Trace Element Partitioning between Iron Oxides and Aqueous Solutions: Evidence for Recrystallization

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Well-crystalline iron oxides (e.g., hematite, goethite) are generally assumed to be stable hosts for trace elements. These phases are highly insoluble under most pH conditions and are slow to be reduced microbially, often persisting in sediments until sulfidic conditions develop. Incorporation of trace into iron oxides is believed to sequester elements contaminants, trap micronutrients, and record ancient fluid compositions. However, evidence suggests that element repartitioning into and out of bulk iron oxide structures occurs when dissolved Fe(II) is present, such as at redox interfaces. In addition, recent work has shown that atom exchange occurs between dissolved Fe(II) and both hematite and goethite, the recrystallization. latter undergoing complete These observations suggest that the remobilization potential of trace elements substituting in iron oxides has been substantially underestimated.

We have investigated the partitioning of trace elements between aqueous solutions and iron oxide structures in the presence and absence of dissolved Fe(II) and how this is impacted by inorganic and organic ligands. At circumneutral pH, Fe(II) promotes Ni and Zn incorporation in and release from goethite and hematite on the timescale of 14 to 30 days. Sulfate has little effect on these processes but both are inhibited by phosphate. While negligible at circumneutral pH, substantial trace element release is observed in the absence of Fe(II) at pH 4 and 5.5, suggesting that there may be a pHdependent background rate of recrystallization. Oxalate and citrate also promote trace element release from goethite and hematite far in excess of what can be explained by ligandpromoted dissolution. These studies demonstrate that trace elements have a surprisingly high potential for remobilization from iron oxide minerals under a range of chemical conditions. Such remobilization will reduce the effectiveness of contaminant sequestration but may enhance micronutrient availability. This work raises uncertainty about the validity of iron oxide trace element contents as records of ancient ocean chemistry.