Transition metal incorporation into layer type FeS

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In sulfide ore deposits, mackinawite, a layer-type FeS mineral, often contains incorporated transition metals, such as Co, Ni, or Cu. However, there are insufficient experimental data on the crystal structure and thermodynamic stability of metal-enriched FeS to establish incorporation mechanisms for these metals. We investigated these mechanisms using density functional theory with dispersion corrections (DFT–D). Our DFT geometry optimizations revealed a metal-specific relationship between mineral composition and crystal structure which depends on whether a metal substitutes at Fe sites or intercalates between FeS_4 tetrahedral sheets (Figure 1). Our substitution results agree with the trends in available experimental data [1, 2], but our intercalation results do not. We then performed free energy calculations for metal incorporation as a function of temperature and the partial pressure ratio $p(H_2S)/p(H_2)$. Our results indicate clearly that substitution, not intercalation, is the more favorable metal incorporation mechanism and that metal incorporation tends to increase the stability of mackinawite, as has long been hypothesized [3].

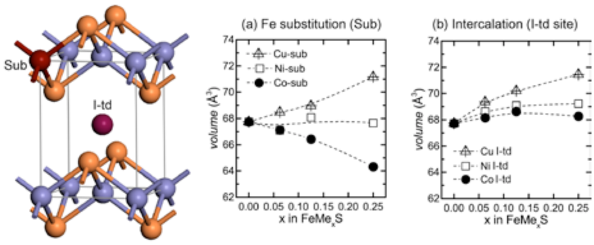

Figure 1. DFT-calculated structural changes of mackinawite crystal when transition metals (a) substitute the Fe sites (Sub) or (b) intercalate between the sheets (I-td). Modified from [4]

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