Time-series analysis of Magnesium isotopes in speleothems

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Magnesium-isotope time series MC-ICP-MS analyses from NW Africa (Morocco) speleothems are reported. In addition, high-resolution C, O and Sr-isotope data, and Mg and Sr element abundances were compiled. The analytical results show clearly co-variant, systematic and cyclical fluctuations for all proxies collected along the growth axis and - with respect to the analytical error - invariant data within one growth increment. Magnesium-isotope ratios (δ^{26}Mg) fluctuate between -4.39‰ ± 0.02 2σ and -4.17‰ ± 0.05 2σ. The difference of 0.22‰ is significantly beyond the error of the external reproducibility of ± 0.03‰ 2 σ for δ^{26}Mg. Considering the analytical error, neither a purely kinetic nor an equilibrium fractionation process explains the observed isotope pattern. Two external factors might drive the speleothem Mg-isotope cyclicity: (1) climate-driven (arid versus humid) variances in the precipitation rate of a carbonate phase from meteoric water; and (2) changing rates of silicate versus carbonate weathering. Both of these processes fractionate the Mg-isotopic composition of runoff/seepage water.

Fractionation of iron isotopes in shallow-marine ferromanganese concretions

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Fe-isotope data for ferromanganese concretions indicate a trend from positive to negative values going from the freshwater environment, via the Arctic Ocean to the Atlantic and Pacific Ocean nodules, possibly following the redox related separation pathway of Fe from Mn in the exogenic cycle. However, the database is still small and additional Fe-Mn concretion data is needed, especially from continental margins, to verify if such a trend exists.

Shallow marine Fe-Mn conretions from the Baltic Sea and the Barents Sea analysed in this study show large variations in δ^{56}Fe, from -1.55 to +1.0, thus spanning the whole range of δ^{56}Fe values presented so far for ferromanganese concretions. There are also large variations in δ^{56}Fe in concretions from the same area. Large positive δ^{56}Fe values are obtained only close to the reduced-oxidised interface in the sediment. Samples taken at some distance from the reduced-oxidised interface with low Fe/Mn ratios generally show negative values. It can be concluded that the local redox conditions strongly influence the Fe-isotope signal in the concretions.

This study indicates that dissolved heavy Fe-isotopes preferentially are trapped close to the reduced-oxidised interface and any dissolved Fe that might escape from the sediment up into the bottom water during early diagenesis should have a clear negative δ^{56}Fe value. Hence, early diagenetic cycling of Fe-oxyhydroxides in shallow marine sediments acts as a sink for heavy Fe-isotopes and as a source of lighter ones.