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+} towards the sediment-water interface. The partitioning of sedimentary Fe has traditionally been studied by applying sequential extractions. We modified an existing leaching method [1] in order to enable δ^{56}Fe measurements on specific Fe mineral fractions. Those are siderite/sorbed Fe, ferrihydrite/lepidocrocite, goethite/hematite, and magnetite. The selectivity of extractions was tested by leaching pairs of ^{58}Fe-spiked and unspiked synthetic minerals. Insignificant amounts of goethite and hematite are dissolved in hydroxylamine-HCl targetting ferrihydrite/lepidocrocite. The determination of reducible oxides leached by dithionite was found to be slightly compromised in presence of magnetite.

Removal of extraction matrix was achieved by repetitive oxidation, heating, Fe precipitation, and column separation. The new method was applied to a short sediment core from the North Sea. Downcore mineral-specific variations in δ^{56}Fe revealed differing contributions of Fe oxides to redox cycling. Acetic acid soluble Fe and ferrihydrite/lepidocrocite-Fe showed increasing δ^{56}Fe values with depth in accordance with progressive dissimilatory iron reduction (DIR). Low δ^{56}Fe in acetic acid soluble Fe relative to ferric hydrous oxide-Fe is consistent with the fractionation pattern between sorbed Fe(II) and ferric substrate during DIR experiments [2]. Goethite/hematite- and magnetite-Fe do not show δ^{56}Fe trends with depth. The results demonstrate the importance of δ^{56}Fe analysis on individual Fe fractions that differ in origin and reactivity. The developed procedure provides a basis for specific Fe isotope studies in past and present environments that undergo or underwent redox changes.

[1] Poulton and Canfield (2005), *Chemical Geology* **214**, 209-221. [2] Crosby et al., *Geobiology* **5** (2007), 169-189.