

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, these then regulate mineral break down rates that dictate the mobility and mass flux of elements.

Two Deccan Trap 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 sub-recent Chhindwara profile has progressed to a moderate degree of alteration (saprolite), whilst the Paleogene Bidar example displays an extremely altered laterite. The Chhindwara profile shows a near uniform Cr and Si concentration and isotopic composition, whereas the Bidar 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 ‰ $\delta^{53/52}\text{Cr}$). 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. 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.

Because 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 CO₂-rich, greenhouse episodes and/or when large landmasses were tectonically arranged at near equatorial latitudes.

Keywords: *laterite; saprolite; weathering; silicon isotopes; chromium isotopes*

1. Introduction

Dissolved silicon (Si) and chromium (Cr) of the modern oceans are supplied primarily by the release during continental weathering of silicate rocks (Reinhard et al., 2013; Tréguer and 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 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, 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 into 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 et al., 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 of 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 sub-Recent 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 (**Figure 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 km² of peninsular India (**Figure 1**), and represent the eroded remnants of an original area of > 10⁶ km², including parts that rifted away and now under the Indian Ocean, thus yielding a total original volume of ~ 1.3 million km³ (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 degree 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 (**Figure 2a,b**). The uppermost, rust red/brown flow is fully exposed and capped by a thin, modern, soil veneer. By contrast, the lower greenish-grey flow was incompletely exposed at the time of sampling and offering samples from only the upper 2.2 m of this flow; thus this profile does not reach unaltered bedrock. It is unclear whether the colour difference between both flows reflects an earlier weathering episode during volcanic quiescence prior to the eruption of the upper flow. The drab colour of the lower flow is presumably the result of higher abundance of pedogenic clays and zeolite minerals and the volcanic textures of the flow; vesicularity, represented by amygdules partly filled by zeolite minerals, increases upwards in the exposed section of the lower flow towards the highly brecciated and vesicular flow-top. By contrast, the upper flow protolith was a more massive and homogeneous basalt flow, and the saprolite is instead dominated by spheroidal weathering textures bearing a wide range in corestone size and alteration intensity. The lower 80 cm of this flow was weakly banded and finer-grained upon emplacement and is more weathered than the overlying saprolite in the centre of the flow. The upper 20 cm of the flow consists of a thin, highly altered soil horizon. The clay mineralogy is relatively consistent throughout the lower flow with a greater alteration of primary basalt textures, indicative of a higher weathering intensity compared to the upper flow. The protolith composition of both flows is represented by the centre area of a large corestone extracted from the upper flow, displaying essentially pristine volcanic mineralogy and texture (sample ChQB12). The detailed major and trace element composition of 27 samples, covering a depth of 6 m across the weathering progression in both flows, are described in detail elsewhere (Babechuk et al., 2014; Babechuk et al., 2015).

2.2 Bidar lateritic profile

The Bidar samples (BB 1 – 9) were taken from a deep, lateritic weathering profile (ca. 50 m depth) located in central India near the hill top city of Bidar (17°54.87' N, 77°32.39' E), in the north-eastern part of Karnataka state in south-central India. This locality has historic precedent since it was here that studies of laterite-capped plateaux prompted Newbold (1846) to suggest that laterite developed as an *in situ* weathering product through the segregation and subsequent rearrangement of minerals and elements that originally comprised the parent rock. The nine samples of the profile have provided the focus for several key studies; the detail of their elemental and isotopic characteristics may be found elsewhere (Babechuk et al., 2014; Babechuk et al., 2015; Kısakürek et al., 2004; Widdowson, 2008; Wimpenny et al., 2007)

