Chromium isotope fractionation during oxidative weathering of a modern basaltic weathering profile.

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Chromium has been used as a tracer of redox sensitive environmental processes. In soils Cr (III) is inert, immobile and resides predominantly in minerals, clays and oxides. Cr (VI) is toxic, soluble and mobile and is usually lost from the soil to runoff. Recent studies on $\delta^{53}Cr$ isotopes in laterites show that oxidative weathering of Cr-bearing rocks is accompanied by an isotopic fractionation, where by the lighter isotopes are retained in the residual soil and the heavier isotope is enriched in runoff [1].

This study aims to quantify the stable Cr isotope composition of two modern basaltic weathering profiles, to help better understand the processes that oxidize Cr (III) to toxic Cr (VI). We sampled two contrasting basaltic weathering profiles and local river waters; 1) Northern Ireland, formed in a peat area, and 2) Uruguay, formed in a grassland area.

Preliminary results show that the oxidation of Cr (III) in soils can be broken down into two important stages;

(i) The breaking down of Cr-bearing minerals in the basalt, which make Cr (III) accessible to oxidizing processes.

(ii) The continuing oxidation of Cr(III) to Cr(VI) oxyanions, CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$. This process predominates in the soil horizon and is accompanied by an isotopic fractionation. Over time Cr (VI) is lost from the system to local run off. In the Uruguay samples, the runoff is isotopically heavy, ($+0.11\pm0.02$‰) while the soils are isotopically lighter (-0.41 ± 0.03‰) with respect to local basalt $\delta^{53}Cr$ values (-0.21 ± 0.02‰).

The Northern Ireland samples show geochemical evidence of oxidative weathering but no significant $\delta^{53}Cr$ isotope fractionation is recorded in the soils. The $\delta^{53}Cr$ values of the soils are within a 95% confidence interval of the local bedrock $\delta^{53}Cr$ values, -0.11 ± 0.01 ‰ to -0.26 ± 0.04 ‰. Here Cr (III) is conversed in the weathering profile due to the low pH ~4.5 of the peat soils and the presence of reducers, Fe^{2+} [2,3] and organic matter which impede Cr(III) oxidation.

This data shows that the $\delta^{53}Cr$ value can be used as a measure of Cr(III) oxidation in a soil, and can give a good indiction of the extent to which toxic Cr (VI) is lost from the soil to local run off.

[1] Crowe *et al* (2013) *EPSL* in press [2] Ellis *et al* (2002) *Science* **295** 2060-2062 [3] Døssing *et al* (2011) *Chem Geol*. **285** 157-166