

## ***Ab initio* thermodynamics of FeS transformation pathways**

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Iron sulfide minerals play an important role in controlling the fate of pollutants in suboxic conditions. Pyrite (FeS<sub>2</sub>), a dominant iron sulfide mineral, forms mainly via transformation of metastable mackinawite (FeS) or greigite (Fe<sub>3</sub>S<sub>4</sub>). Multiple transformation pathways have been proposed in synthetic experiments, but they often conflict among different experiments. The conflict may be resolved by separating kinetic effects from thermodynamics involved in the mineral transformation. However, calorimetric data are sparse for the metastable iron sulfide minerals. In this study, we investigated the transformation thermodynamics of the metastable phases using density functional theory (DFT) with the SCAN functional. We present DFT-calculated pH-Eh Pourbaix diagrams for H<sub>2</sub>O, FeS, Fe<sub>3</sub>S<sub>4</sub>, Fe<sub>7</sub>S<sub>8</sub>, and FeS<sub>2</sub> and possible transformation pathways of the minerals as a function of H<sub>2</sub>S/H<sub>2</sub> ratio. Our theoretical calculations, which use no experimental data for iron sulfide minerals, provide thermodynamics missing in experiment that allows one to separate kinetic effects and thus help understand the transformation pathways of iron sulfide minerals.