Ce isotope fractionation during oxidation reaction

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Cerium belongs to the Rare Earth Element (REE) group and unlike any other Light REE can be stable under two oxidation states (Ce(III) and Ce(IV)). The Ce aqueous chemistry is interesting because Ce(III) and Ce(IV) behave differently. While Ce(III) behaves like its REE neighbours and is readily soluble, Ce(IV) is less soluble in natural waters and can therefore be easily decoupled from other LREE. Variations in Ce concentration relative to its neighbours have been extensively used to study changes in redox conditions in natural systems. For example, seawater is characterised by a large negative Ce anomaly (i.e. Ce is depleted relative to its neighbours) and this has been interpreted as reflecting the insoluble behaviour of Ce(IV) under oxic conditions.

Cerium has four stable isotopes (^{136}Ce, ^{138}Ce, ^{140}Ce, ^{142}Ce) and mass dependent variations have been previously reported in Fe-oxides and during chemical precipitation experiments (Nakada et al. 2013, 2016). The main conclusion is that redox reactions play a major role in fractionating Ce isotopes. The study of mass dependent Ce isotope variations can therefore help us constrain the behaviour of Ce and the conditions in which Ce isotopes are fractionated in natural waters. To date, however, there is no laboratory experiments that investigate the behaviour of Ce isotopes during oxidation reactions.

We have developed a new triple spike analytical method to measure mass-dependent Ce isotope variations (Bonnand et al. 2019, JAAS). In order to investigate the behaviour of Ce during oxidation reaction, we performed a number of laboratory experiments in which we partially oxidised a Ce(III) solution. We then measured the Ce isotopic composition in the Ce(III) and Ce(IV) fractions. While the oxidation reactions proceeds, the Ce(III) remaining become isotopically heavy (up to 0.6 ‰) relative to the starting isotopic composition. The isotopic composition of the Ce(IV) fraction is lighter than that of the Ce(III) fraction typical of isotopic fractionation during a kinetic reaction. These results confirm the redox control on the Ce isotopes behaviour and suggest that Ce isotope could become a useful tool to study redox reactions and past atmospheric oxygenation.

Nakada et al. 2013, GCA, 121, 105-119. Nakada et al. 2016, GCA, 191, 89-100. Bonnand et al. 2019, JAAS, 34, 504-516.