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 (FeS0.9), and after experimental diagenesis to pyrite (FeS2) using S8 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 FeS0.9 transformed to pyrite, with residual FeS0.9 detectable. Co- and Ni-containing FeS0.9 also transformed to pyrite, but with multiple techniques detecting FeS0.9 as well as S8, implying less complete transformation to pyrite as compared to metal-free FeS0.9. These results indicate that Co and Ni may inhibit transformation for FeS0.9 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 FeS0.9 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

INTRODUCTION

Pyrite (FeS2) is the most abundant iron sulfide mineral on the surface of the Earth (Rickard and Luther 2007) and has formed in marine sediments (e.g., “diagenetic” pyrite) for at least 3.5 billion years (Gy) (Shen et al. 2001). The presence of pyrite, as well as its isotopic and elemental composition, has been applied to determining the redox conditions of the site of deposition, as well as the atmosphere and oceans. For instance, the presence of detrital pyrite in sediments >2 Gy old was one of the early indications of an anoxic Archean atmosphere (Holland 1984). Because of the enhanced mobilization of sulfate to the oceans from weathering of continental pyrite as oxygen appeared in the atmosphere, the presence of marine pyrite, formed either authigenically or diagenetically, tracks the timing of oxidation of the Earth and atmosphere. Pyrite Fe and S isotopes are exploited to track the magnitude of pyrite burial through time (Rouxel et al. 2005; Tostevin et al. 2014), the amount of sulfate in the oceans (Canfield and Farquhar 2009), as well as atmospheric and ocean oxygenation (Mojzsis et al. 2003; Rouxel et al. 2005; Konhauser et al. 2011; Fakhraee et al. 2018).

Increasingly, though, scientists are also looking into the trace metal inventory of sedimentary pyrite as a reflection of the trace metal contents and redox conditions of the overlying water column. While investigations of trace metals in bulk clastic sediments, such as shales, are useful for this purpose, these studies tend to better highlight the utility of elements that undergo extreme authigenic enrichments in sediments under certain redox conditions (Algeo and Maynard 2004; Algeo and Rowe 2012), rather than those that are specifically incorporated by pyrite. The trace metals that become incorporated into pyrite by coprecipitation can reflect either the abundance of these elements in seawater (Huerta-Diaz and Morse 1992), and the metals can be