Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.6939

A sequential extraction procedure for manganese and its application to marine sediments

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Manganese (Mn) is a key element in marine systems and its dynamics can affect the cycling of many elements, such as iron (Fe), phosphorus (P) and carbon (C). The biogeochemical impact of Mn depends on its form in the sediment. For example, Mn oxides can be involved in the oxidation of dissolved Fe(II), organic matter and methane. Mn(II)-phosphates and P-bearing Mn carbonates may promote the burial of P in sediments. While sequential extractions are widely used to discern between various sediment forms of Fe, P and sulfur, no sequential extraction procedure is currently available to investigate the solid phase speciation of Mn.

In this study, an extraction procedure that is widely used for the speciation of Fe in sediments, is calibrated for Mn using a range of standards. The standards consist of various Mn oxides, Mn carbonates, Mn(II)-phosphate minerals, Mn sulfides and clays. We show that the extraction procedure allows us to separate most of the Mn phases, and is especially successful in distinguishing between Mn oxides, Mn carbonates and Mn associated with pyrite.

Additionally, we applied the sequential extraction to a range of marine sediments with varying bottom water redox conditions. The results show that, in sediments deposited in euxinic bottom waters, Mn is mainly present in Mn carbonates and bound in clays and pyrite, in approximately equal amounts. In sediments deposited in periodically euxinic and hypoxic bottom waters, Mn carbonates dominate over the other two fractions and small but variable amounts of Mn oxides are also observed. In sediments deposited in oxygenated bottom waters, Mn oxides, Mn-rich vivianite-type minerals and Mn carbonates dominate and no pyrite bound Mn is observed. We also find evidence for the presence of Mn oxides below the sulfate methane transition at one location, suggesting that at this site, Mn oxides could potentially contribute to the anaerobic oxidation of methane.