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A combined Y/Ho, high field strength element (HFSE) and Nd isotope perspective on basalt weathering, Deccan Traps, India

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High-precision high field strength element (HFSE: Zr, Hf, Nb, Ta, Th, U, W, Mo), Y/Ho, and Nd isotope chemostratigraphy of two contrasting Deccan Traps weathering profiles – an ancient, deeply weathered laterite, and a younger (Quaternary), more moderately weathered saprolite – are used to reconstruct different aspects of basalt weathering. Precision of the HFSE analyses is demonstrated through a report of the long-term concentrations and ratios determined in United States Geological Survey (USGS) and Geological Survey of Japan (GSJ) basalt rock standards (BHVO-1, BHVO-2, BIR-1, BCR-2, JB-2).

The oxyanion-forming members (U, Mo, W) are the most mobile of the considered HFSE group. Extreme loss of W, far exceeding those of U and Mo during certain stages of basalt alteration, is first reported here. The ability to strongly fractionate Mo and W during weathering may contribute to solving the unresolved mass imbalance between the crustal and marine inventories of W. By contrast, Zr, Hf, Nb, and Ta preserve the ratios of the parent basalt in the profiles due to their limited mobility; these are therefore of great potential value in reconstructing basalt flow stratigraphy and correlating lava flows in weathered flood basalt provinces. Of the HFSE, Th is not a good choice as a conservative element because it is strongly susceptible to addition of aeolian dust; this is evidenced by strong excursions in Th/Nb that are correlatable with alkali element enrichment and less radiogenic $^{143}Nd/^{144}Nd$ ratios.

The chemical fingerprints of dust were identified in a paleo-flow top of the saprolite profile, suggesting that dust accumulation occurred during periods of quiescence between basaltic eruptions. During protracted exposure and laterite development, the magnitude to which dust overprints the basalt chemistry increases substantially as evident from much less radiogenic Nd isotope ratios and higher Th/Nb ratios in the Bidar profile relative to the protolith basalt. Attempts at quantifying the magnitude of dust accumulation in the laterite based on Th enrichment indicate a mass fraction of greater than 0.5 when the dust is assumed to have the chemistry of average upper continental crust. Although mixing models between the basalt and assumed dust composition cannot unambiguously constrain the dust source, the Nd isotope mixture preserved in the laterite points to a relatively young crustal dust source (e.g., similar to loess in composition) rather than the Precambrian shield rocks in the vicinity of the Deccan Traps. The contrasting topologies of dust-derived Nd and dust-derived Th in the laterite appears to record both physical transport of dust (Th) through permeable laterite horizons as well as transport by chemical dissolution and precipitation (Nd) at an inferred paleo-water table and in deep saprolite zones.

Yttrium and Ho fractionate substantially during all observed stages of weathering, with Y/Ho ratios ranging from 26.5 to 21.9 in the moderately weathered saprolite profile and from 30.2 to 14.7 in the laterite profile. The single strongly superchondritic Y/Ho ratio of 30.2 in the laterite is restricted to a sample at depth, and appears to fingerprint the deposition of REE derived from dissolution higher in the profile. Decrease in the Y/Ho ratio relative to the protolith basalt (24.4–24.7) in both profiles inversely correlates with chemical weathering indices, and suggests that Y/Ho ratios have significant potential as a silicate weathering proxy. Consequently, suspended vs. dissolved river loads may record the differing behaviour of these elements during weathering.

1. Introduction

Weathering of large continental flood basalt provinces (CFBPs) represents a major sink of atmospheric carbon dioxide (Louvat and Allègre, 1997, 1998), and their long-term weathering plays an important part of

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the geochemical cycle of many other elements (e.g., Dessert et al., 2001, 2003). The contribution of basaltic rocks to the continental weathering flux is known to have fundamentally affected ocean chemistry because the geologically rapid (~1–4 Myr) emplacement and associated subaerial alteration and erosion of CFBPs such as the Deccan Traps (67–64 Ma) can be readily identified in the marine Sr and Os isotope record (e.g., Vonhof and Smit, 1997; Ravizza and Peucker-Ehrenbrink, 2003). However, such well-documented signatures serve to highlight a need to better constrain the proportion of elements delivered from these basaltic terrains, and to determine the relative contributions of the processes that release them.

Detailed geochemical investigation is crucial to understanding the modern and ancient development and evolution of the 'critical zone' — the complex, near surface environment in which rock, soil, water, air, and living organisms interact (e.g., Brantley and Lebedeva, 2011). One of the major, yet still poorly understood, processes in the geochemical evolution of the critical zone, is the accumulation and downward migration of aeolian dust. The strongest evidence for this comes from the presence of "foreign" minerals (e.g., Rex et al., 1969; Jackson et al., 1972; Kurtz et al., 2001) in the profile and isotopic compositions (e.g., Nd, Hf, Sr, or Li isotopes) that are outside the limits achievable from simple alteration of the parent rock (Borg and Banner, 1996; Kurtz et al., 2001; Kisakürek et al., 2004; Viers and Wasserburg, 2004; Pett-Ridge et al., 2009; Liu et al., 2013). Although this allochthonous input introduces an obvious complication to chemical mass balance determinations, it is becoming increasingly apparent that dust plays an important role in the long-term evolution of weathering profiles through resupplying nutrients and altering the chemical signature of the weathering flux. Assessing the dust contribution in weathering profiles thus has the potential to help reconstruct the exposure history of landmasses and provide insight into certain paleoclimatic conditions (e.g., Brimhall et al., 1988; Chadwick et al., 1999; Vitousek, 2004).

