



# Processes controlling the chromium isotopic composition of river water: Constraints from basaltic river catchments

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## Abstract

We report chromium (Cr) isotope compositions and concentrations (and additional geochemical and physicochemical data) of bedrock, soils and river waters from two geographically distinct basaltic river catchments, the Uruguay River catchment (Uruguay) and the Glenariff River catchment (Northern Ireland, United Kingdom), to investigate the processes that control Cr mobilisation and fractionation during weathering and riverine transport to the sea. Our results show that the Cr isotope compositions of soils are a function of the modal abundance and weathering rates of Cr-bearing minerals. The accumulation of weathering resistant Cr-spinels in the soils of Northern Ireland results in soils which are enriched in Cr and have  $\delta^{53}\text{Cr}$  values within the range of local bedrock ( $\delta^{53}\text{Cr}$  value of  $-0.21 \pm 0.12\text{‰}$ ,  $2\sigma$ ,  $n = 4$ ). By contrast, the more easily weathered Cr-silicates in the bedrock of Uruguay results in greater Cr loss from the soil and a depletion in the heavy isotopes of Cr (with average  $\delta^{53}\text{Cr}$  value of  $-0.32 \pm 0.04\text{‰}$ ,  $2\sigma$ ,  $n = 4$ ) relative to the local bedrock ( $\delta^{53}\text{Cr}$  value of  $-0.22 \pm 0.08\text{‰}$ ,  $2\sigma$ ,  $n = 4$ ). The river waters in both catchments are predominantly enriched in the heavy  $^{53}\text{Cr}$  isotope relative to bedrock, although the range and average river water  $\delta^{53}\text{Cr}$  values differ significantly between each. The Uruguay rivers exhibit a restricted range in  $\delta^{53}\text{Cr}$  values, with a mean of  $+0.08 \pm 0.06\text{‰}$  ( $2\sigma$ ,  $n = 5$ ) that represents a positive fractionation of  $+0.2\text{‰}$  relative to bedrock, and is best explained by the unidirectional formation of Cr(VI) during weathering that has not been significantly modified by back-reduction to Cr(III). By contrast, the Glenariff stream and river waters (Northern Ireland) exhibit a wide range in  $\delta^{53}\text{Cr}$  values from  $-0.17 \pm 0.3\text{‰}$  ( $2\sigma$ ,  $n = 4$ ) to  $+1.68 \pm 0.3\text{‰}$  ( $n = 1$ ) that appears to reflect the variable redox conditions of the catchment. In general, the values with the lowest  $^{53}\text{Cr}$  enrichment have higher Cr concentrations, the lowest pH, highest dissolved organic carbon (DOC), and exhibit minimal Ce anomalies that is consistent with a greater proportion of Cr(III) released from more reducing (bog influenced) stream waters. The remaining waters have lower Cr concentrations, lower DOC, and more pronounced Ce anomalies, indicating that a greater proportion of Cr(VI) underwent partial back-reduction to Cr(III) either during weathering, or during riverine transport. Overall, the DOC appears to exert a control on the dissolved Cr speciation and magnitude of isotope fractionation in these river waters. The broader implications of these observations are that the prevailing redox conditions in a river catchment strongly influence the  $\delta^{53}\text{Cr}$  value of the river water flux emptying into seawater. Observations for this study need to be considered when developing a framework for interpreting palaeo-climates from the  $\delta^{53}\text{Cr}$  values of ancient authigenic marine sediments.

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## 1. INTRODUCTION

Chromium stable isotopes are a useful tracer of changes in redox conditions. Recent experimental work has shown that changes in its oxidation state are accompanied by an isotopic fractionation (Ellis et al., 2002; Sikora et al., 2008; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012). Initial research has focused on the use of Cr isotopes in monitoring the remediation of toxic Cr(VI) in contaminated soils and groundwater (Ellis et al., 2002; Izbicki et al., 2008). More recently researchers have become interested in using Cr isotopes as a tool to record present and past variations in the global Cr biogeochemical cycle, with a view towards using the Cr isotopic composition of authigenic marine sediments as a new proxy to interpret ancient climates and redox conditions (Frei et al., 2009, 2011; Crowe et al., 2013; Planavsky et al., 2014). In order to reliably use this proxy in ancient settings we first need to define the Cr isotopic composition of fluxes into and out of the modern oceans. Continental weathering accounts for upwards of 70% of the overall Cr flux into the oceans (Reinhard et al., 2014). Hence, quantifying the Cr isotopic composition of riverine input and understanding the processes on land that influence it is an important factor to consider when interpreting ancient climates from authigenic marine sediments.

