The isotope signature of benthic Fe cycling in glacially influenced fjord sediments

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Western Svalbard fjords are an excellent environment to study the benthic Fe cycle and associated Fe isotope composition of marine sediments in which dissimilatory Fe reduction and extensive oxidative sulfur cycling are prevalent. Pore-water concentrations and isotope values with depth in Van Keulenfjorden sediments are imprinted by the (i) occurrence of dissimilatory Fe reduction throughout the sampled interval and (ii) the oxidation of dissolved Fe in distinct reaction zones. This process occurs predominently via oxygen at the mid- and outer fjord sites and Mn oxides at the inner fjord site. These processes drive the pore-water Fe isotope composition to light values, reaching -2.3‰ at the top of the reaction zone at the inner fjord site. Iron isotope profiles of labile Fe phases (0.5 M HCl extractable; Fe_{HCl}) display trends from heavier values at the bottom of the reaction zones to lighter values at the top where the pore-water Fe pool is (almost) completely oxidized. Our results support previous studies suggesting that Fe-oxidation in the sediment oxic layer is an important contributor to generating very light isotope compositions of benthic dissolved Fe flux.

Away from the reaction zones, the Fe_{HCl} fraction is comprised mostly of carbonate-bound (sodium acetate extractable) Fe (Fe_{NaAc}; 70-90%) and “fresh” (ascorbic acid extractable) ferric (oxyhydr)oxide phases (Fe_{ASC}; 10-30%), while acid volatile sulfide plays a minor role (<1.5%). Mixing diagrams suggest that the Fe_{ASC} pool has an isotope composition that is distinctly heavier (+0.7 to +1.3 ‰) than the Fe_{NaAC} fraction (-0.60 to -0.80 ‰). The observed values likely reflect the composition and formation history of the local bedrock, a Paleocene nearshore environment, that is undergoing mechanical and chemical breakdown, suggesting an important connection between the reworking of Fe mineral phases by weathering and erosion in the glacial environment and their deposition in the adjacent fjord archive.