It is generally accepted that the isotopic ratios of elements with relatively high atomic numbers, such as those of Hf and Nd (e.g. $^{143}Nd/^{144}Nd$) are not significantly fractionated by incongruent weathering (cf. Ma et al., 2010). It is for this reason that radiogenic isotope ratio variations can be used to quantify, through end-member mixing models, the mass balance between indigenous material and foreign matter such as dust in weathering profiles if they differ in chemical composition (e.g., Borg and Banner, 1996; Kurtz et al., 2001; Viers and Wasserburg, 2004). In this regard, the strongly contrasting chemistry of depleted mantle-derived basalt from that of the average upper continental crust, a typical approximation of dust, makes basalt weathering profiles an ideal substrate to fingerprint aeolian dust accumulation.

In this study, a selection of the high field strength elements (HFSE; Nb, Ta, Zr, Hf, Th, U, W, Mo, Y, Ho), those with a high charge to mass ratio, is combined with Nd isotopes to address different aspects of basalt weathering profile evolution. Analysis is performed on two profiles from the Deccan Traps, India: the deep, Paleogene Bidar laterite and a sub-Recent (Quaternary) profile near Chhindwara that spans incipient to intermediate stages of weathering. The geology and preparatory geochemical studies of the profiles have been reported previously (Kisakürek et al., 2004; Wimpenny et al., 2008; Babechuk et al., 2014). The aim of the study is to address three central topics related to the critical zone:

1) The first pre-requisite in geochemical studies of weathering is identifying the least mobile elements during the alteration of the parent rock. The HFSE (Zr–Hf–Nb–Ta–Th) are typically hosted in weathering-resistant minerals (e.g., Fe–Ti oxides) and exhibit generally limited solubility, apart from those that can form more soluble oxyanions (U, W, Mo). For this reason, the HFSE are often assumed to be immobile, yet this is not always the case, and they may additionally be modified by dust (e.g., Kurtz et al., 2000). In this study, ratios of the HFSE in the basalt profiles are used to assess which elements are least mobile and least influenced by dust. These elements are then used to investigate certain aspects of the pre-weathering characteristics of the basalt protolith, including fingerprinting variations in HFSE chemistry of adjacent flows and the use of HFSE in correlating flow units in lateritised regions. Next, since little is known about bedrock weathering of W and Mo, the comparative mobility of U, Mo, and W is considered. The importance of constraining their weathering behaviour is discussed in the context of their flux from the crust, both at present and in deep geological time, since both elements have importance serving a bioessential function as metal cofactors.
2) Previous studies of the Bidar laterite presented tentative geochemical evidence for dust addition to the Deccan Traps region (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2008), which is further explored in this study with more sensitive and conclusive geochemical fingerprints in the form of Nd isotopes and element Th–U–Nb–Nd systematics of the profile. An attempt is made to further resolve the magnitude of dust accumulation and the post-addition redistribution of the dust-derived components during protracted evolution of the weathering profile, which is of relevance to reconstructing the exposure and uplift history of the Deccan Volcanic Province. New evidence for dust addition during the periods of quiescence between volcanic eruptions during Deccan Traps emplacement, prior to the extended period of lateritisation, is also provided. This has significance when assessing total eruptive duration for the Deccan episode (Chenet et al., 2008).
3) The final aim of this study is to explore the weathering-related fractionation of the geochemical twin elements Y and Ho (Babechuk et al., 2012; Thompson et al., 2013). The contrasting alteration history of the geochemically similar parent basalt of the two profiles allows an evaluation of the degree of Y/Ho fractionation across a wide range of weathering conditions, and this preliminary work indicates that the this ratio has potential as a novel tracer of weathering intensity. Weathering-induced changes of Y/Ho from parent rock ratios are predicted to result in observable fractionation in derived sediments and riverine waters; this is briefly explored using a pre-existing data set of dissolved rare earth elements and yttrium (REE + Y) from rivers in eastern Australia (Lawrence et al., 2006a,b).

From a broader perspective, this study contributes to the understanding of the geochemical evolution of basaltic weathering profiles, which is relevant to reconstructing how basalt weathering has influenced ancient Earth systems. More broadly still, it may also provide a context for better understanding basalt alteration behaviour on the Martian surface (Morris et al., 2006). Further, this study also adds to mounting evidence that dust addition to weathering profiles, although most easily fingerprinted in basaltic environments, is a fundamental process in shaping the geochemistry of the critical zone and is thus of essential consideration with regards to modelling mass balance and nutrient availability.

2. Methods

2.1. High-precision trace element analysis

Trace element analysis was performed at Laurentian University, Canada, via solution quadrupole ICP-MS (SQ-ICP-MS) measurement with an XSeriesII as described below and in Babechuk et al. (2014). For sample digestion, 100 mg of sample powder was transferred into Savillex® beakers into which a HF–HNO_3 (4:1) mixture was added. The beakers were left sealed on a hotplate at 160 °C for 72 h and agitated at least once every 24 h. The residue was evaporated and the resulting fluorides were attacked with 6 N HCl (twice using 0.5 mL) and converted to nitrates using concentrated HNO_3 (twice using 1 mL) with evaporation to dryness between and following each step. The ensuing nitrate residue was dissolved in a final 10 g 20% HNO_3 stock solution. Inspection