



# Silicon and chromium stable isotopic systematics during basalt weathering and lateritisation: A comparison of variably weathered basalt profiles in the Deccan Traps, India



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## ABSTRACT

Global biomass production is fundamentally affected by the hydrological cycling of elements at the Earth's surface. Continental weathering processes are the major source for most bio-essential elements in marine environments and therefore affect primary productivity. In addition, critical zone biomass depends on energy and chemical exchange reactions in weathering profiles. The latter reservoirs are in turn influenced by different climatic conditions that control weathering and pore water parameters like pH and Eh, which regulate mineral break down rates and dictate the mobility and mass flux of elements.

Two Deccan Traps basalt weathering profiles of contrasting age and alteration intensity provide a natural laboratory for investigating the effects of rock alteration on Si and Cr and their isotopic systematics. The Quaternary Chhindwara profile has progressed to a moderate degree of alteration (saprolite), while the Paleogene Bidar example displays an extremely altered laterite. The Chhindwara saprolite profile shows a near uniform Cr and Si concentration and isotopic composition, whereas the Bidar laterite profile is characterised by an intense loss of Si, a large enrichment of Cr within the most altered uppermost levels, and a wide range of Cr stable isotope ratios ( $-0.85$  to  $0.36\text{‰}$   $\delta^{53/52}\text{Cr}$ ). A co-variation between Si and Cr isotopes, as well as their co-variation with iron content, provides empirical evidence that iron redistribution within the profile has a large effect on Cr mobility and Si isotopic fractionation. Therefore, it is concluded that iron oxides exert a primary control over the isotopic composition of both Cr and Si in pore waters of laterites.

Since laterite formation is promoted by tropical climates, the results of this study provide new evidence to suggest that the hydrological Cr and Si fluxes originating from continental weathering have changed in accordance with large-scale, deep time climate variation and continental plate configuration. An increased flux of Si and greater magnitude of Cr mobility and isotopic fractionation are possibly amplified under  $\text{CO}_2$ -rich, greenhouse episodes and/or when large landmasses were tectonically arranged at near equatorial latitudes.

## 1. Introduction

Dissolved silicon (Si) and chromium (Cr) of the modern oceans are supplied primarily by their release during continental weathering of silicate rocks (Reinhard et al., 2013; Tréguer and De La Rocha, 2013). The initial isotopic composition of soluble Cr supplied to the oceans is thought to be dominated by Cr(VI), which itself is released from soils as a result of Cr(III) oxidation reactions catalysed on Mn oxide surfaces (Cranston and Murray, 1980; Ellis et al., 2002; Zink et al., 2010).

Oxidative weathering reactions are therefore necessary to transform particle reactive Cr(III) within crustal rocks to more soluble Cr(VI). Furthermore, oxidation processes coupled with partial back reduction of aqueous Cr(VI) to Cr(III) by ferrous iron or organic matter (Døssing et al., 2011) are likely to leave an isotopic fingerprint in weathering profiles (D'Arcy et al., 2016; Frei and Polat, 2013). The dissolved Cr isotope and speciation signatures in the hydrosphere are therefore interpreted to be controlled initially by the redox state and biogeochemical conditions of the weathered rocks (D'Arcy et al., 2016). The

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weathering of primary minerals containing Cr(III) (silicates, oxides; e.g., pyroxene, magnetite) and the oxidative transformation of liberated Fe results in pedogenic Fe(III)-(oxyhydr)oxides. These pedogenic Fe(III) minerals become influential as scavengers for numerous particle reactive aqueous metals/metal complexes, including those of Cr(III) and Cr(VI), such that the Cr budget and isotope systematics could be predicted to be coupled to iron behaviour within weathering profiles (Zhong et al., 2015; Schwertmann and Pfab, 1996). Thus, in addition to the direct redox influence of Mn-oxides in forming Cr(VI), Fe-oxides are an integral part of the Cr weathering cycle. On a global scale, climatic conditions are likely to have exerted a large influence on the dissolved Cr isotopic composition over geological time when enhanced silicate weathering overlapped with highly oxidative conditions. To date, several studies have started to shape the basis of Cr isotopic systematics in ancient marine and continental deposits serving as a paleo-environmental redox proxy (e.g., Crowe et al., 2013; Frei et al., 2016; Frei et al., 2009; Scheiderich et al., 2015; Holmden et al., 2016).

Unlike Cr, aqueous Si mobility is not a direct function of redox state but released, predominantly as silicic acid, during the dissolution of silicate minerals. Chemical weathering releases isotopically heavy Si into solution due to preferential adsorption of isotopically light Si on neo-formed secondary phases such as Al and Fe oxides (Delstanche et al., 2009; Oelze et al., 2015; Oelze et al., 2014). Both the kinetic sorption and incorporation of the lighter Si isotopes into secondary formed oxides, as well as biological utilisation of isotopically lighter Si, drive aqueous Si towards heavier isotope compositions (Qin and Wang, 2017; Oelze et al., 2014). Thus, apart from biological Si utilisation, the Si isotopic variability of surface waters is controlled by mineralogy, weathering kinetics, and pore water variables like pH and Eh (Cardinal et al., 2010; Ding et al., 2004; Ding et al., 2011; Georg et al., 2006; Georg et al., 2007). Accordingly, like Cr, the mobility and mineralogy of Fe within a weathering profile might also exert an influence on the isotopic composition of the dissolved Si pool. Here, the effects of iron mobility and oxidation might be of particular interest since experiments conducted upon natural soil samples have demonstrated the adsorption of isotopically light Si on Fe-oxides (Opfergelt et al., 2009). Importantly, an unusually light Si isotopic composition of  $+0.02 \pm 0.15\% \delta^{30/28}\text{Si}_{\text{NBS28}}$  was found in organic-rich river waters of the Congo Basin draining a lateritic catchment that has developed under prevailing tropical climate conditions (Cardinal et al., 2010). These examples highlight a need to further examine Si isotopic fractionation in lateritic profiles, since documentation of the Si isotope distribution within these environments and its influence on the Si isotopic composition of the riverine flux remains sparse.