In oxygenated, circum-neutral surface waters, Cr(VI) oxyanions are the predominant Cr species (Cranston and Murray, 1980; Vos, 1985; Isshiki et al., 1989; Mugo and Oriens, 1993; Achterberg and Van den Berg, 1994; Sirinawin et al., 2000; Comber and Gardner, 2003; Connelly et al., 2006). Modern seawater is enriched in the heavy  $^{53}\text{Cr}$  isotope relative to unweathered magmatic bedrock ( $\delta^{53}\text{Cr}$  value of  $-0.12 \pm 0.1\%$ ) (Schoenberg et al., 2008). To date reported seawater  $\delta^{53}\text{Cr}$  values range from  $\sim +0.4\%$  (Argentine Basin, South Atlantic; Bonnand et al., 2013) to  $+1.5\%$  (Beaufort Sea, Arctic Ocean; Scheiderich et al., 2015).  $\delta^{53}\text{Cr}$  values of continental runoff measured to date is limited to; (1) an ultramafic (serpentinized) stream catchment from Mohelno, Czech Republic (Farkaš et al., 2013) with an average  $\delta^{53}\text{Cr}$  value of  $+3.94\%$  (27.3 nM), (2) the predominantly basaltic river catchment of the Paraná river, Argentina (Frei et al., 2014) with an average  $\delta^{53}\text{Cr}$  value of  $+0.35\%$  (31.3 nM), and (3) the Damsel River, Sukinda valley, India – an area heavily influence by local mining activity – with  $\delta^{53}\text{Cr}$  values from  $-0.06\%$  to  $+1.33\%$  (6 nM to  $2 \times 10^4$  nM).

In this study we aim to investigate the processes that control the variability in Cr isotopic composition of continental runoff by focusing on the factors controlling Cr mobilisation and fractionation during continental weathering and riverine transport to the ocean. To do this we measured Cr concentrations and isotopic compositions of bedrock, soils and river waters from two catchments with dominantly mafic bedrock from two distinct geographical locations: the Uruguay River catchment, Uruguay and the Glenariff River catchment, Northern Ireland, U.K.

## 2. CR FRACTIONATION AND CONTINENTAL WEATHERING

Chromium isotope fractionation at the Earth's surface is driven by oxidation and reduction reactions (Kotaš and Stasicka, 2000). Cr(III) oxidation reactions are thought to induce equilibrium isotopic fractionation, and Cr(VI) reduction induces kinetic isotopic fractionation (Schauble et al., 2004). During equilibrium fractionation isotope partitioning is associated with bond strength, whereby the heavy isotope preferentially forms stronger bonds. During oxidation of Cr(III), the heavy  $^{53}\text{Cr}$  isotope preferentially partitions into Cr(VI) oxyanions ( $(\text{H}_x\text{CrO}_4^{x-2})$  with tetrahedral coordination, because they form stronger bonds than octahedral bonds typically formed between Cr(III) and water molecules ( $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ). In contrast, kinetic fractionations are rate dependant and associated with unidirectional chemical reactions. Lighter isotopes form weaker bonds which can be broken easily, so they react faster. During kinetically regulated reduction reactions the product Cr(III) preferentially incorporates the lighter  $^{52}\text{Cr}$  isotope, further enriching Cr(VI) in the heavy isotope (Ellis et al., 2002; Sikora et al., 2008; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012). Thus, both oxidation and reduction reactions enrich Cr(VI) in the heavy  $^{53}\text{Cr}$  isotope.

Cr(III) is found mostly in mafic and ultramafic rocks in spinel group minerals such as chromite ( $\text{FeCr}_2\text{O}_4$ ), magnetite ( $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ , with partial substitution for  $\text{Fe}^{3+}$ ), and as a trace constituent in pyroxenes and sheet silicates such as chlorite and serpentine (Deer et al., 1992; Oze et al., 2004; Roeder et al., 2006). During weathering processes Cr(III) is leached and hydrolysed to  $\text{CrOH}^{2+}$ ,  $\text{Cr}(\text{OH})_2^+$  and  $\text{Cr}(\text{OH})_3$ . This process is proportional to the dissolution rates of Cr(III)-bearing minerals (Oze et al., 2007; Garnier et al., 2008). The hydrolysed species are more reactive, and can be readily oxidised to Cr(VI) oxyanions. In soils Cr(III) oxidation is catalysed by Mn-oxides, which act as an electron acceptor (Bartlett and James, 1979; Manceau et al., 1992; Fendorf, 1995; Oze et al., 2007). The resulting Cr(VI) pool is enriched in the heavy  $^{53}\text{Cr}$  isotope (Zink et al., 2010; Frei et al., 2014). Cr(VI) is highly soluble and is released to soil pore waters, although it can be partially retained in the soil by adsorption and/or back-reduction to insoluble Cr(III). Retention of Cr(VI) by adsorption to Fe/Al hydrous oxides (Zachara et al., 1989; Manceau et al., 1992; Fendorf, 1995) can result in discrete enriched horizons within weathering profiles (Frei et al., 2014). Common Cr(VI) reducers include dissolved ferrous iron (Ellis et al., 2002; Døssing et al., 2011), organic substances (Kitchen et al., 2012) and biological reducers (Sikora et al., 2008; Basu et al., 2014). Back-reduction reactions further enrich Cr(VI) in the heavy isotopes (Ellis et al., 2002; Sikora et al., 2008; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012). Isotopically heavy Cr(VI) in pore water can be lost to local runoff leaving behind an isotopically light Cr pool in the residual soils (Berger and Frei, 2014; Frei et al., 2014).

Once Cr(VI) oxyanions are liberated to local stream and river waters, two processes (adsorption and reduction),

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