Effects of solution pH, atmospheric oxygen concentrations and weathering state on the mobilization of redoxsensitive trace elements during waterrock interaction in presence of siderophores

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Siderophores are important biogenic chelators which facilitate the mobilization of iron and other highly-charged cations in the natural environment. Our previous research indicated that the hydroxamate siderophore desferrioxamine B (DFO-B) enhances the mobilization of certain trace elements that hydrolyze easily and which hence are traditionally assumed as being 'immobile' during water-rock interaction. Leaching of different rock material with DFO-B under ambient conditions, for example, facilitates the formation of a very pronounced Ce anomaly in bulk-normalized patterns and fractionates the Th/U element pair. This was tentatively attributed to an oxidation of Ce(III) to Ce(IV) and U(IV) to U(VI) during DFOB leaching. In this contribution, we investigated the effects of solution pH, fO₂ and weathering state of different rocks on the mobilization of redoxsensitive trace elements during water-rock interaction in presence of DFO-B. Redox-sensitive trace elements and their isotopes are used in many geoscientific studies as geochemical proxies for the presence of free atmospheric oxygen. However, the impact of natural organic ligands on these proxies may be largely underestimated. Many studies, for example on the reconstruction of the oxygen content of the early Earth's atmosphere, are based on the assumption that bacteria, fungi and plants had little or no influence on geologic archives. However, siderophores are omnipresent today and may also have been present in the geological past, during or after deposition of the geologic archives. Our preliminary results indicate that the fractionation of redox-sensitive trace elements is largely independent of solution pH, but fractionation is strongly controlled by atmospheric oxygen concentrations and by the weathering state of the studied rock. Hence, siderophores may have the potential to significantly catalyze the oxidation of these elements even under strongly hypoxic conditions. Here, we provide trace element data for batch leaching experiments run under different experimental conditions and constrain the amount of free oxygen needed for fractionation of Ce and U in presence of the siderophore DFO-B.