

Comparison between Co(II) and Ni(II) cycling at goethite-water interfaces: Interplay with Fe(II)-catalyzed recrystallization

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Cobalt (Co) and nickel (Ni) are among the list of essential micronutrients for plant health and critical metals for modern renewable technologies. Both metals are commonly associated with iron (oxyhydr)oxide minerals, e.g., goethite (α -FeOOH), that are ubiquitously present in terrestrial and aquatic systems. While Ni(II) cycling has a negative feedback on Fe(II)-catalyzed goethite recrystallization [1], the interplay between Co(II) cycling through goethite and its recrystallization induced by Fe(II) remains poorly understood. Here we compare Co(II) and Ni(II) cycling at goethite-water interfaces during Fe(II)-catalyzed recrystallization. At circumneutral pH and anoxic conditions, we performed reaction experiments on synthesized Co(II)-substituted goethite and aqueous Fe(II) and sorption experiments on synthesized pure goethite in Co(II) and Ni(II) solutions with and without addition of aqueous Fe(II). The redox state and coordination environment of Co in substituted goethite were determined at Co K-edge using high energy resolution fluorescence detection (HERFD) synchrotron X-ray absorption spectroscopy (XAS), and the distribution of solid-bound Co and Ni in goethite following sorption was revealed by sequential dissolution. Our results show that substitution of Co(II) for Fe(III) in goethite structure does not have as much negative feedback as Ni(II) does on Fe(II)-catalyzed recrystallization, which may be related to their differing structural distortions as evidenced by EXAFS. In the absence of Fe(II), aqueous Co(II) is more favourably adsorbed onto and deeply incorporated into goethite than Ni(II). This is presumably due to the potential transition of Co(II) from high-spin to low-spin configuration that renders it more structurally compatible to goethite. The presence of Fe(II) markedly enhances the structural incorporation of both Co(II) and Ni(II) as a result of goethite recrystallization, which in turn can be inhibited by the accumulation of metals at mineral surface. Furthermore, structurally-incorporated Co(II) is more difficult to be released back into solution than Ni(II) during Fe(II)-catalyzed goethite recrystallization. Overall, our work highlights the nuanced differences between Co(II) and Ni(II) in their cycling at goethite-water interfaces and interplay with Fe(II)-catalyzed recrystallization, which improves our understanding of their mobilization and distribution in anoxic goethite-rich systems.

References: [1] Frierdich et al. (2019), *ACS Earth Space*