This profile developed on the last major DVP basalt package (i.e., Ambenali formation) to be emplaced in the eastern Deccan region (Jay and Widdowson, 2008), and thus marks the most topographically elevated lava sequence. The profile displays an upwardly increasing alteration progression, whereby unweathered basalt gradationally transitions into corestone-rich saprolite and further through individual lateritised horizons that are capped with an indurated Fe-crust. The indurated laterite cap is characterised by a 'tubular' (vermiform) fabric (Babechuk et al., 2014; Widdowson, 2008) (**Figure 3 a,b**). Along this weathering progression, primary silicates are progressively replaced by pedogenic sesquioxides, initially as pseudomorphs, and with a mineralogy dominated by kaolinite and goethite. Beyond this stage in the upward alteration progression the primary igneous texture is lost, and sesquioxides of Fe and Al begin to predominate with Fe-mottling and micro-aggregation textures that finally gives way to the capping Fe crust that is dominated by interlocking Fe and Al sesquioxides with no remaining phyllosilicates. The corresponding major element chemistry of this alteration progression is characterised by an upward loss of Si and Al relative to Fe, which is typical for *in situ* lateritisation (Schellmann, 1986). Departure from this progression is only observed at the location of a paleo-water table at a depth in the profile between ~ 15 and 10m, where Fe

abundances are stratigraphically higher than above and below as a result of enhanced, laterally driven Fe (and other metal) deposition (Widdowson, 2008).

3. Analytical Methods

3.1 Silicon isotope analysis

The bulk rock sample powders of the Bidar profile were prepared using a tungsten carbide mill, whereas the Chhindwara powders were prepared in an agate mill. Previous studies have demonstrated previously that the employment of an agate mill causes no resolvable Si isotopic contamination (Savage et al., 2011; Zambardi and Poitrasson, 2011). Splits of all 9 Bidar profile and 15 Chhindwara profile sample powders were selected for Si isotope composition.

Sample decomposition and Si purification procedures followed the general method described in van den Boorn et al., 2006; Wille et al., 2010. Briefly, 1-2 mg of homogenised sample powder was digested using 2 M sodium hydroxide produced from sodium hydroxide monohydrate (Fluka, TraceSelect) in Berghof DAB-3 high pressure digestion vessels. The solid residue was separated from the NaOH supernatant and decomposed with concentrated aqua regia. After complete sample digestion, supernatant was evaporated and re-dissolved in 0.25 ml of 0.25 M HNO₃. To purify Si from major cations, HNO₃ and NaOH supernatant was passed through 0.5 ml of cation exchange resin (Dowex AG-X8, 100-200 mesh, Bio-Rad) Subsequently, HNO₃ was added to the eluted Si-bearing solution in order to attain ~2 ppm Si in a 1% (v/v) HNO₃ solution. Silicon isotopes were determined by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Neptune Plus, ThermoFisher Scientific) at the Isotope Geochemistry Lab, Department of Geosciences, University of Tübingen. Measurements were performed in medium resolution and dry plasma mode using the ESI Apex Q desolvating system. A sapphire injector was used to direct sample aerosol into the Ar-plasma. Data acquisition and reduction were carried out using a standard bracketing technique (Albarede et

al., 2004). All values are reported relative to the silicon isotope reference standard NBS-28 reported in delta (δ) notation in ‰ units: $\delta^{30/28}\text{Si} = [({}^{30}\text{Si}/{}^{28}\text{Si}_{\text{sample}})/({}^{30}\text{Si}/{}^{28}\text{Si}_{\text{NBS-28}}) - 1] \times 1000$. The isotopic difference between two Si reservoirs A and B are expressed as $\Delta^{30/28}\text{Si}_{\text{A-B}} = \delta^{30/28}\text{Si}_{\text{A}} - \delta^{30/28}\text{Si}_{\text{B}}$. Repeated decomposition and measurement of an in-house homogenised sponge material SP150 (n=10) (Wille et al., 2010) and Herkimer “diamond” quartz (n=13) (Douthitt, 1982) yielded a 2SD reproducibility of $\delta^{30/28}\text{Si}_{\text{NBS28}}$ of ± 0.12 ‰ which is used for error bars in illustrated figures. Further details of the Si isotopic methods can be found in the Supplementary Material.

