Lower Mantle: New Insights into the Sulfur Excess Paradox

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Recent studies suggest that approximately 46.5 Tg of sulfur is subducted into Earth's interior annually^[1]. Pyrite is the predominant sulfide mineral in marine sediments, accounting for more than 50% of the total sulfur content in oceanic sediments^[2]. Pyrite plays a vital role in sulfur transport in the Earth's interior. The physical and chemical properties of pyrite under high pressure and temperature (*PT*) are essential for understanding the deep sulfur cycle.

We investigated the thermodynamic and elastic properties of pyrite under mantle *PT* conditions using Density functional theory (DFT) calculations. We predict that pyrite remains stable at 137.8 GPa and 4000 K. The elastic modulus of pyrite shows a significant nonlinear response to variations in pressure and temperature. Pyrites show lower compressional (V_p) and shear (V_s) wave velocities. Additionally, the elastic anisotropy of pyrite is significantly pronounced. We calculated density and wave velocity profiles for pyrite along mantle geotherms, revealing lower bulk and shear moduli and higher density compared to the reference state (PREM). Thus, pyrite maybe potentially contribute to the formation of ultralow velocity zones (ULVZs). Besides, we explored the possibility of Fe acting as a reducing agent with FeS₂, or FeS₂ acting as an oxidizing agent with FeOOH to undergo oxidation reactions that produce S₃O₄ along the cold mantle geotherm as follows:



We explored the redox mechanisms of pyrite, producing compounds such as S₃O₄ that transport sulfur in the deep lower mantle. These findings provide new evidence for the deep mantle sulfur reservoir and the volcanic degassing of excess sulfur.

References

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- [2] Raiswell, R., Canfield, D.E., (2012). *Geochemical perspectives* 1, 1-2.