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Cobalt incorporation into low temperature pyrite: toward a further understanding of the polysulfide pathway to pyrite

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Authigenic pyrite (FeS_2) is often considered as a geochemical archive for reconstructing past marine conditions. Notably, cobalt (Co) abundance in marine sedimentary pyrite is considered as reverse proxy for atmospheric oxygen levels (Large et al., 2017). As a bio-essential nutrient, Co plays a significant role in present and past biogeochemical processes such as methionine synthesis and anaerobic metabolisms (Swanner et al., 2014; Robbins et al., 2016). However, Co can reach harmful concentrations in mine drainages (e.g., Ziwa et al., 2021), which questions its potential toxicity towards humans and ecosystems. Thus, better understanding the mechanism of Co incorporation into diagenetic pyrite is crucial for evaluating the ability of this mineral to act as source or sink for Co in contaminated environments, as well as for refining the use of sedimentary pyrite as a paleo-proxy. In this study, pyrites were synthesized via the polysulfide pathway under anoxic conditions at ambient temperature with varying initial aqueous Co concentrations. Using High Energy Resolution Fluorescence Detected (HERFD) Co K-edge X-ray Absorption Near Edge Structure (XANES) and Extended X-ray absorption fine structure (EXAFS) analyses, we obtain key information on the partition of Co between pyrite and its precursors during the pyritization process (Deng et al., submitted). Moreover, the Co^{2+} ion acts as geochemical probe revealing unprecedented information on the molecular structure of the precursors to pyrite. Beyond the single case of Co, it yields mechanistic explanations for the reported role of trace metals such as Ni and As on the kinetic of low temperature pyrite formation. This study has implications for further understanding the mechanisms of pyrite formation via the polysulfide pathway and of trace metal incorporation in this mineral during early diagenesis.

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