The impact of the biogenic siderophore desferrioxamine B on Cr oxidation and fractionation of Cr isotopes

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The isotopic composition of Cr in marine chemical and clastic sediments and in paleosols is commonly used as a quantitative proxy for oxidative weathering. The oxidation of Cr(III) to Cr(VI) in presence of atmospheric oxygen is coupled to a fractionation of Cr stable isotopes, i.e., oxidized Cr species are isotopically heavier than the reduced species. Here we present results of batch experiments, where different Cr-bearing (igneous) rocks were incubated with the biogenic siderophore desferrioxamine B (DFOB). Siderophores are organic molecules which are produced and excreted by a wide range of bacteria, fungi and plants to enhance the bioavailability of key nutrients like Fe. Siderophores such as DFOB not only have a high affinity for Fe(III), but they also show exceptionally high stability constants with other highly-charged metals. Several studies demonstrated that siderophore chelation of heavy metals reduces metal uptake by bacteria, fungi and plants, and thus, these biomolecules apparently also play a vital role in heavy metal detoxification.

Here we show that leaching of pristine igneous rocks with DFOB results in stable isotope fractionation of Cr due to siderophore-promoted oxidation of Cr(III) to Cr(VI) during liberation from the mono- or polymineralic rocks. Although little is known about the abundance and the diversity of simple and complex organic acids in Earth's history, the ability to detoxify heavy metals by selective ligand binding as observed for modern siderophores might have been useful during the dawn of life in the Archean, to tackle any kind of heavy metal stress.

Our experiments show that Cr stable isotope fractionation, besides acting as a quantitative indicator for atmospheric oxygenation in marine chemical and clastic sediments, may also be indicative of the presence of (organic ligand-producing) biota on Early Earth. Moreover, the presence of biomolecules like siderophores during (bio)weathering leads to an enhanced production of Cr(VI) species and may thus significantly increase the level of environmentally harmful chromate or dichromate in natural and potable water.