3.2 Chromium isotope analysis

Splits of all 9 Bidar profile and 16 Chhindwara profile sample powders were selected for stable Cr isotope analysis. Based on the previously determined Cr concentration (Babechuk et al., 2015), a mass of powder sufficient to yield at least 500 ng of Cr for isotopic measurement was weighed and transferred into a Savillex PFA Teflon beaker. The sample powder was then tagged with a Cr double spike enriched in isotopes ${}^{50}\text{Cr}$ and ${}^{54}\text{Cr}$ to yield a 1:1 sample:spike Cr abundance ratio. Sample digestion and spike-sample homogenisation was achieved by the successive addition of a concentrated HF/HNO₃ and 6 M HCl. Decomposed sample matrix was re-dissolved in 1 ml 6 M HCl in preparation for chromatographic Cr separation. The purification of Cr from matrix elements was achieved with one of two protocols. The first protocol is described in detail by Schoenberg et al. (2008) and involves a liquid-liquid extraction followed by an anion resin (Biorad Dowex© AG1-X8, 100-200 mesh) exchange chemistry. The second recipe is described in detail by Schoenberg et al. (2016) and involves a three-step chromatography using an anion resin (Biorad Dowex© AG1-X8, 100-200 mesh) and two cation resin (Biorad Dowex© AG50W-X8, 200-400 mesh) steps. Samples processed using both chemistries have been shown to produce matching Cr isotope ratios (Babechuk et al., 2017; Schoenberg et al., 2016). In preparation for Cr isotope analysis, all purified samples were dissolved in 0.15 M HNO₃ to produce a matched measurement concentration of ~ 150 ng g⁻¹. The Cr isotope analyses were performed over three analytical sessions on a ThermoFisher

Scientific NeptunePlus MC-ICP-MS in the Isotope Geochemistry Lab, Department of Geosciences, University of Tübingen. The MC-ICP-MS was operated in medium resolution mode using an Aridus II desolvating system to generate dry plasma conditions. The double spike-deconvoluted $^{53}\text{Cr}/^{52}\text{Cr}$ ratios of the experiment session were normalised to the mean of this ratio measured for the SRM979 standard and reported in delta (δ) notation ‰ units, consistent with other studies, as: $\delta^{53/52}\text{Cr} = [({}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{sample}})/({}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{SRM979}}) - 1] \times 1000$. The reproducibility of $\delta^{53/52}\text{Cr}$ in natural samples is conservatively estimated at 0.05 ‰ (Schoenberg et al., 2008), which is the error value used in all data plots unless the internal standard error of an individual sample measurement exceeded this value. Further details of the Cr isotopic methods can be found in the Supplementary Material.

3.3 Weathering progression and elemental characteristics of the profiles

To express the magnitude of alteration of samples in each profile, relatively immobile major elements (i.e., Al and Ti) are used to track the loss of highly mobile elements (e.g. Ca, Mg, Na, K, Mg). Specifically, the chemical index of alteration, CIA (Fedo et al., 1995), the mafic index of alteration, MIA, and the index of lateritisation, IOL (Babechuk et al., 2014; Schellmann, 1986) are employed. Further details of these major element trends were reported for both profiles previously in Babechuk et al. (2014). Losses and gains of other elements not included in the weathering indices are calculated individually by normalising to concentrations of the immobile element Ti assuming minimal allochthonous Ti addition (see supplemental material).

4. Results

4.1 Cr and Si isotope composition

The first key observation is that the difference in major and trace element behaviour of both weathering profiles are similarly expressed in their Cr and Si isotopic variability. Therefore, we next consider first the broad isotopic composition of the analysed samples and their comparison with published ranges, and secondly discuss the observed variation within each profile.