To date, no studies exist that document coupled isotopic fractionation and cycling of Si and Cr within the terrestrial realm. Although Si and Cr do have different physical and chemical properties, both elements share isotopic reservoir characteristics (Poitrasson, 2017; Qin and Wang, 2017) in terms of their limited isotopic variation within magmatic rocks and heavy average river and seawater isotopic compositions (Poitrasson, 2017; Savage et al., 2010; Savage et al., 2013; Scheiderich et al., 2015; Schoenberg et al., 2008). Further, the mobility, concentration, and isotopic composition of both elements in meteoric waters appear to respond to adsorption onto mineral surfaces and pore water Eh-pH conditions (Babechuk et al., 2017; Bern et al., 2010; Cardinal et al., 2010; Chemtob et al., 2015; D'Arcy et al., 2016; Delstanche et al., 2009; Farkaš et al., 2013; Frei et al., 2014; Opfergelt et al., 2009; Paulukat et al., 2015; Ziegler et al., 2005a; Ziegler et al., 2005b). The relative impact of each of these processes on Si and Cr isotopic signatures are likely to vary within different weathering regimes (e.g., desilication favoured under acidic conditions, and Cr being both acid soluble and redox-sensitive). Accordingly, it may potentially become possible to distinguish reactions and transportation processes using combined data from the two isotopic systems.

Our study investigates the Si and Cr isotope composition of two well-documented basaltic weathering profiles in the Deccan Traps

(India); these being the Paleogene Bidar laterite and the Quaternary Chhindwara saprolite (Babechuk et al., 2014). Both profiles have developed at different times, under different climatic conditions and exposure times, and thus represent a range of alteration intensities. The Si and Cr isotopic signatures of both profiles are compared to investigate conditions within the profiles that led to the greatest Cr and Si release and accompanying isotopic fractionation. Notably, the Paleogene lateritic profile represents an end-member of chemical weathering where the coupled loss of Si and enrichment of Fe becomes extreme.

The element and isotopic geochemistry of samples from both profiles have been investigated in previous studies in great detail (Babechuk et al., 2014; Babechuk et al., 2015; Kısakürek et al., 2004; Widdowson, 2008; Wimpenny et al., 2007) and thus provide a foundation to understand the chemical weathering evolution that can be linked to changing Si and Cr isotopic signatures. The Cr isotope geochemistry of the Bidar profile are the first reported values from a deeply weathered Paleogene laterite profile.

## 2. Geological setting and sample material

The Deccan Volcanic Province (DVP), located in western to central India (Fig. 1), is one of the largest flood-basalt provinces on Earth. Emplacement of basaltic lava flows took place between ~67 and 63 Ma (Jay et al., 2009; Venkatesan et al., 1993; Widdowson et al., 2000), and thus volcanism occurred before, during, and after the Cretaceous-Paleocene (K-Pg) mass extinction event (Chenet et al., 2007; Courtillot et al., 1986; Duncan and Pyle, 1988; Kelley, 2007), with the majority of flows and the largest volume being erupted during a very brief period c. 65–66 Ma (Chenet et al., 2009; Chenet et al., 2007; Renne et al., 2013 and references therein). The basaltic units presently cover c. 500,000 km<sup>2</sup> of peninsular India (Fig. 1), and represent the eroded remnants of an original area of > 10<sup>6</sup> km<sup>2</sup>, including parts that rifted away and located now under the Indian Ocean, thus yielding a total original volume of ~1.3 million km<sup>3</sup> (Jay and Widdowson, 2008).

Since eruption, a long history of equatorial to sub-equatorial weathering conditions and development of the monsoonal climate led to the development of deep weathering profiles characterised by extreme alteration and the development of a widespread regional laterite between 65 and 40 Ma (Bonnet et al., 2016; Kısakürek et al., 2004). Continued, northward movement of the Indian plate and uplift of the Deccan province caused rejuvenation of fluvial erosion of the deeply weathered lava surface, and widespread abandonment of the established paleo water-table. This led to a decrease in chemical weathering intensities and physical erosion (Widdowson and Cox, 1996). During the Neogene further increase of physical erosion due to the monsoon-influence extensively eroded the old lateritic profiles and excavated unweathered basalt surfaces which, themselves, then provided a substrate for the formation of Quaternary weathering profiles. These neo-formed profiles display considerably less intense chemical weathering alteration (Babechuk et al., 2014).

Therefore, the two DVP weathering profiles chosen for investigation of Cr and Si fractionation in this study are chronologically separate, represent differing climatic weathering regimes and associated degrees of alteration.

### 2.1. Chhindwara profile

The Chhindwara samples were taken from a 6 m deep, saprolite-dominated profile exposed in a quarry (22°04.213' N, 79°01.393' E) situated on a basaltic plateau (600–750 m elevation) in the Chhindwara District of the Madhya Pradesh state (Babechuk et al., 2014). The weathering profile spans across two separate lava flows clearly identifiable by a sharp colour (rust red/brown to greenish grey) and textural boundary where relict volcanic textures, such as flow banding and flow-top breccia, are still recognisable (Fig. 2a, b). The uppermost, rust red/brown flow is fully exposed and capped by a thin, modern, soil veneer.

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