Reactivity and cycling of trace-metals in marine sediments

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Despite their relatively low abundance in marine sediments, iron (Fe) and manganese (Mn) minerals, through coupled sorption and redox, exert a primary control on the reactivity and cycling of trace-metals in the marine environment. Directly, these often transient minerals impart a first order effect on the concentration and stable isotope composition of metals in seawater, including nickel (Ni) and copper (Cu). Indirectly, as a result of mineral-promoted preservation of organic carbon (OC), these phases present an important but little understood link between the Earth's major and trace element cycles.

In order to quantify the role of Fe and Mn minerals in global element cycles, it is necessary to understand their sorption and redox processes at the molecular level, because the precise mechanism by which trace-metals are sequestered can determine sediment-seawater exchange, and can induce significant trace-metal stable isotope fractionation, thought to control modern seawater composition for a number of micronutrients. This presentation will discuss several current research projects, where understanding the complex interplay between ferromanganese minerals and trace-metals at the molecular level has shed light on global element cycles. For example, in the modern oceans, Mn oxides provide the primary sedimentary sink for Ni, where Ni concentration in seawater is coupled to an equilibrium sorption reaction between dissolved Ni and the phyllomanganate birnessite. During diagenesis, birnessite transforms into the tectomanganate todorokite and, across significant areas of the seafloor, the primary authigenic Mn oxide in marine sediments therefore exists as a transient mineral phase. The transformation of birnessite results in significant release of Ni into marine sedimentary porewaters and the diagenesis of Mn oxides might therefore provide a benthic source of micronutrients to seawater. Similarly, equilibrium sorption reactions between dissolved Cu and both Fe and Mn (hydr)oxides exert a significant control on modern oceanic Cu. Coupled with these processes, the formation, transformation and sorption behaviour of Fe (hydr)oxides in particular is fundamentally modified by the intimate association of Fe minerals with OC. Coupling of the Fe and C cycles in marine sediments changes the mechanism of Cu sequestration at the molecular level and results in significantly altered Cu mobility.