

Fate of cobalt and nickel in mackinawite during diagenetic pyrite formation

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ABSTRACT

As iron sulfide mineral phases are important sedimentary sinks for naturally occurring or contaminant metals, it is important to know the fate of metals during the diagenetic transformation of primary sulfide minerals into more stable phases, such as pyrite (FeS₂). Furthermore, the trace metal content of pyrite has been proposed as a marine paleoredox proxy. Given the diverse low-temperature diagenetic formation pathways for pyrite, this use of pyrite requires validation. We, therefore, studied nickel (Ni) and cobalt (Co) incorporation into freshly precipitated mackinawite (FeS_m), and after experimental diagenesis to pyrite (FeS₂) using S⁰ as an oxidant at 65 °C. Metal incorporation was quantified on bulk digests using ICP-OES or ICP-AES. Bulk mineralogy was characterized with micro-X-ray diffraction (micro-XRD), documenting the transformation of mackinawite to pyrite. Epoxy grain mounts were made anoxically of mackinawite and pyrite grains. We used synchrotron-based micro-X-ray fluorescence (μXRF) to map the distribution of Co and Ni, as well as to collect multiple energy maps throughout the sulfur (S) *K*-edge. Iron (Fe) and S *K*-edge micro-X-ray absorption near edge spectroscopy (μXANES) was used to identify the oxidation state and mineralogy within the experimentally synthesized and diagenetically transformed minerals, and map end-member solid phases within the grain mounts using the multiple energy maps. Metal-free FeS_m transformed to pyrite, with residual FeS_m detectable. Co- and Ni-containing FeS_m also transformed to pyrite, but with multiple techniques detecting FeS_m as well as S⁰, implying less complete transformation to pyrite as compared to metal-free FeS_m. These results indicate that Co and Ni may inhibit transformation for FeS_m to pyrite, or slow it down. Cobalt concentrations in the solid diminished by 30% during pyrite transformation, indicating that pyrite Co may be a conservative tracer of seawater or porewater Co concentrations. Nickel concentrations increased several-fold after pyrite formation, suggesting that pyrite may have scavenged Ni from the dissolution of primary FeS_m grains. Nickel in pyrites thus may not be a reliable proxy for seawater or porewater metal concentrations.

Keywords: Mackinawite, pyrite, diagenesis, cobalt, nickel, X-ray absorption spectroscopy, X-ray fluorescence; Understanding Paleo-Ocean Proxies: Insights from in situ analyses