Isotopic fractionation and reaction kinetics of Cr in aqueous solutions

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Mass-dependent variations in the isotope composition of redox-sensitive elements like Cr, Fe, Mo, and U show great potential to decipher redox-changes in the present and past oceans, and as such to unravel Earth's climate history. However, to correctly interpret isotope variations of these elements in geological archives, it is imperative to understand their fractionation behaviour during redox transitions and the involved reaction kinetics. Therefore, we experimentally determined the mass-dependent chromium isotope fractionation during Cr(VI) reduction, Cr(III) oxidation, as well as the isotope exchange kinetics between soluble Cr(III) and Cr(VI).

All chromium isotope measurements were performed by high-resolution MC-ICP-MS [1]. The influence of the pH conditions on the Cr isotope fractionation factor and the type of fractionation (i.e. equilibrium vs. kinetic) were investigated during Cr(VI) reduction. The constant difference in $\Delta(^{53,52}Cr)_{Cr(III)-Cr(VI)}$ of -3.54 ± 0.35 ‰ (1 SD, N = 4) with different fractions of Cr(VI) reduction under strongly acidic conditions clearly demonstrates equilibrium Cr isotope fractionation. This $\Delta(^{53,52}Cr)_{Cr(III)-Cr(VI)}$ value is within uncertainty equal to that of -3.4 ± 0.1 ‰ that was published for Cr isotope fractionation at pH 6 to 7 [2]. The outcome of our reduction experiments at pH = 7 is less clear as they invoke overlapping processes, some of which are clearly kinetic in origin. The oxidation experiments in alkaline milieu indicate much smaller Cr isotope fractionation – ≈ 0.5 ‰ on the $^{53}Cr/^{52}Cr$ ratio – than the reduction experiments.

The isotope exchange kinetics between soluble Cr(III) and Cr(VI) were investigated by means of enriched ^{50}Cr isotope tracer experiments. Over the timescale of weeks, no measureable isotope exchange between soluble Cr(III) and Cr(VI) was found, independent of differencies in pH conditions and Cr(III):Cr(VI) ratios.

[1] Schoenberg, R. *et al.* (2008) *Chemical Geology*, **249**, 294ff. [2] Ellis, A. *et al*. (2002) *Science*, **295**, 2060ff.

Tracking the movement of the ITCZ from the last interglacial to the present: Evidence from Seychelles corals, western Indian Ocean

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In climate models the Indian Ocean is the region with the largest spread and the austral summer season is often not cosidered. However, the winter monsoon is crucial for precipitation over sub-Saharan Africa, Madagascar, Indonesia and West Australia. In addition, the winter monsoon season is strongly affected by the El Niño-Southern Oscillation (ENSO). Little is known about past changes of austral summer intra-seasonal variability (ISV) and its linkage with the position of the ITCZ. Here, we investigate changes in past seasonality and ISV during former Interglacials and from the Mid-Holocene to the present obtained from geochemical proxies (Sr/Ca, $\delta^{18}O$) in corals from the Seychelles located in a key region of ISV in the western Indian Ocean.

We hypothize that the strength of the ISV variability over the western Indian Ocean in combination with changes in incoming solar radiation are crucial to explain the weak ENSO magnitude during Interglacials and the Mid-Holocene.