

Paper Number: 4438

Chromium isotope fractionation during extreme basalt weathering

Babechuk, M.G.¹, Kleinnhans, I.C.¹, Wille, M.¹, Schoenberg, R.¹, Widdowson, M.²

¹Department of Geosciences, University of Tübingen, 72074 Tübingen, Germany

²Department of Geography, Environment and Earth Sciences, University of Hull, Hull, HU6 7RX, UK

Fractionation of the stable isotopes of Cr has been documented during surficial Cr redox cycling [e.g., 1] and seafloor hydrothermal alteration [2], and the system is now gaining momentum as a paleo-redox tracer [3]. Here, Cr isotopes are reported for the early Paleogene Bidar laterite profile developed on Deccan Traps basalt, with the aim to document the isotopic fractionation associated with extreme oxidative basalt weathering.

Chromium is known to be one of the elements most highly concentrated in mafic lateritic residues with a behaviour that is closely linked to that of Fe. The Bidar profile is a classic example of water-table controlled lateritisation and preserves a progressive upward increase in alteration intensity and Fe enrichment. One prominent departure from this progression occurs at the position of the paleo-water table where extensive lateral element transfer occurred, resulting in Fe and Cr abundances that are highly elevated compared to the bounding horizons – this allochthonous transport influx is substantiated by mass balance calculations (assuming Nb immobility).

We observe that Cr shifts to isotopically heavier and lighter values from the composition of the protolith basalt ($\delta^{53/52}\text{Cr}$ of -0.25 ‰) in the overlying saprolite horizons (-0.47 to -0.12 ‰). Further, the Cr isotope composition switches between -0.85 to +0.36 ‰ within the paleo-water table influenced horizon, indicating a zone of complex Cr cycling that results in re-deposition of isotopically heavy Cr. Above the paleo-water table, in the horizons experiencing the most extreme residual Fe enrichment, the Cr isotope composition ranges from -0.58 to +0.02 ‰.

A correlation of Fe and Cr abundance in the profile ($r^2=0.725$) indicates that the majority of Cr is present as component of Cr(III) in the lattice of neo-formed hematite and goethite, consistent with the profile mineralogy. However, a detailed evaluation of the preserved Cr redox state in the profile has yet to be performed. Nevertheless, one group of samples in the profile shows a systematic decrease in $\delta^{53/52}\text{Cr}$ with increasing Fe abundance, which can be explained by the scavenging of Cr(III) by Fe(III)-oxides formed in the presence of a growing pool of isotopically heavy Cr(IV).

The $\delta^{53/52}\text{Cr}$ and Cr concentrations appear to be decoupled from variations in Mn abundance and Ce anomalies (another element forming a redox couple with Mn), such that it is difficult to establish a direct link between Mn and Cr at present. The samples bearing $\delta^{53/52}\text{Cr}$ values greater than the protolith indicate that not all of the isotopically heavy Cr escaped the profile as Cr(VI) and, instead, must have been adsorbed on mineral surfaces and partially back-reduced.

Lateritisation occurs under generally high Eh and fluctuating but periodically very low (2-5) pH conditions. Given the strong pH dependency of the adsorption of both Cr(III) and Cr(VI) aqueous species, it is also anticipated that mobilisation of isotopically fractionated pools of species in both redox states played a role in the stratigraphic variability. Top-down addition of Cr associated with aeolian dust and its subsequent redistribution in the profile may also have been a contributing factor but is significantly subordinate to the internally-mobilised Cr load.

References:

- [1] Paulukat C et al. (2015) *App Geochem* 59: 125-138
- [2] Farkaš et al. (2013) *Geochim Cosmochim Acta* 123: 74-92
- [3] Frei et al. (2016) *Nature Scientific Reports* 6: 21058

