

## **Iron isotope fractionation in iron-organic matter associations: Experimental evidence using filtration and ultrafiltration**

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Our aim in this work is to address the importance of Fe physical speciation in controlling the Fe isotopic composition in natural waters. Iron-organic matter (OM) associations were synthesized at various pH (1, 2 and 6.5) through binding and titration experiments. These suspensions were (ultra)filtered at 0.2  $\mu\text{m}$ , 30 kDa and 5 kDa. Significant Fe isotopes fractionation cannot be attributed to abiotic Fe precipitation, the (ultra)filtration technique or clogging. However, the Fe-OM binding and titration experiments displayed a Fe isotopic fractionation of approximately  $0.35 \pm 0.09\%$  and  $0.26 \pm 0.10\%$  between the total sample and the  $<30$  kDa fractions, respectively, at circumneutral pH. This fractionation of the Fe isotopes results from the complexation of Fe by OM. The results were subsequently used to interpret the Fe isotope fractionation in natural Fe-OM associations. These associations were produced from the oxidation of a reduced soil solution which itself was produced by the anoxic incubation of a wetland soil. The highest  $\delta^{56}\text{Fe}$  values were obtained in the smallest size fraction ( $<5$  kDa) demonstrating an isotopic fractionation of  $0.23 \pm 0.10\%$  in response to Fe(III) complexation by small humic OM molecules as monomers or small clusters.