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Fe isotopes revealing mineral-specific redox cycling in sediments

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Reactive Fe (oxyhydr)oxides preferentially undergo early diagenetic cycling and cause a diffusive flux of dissolved Fe^{2+} from sediments towards the sediment-water interface. The partitioning of Fe in sediments has traditionally been studied by applying sequential extractions based on reductive dissolution of reactive Fe (oxyhydr)oxide minerals. In order to trace back sources of bioavailable Fe in the water column, Fe isotope analyses on water, pore water and specific precursor-minerals represent a tool of increasing interest. Therefore, we modified an existing sequential leaching method by Poulton and Canfield [1] in order to be able to gain δ^{56}Fe data for specific Fe minerals. Those are a) Fe-carbonate, b) ferrihydrite and lepidocrocite, c) goethite and hematite, and d) magnetite. Leaching was performed with acetic acid, hydroxylamine-HCl, Na-dithionite and oxalic acid, respectively. The selectivity of the extraction steps was tested by leaching pairs of ^{58}Fe-spiked and unspiked lab-made minerals. Hydroxylamine-HCl leaching for ferrihydrite and lepidocrocite dissolves insignificant amounts of goethite and hematite. The determination of reducible oxides (ferrihydrite, lepidocrocite, goethite, hematite), however, is slightly compromised in presence of significant magnetite. Processing the leachates for δ^{56}Fe analysis involved boiling the samples in $HCl/HNO_3/H_2O_2$, Fe precipitation and anion exchange column chromatography. Fractionation during the chemical treatment could be excluded by monitoring processed standards and replicate samples.

The new method was applied to short sediment cores from the North Sea and a bay of King George Island (Potter Cove, South Shetland Islands, Antarctica). Acetic acid, used to extract Fe-carbonates, also dissolved acid volatile sulfides. Downcore mineral-specific variations in δ^{56}Fe revealed differing contributions of Fe (oxyhydr)oxides to redox cycling. In the North Sea core, the fractions of acetic acid soluble Fe and the ferrihydrite/lepidocrocite-Fe showed increasing δ^{56}Fe values with depth. Low δ^{56}Fe in acetic acid soluble Fe relative to ferric hydrous oxide-Fe is consistent with isotope fractionation via adsorption during dissimilatory iron reduction (DIR) experiments [2]. Increases of δ^{56}Fe with depth in both the acetic acid soluble Fe and the ferrihydrite/lepidocrocite-Fe fraction, are consistent with progressive DIR [2,3]. With the exception of the acetic acid soluble fraction, the Fe pools in the Antarctic core do not show any isotopic trend with depth. This is either due to a masking of DIR-related isotope effects by the generally large pools of reducible Fe (oxyhydr)oxides, or to intense mixing of the sediment column by iceberg rafting. These preliminary results show diagenetic Fe isotopic variability that could not have been revealed by analyzing δ^{56}Fe of the total reactive Fe pool in the sediment.

[1] Poulton and Canfield (2005), Chemical Geology 214, 209-221.

[2] Crosby et al., Geobiology 5 (2007), 169-189.

[3] Staubwasser et al., Geology 34 (2006), 629-632.