Considering the data from both profiles, the overall Si isotopic range is 1.25 ‰ $\Delta^{30/28}\text{Si}$ (-0.04 to -1.29 ‰ in $\delta^{30/28}\text{Si}_{\text{NBS28}}$), which is relatively small compared to the overall published Si isotopic range of soils and clay minerals formed during weathering (up to 3 ‰ $\Delta^{30/28}\text{Si}$) (Douthitt, 1982; Opfergelt and Delmelle, 2012; Ziegler et al., 2005b). However, this measured isotopic range exceeds that reported for unweathered mafic rocks (Savage et al., 2010). In addition, the Si isotopic variability within the sample set of both weathering profiles is significantly larger than that of the Si isotopic range defined by the two protolith Deccan Traps basalt samples (BB-1 -0.18 ‰ $\delta^{30/28}\text{Si}_{\text{NBS28}}$ and ChQB-12 -0.12 ‰ $\delta^{30/28}\text{Si}_{\text{NBS28}}$) even after considering Si isotopic experimental reproducibility of ± 0.12 ‰ in $\delta^{30/28}\text{Si}$ (**Figure 2b, 3b, Table 1**). The Cr isotopic variability of 1.21 ‰ $\Delta^{53/52}\text{Cr}$ (0.36 to -0.85 ‰ $\delta^{53/52}\text{Cr}_{\text{NBS97}}$) of both profiles is larger than that reported for magmatic rocks (Schoenberg et al., 2008), $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ of -0.12 ± 0.10 (2 SD), and in the range of previously reported weathering profiles and paleosols ($\delta^{53/52}\text{Cr}_{\text{NBS979}}$ of -1.29 to +2.38 ‰) (Babechuk et al., 2017; Berger and Frei, 2014; Crowe et al., 2013; D’Arcy et al., 2016; Frei et al., 2014; Frei and Polat, 2013; Paulukat et al., 2015).

In the Chhindwara profile, the Si (-0.12 to -0.47 ‰ $\delta^{30/28}\text{Si}_{\text{NBS28}}$) and Cr (-0.01 to -0.19 ‰ $\delta^{53/52}\text{Cr}_{\text{NBS979}}$) isotopic variability is small, and for Si only slightly beyond that of unweathered mafic rocks (Savage et al., 2010). Low variability of $\delta^{30/28}\text{Si}_{\text{NBS28}}$ accord with Si/Ti which do not depart significantly from the that of the protolith, and indicate that weathering reactions and any concomitant clay mineral formation within the profile have let to only moderate amounts of Si mobilisation within the Chhindwara profile (**Figure 2b**). The low variability in $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ and Cr/Ti ratios is evidence for a conservative weathering behaviour of Cr within the Chhindwara Profile and demonstrate that even during weathering of pyroxenes, the primarily host for Cr (**Figure 4**), an insufficient amount of Cr is mobilised to imprint an isotopic shift within the weathered rock. However, a slight offset in $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ between upper (-0.15 ± 0.05 ‰ (2SD)) and lower (-0.06 ± 0.06 ‰ (2SD)) is visible.

The magnitude of the overall Cr and Si isotopic variability observed is much greater in the extensively weathered, Fe-oxide rich samples of the Bidar profile. This observation is

accompanied by the fact that Cr within the Bidar profile is enriched in areas where Fe concentrations are particularly high (e.g. within the nodular cap, **Figure 5a**; or within the paleo-water table, **Figure 5b**). This observation differs from the element distribution map of the unweathered basalt where regions of highest Fe concentrations do not contain the highest amount of Cr (**Figure 5c**). By contrast to Chhindwara, the Bidar profile shows a larger variability of Cr isotope ratios, with $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ ranging from +0.36 to -0.85 ‰, with increasing variability towards the top of the lateritic profile where higher Fe concentration and Si depletion is evident (**Figure 3a,b, Table 1**). In the saprolitic zone of the Bidar profile, samples BB-2 and BB-3 show an alteration intensity that is comparable to samples from the Chhindwara profile, with a limited range in $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ and slightly heavier isotopic composition compared to the protolith BB-1. These values still lie within the range of unaltered igneous rocks (Schoenberg et al., 2008). By contrast, samples BB-4 and BB-5 show lighter $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ down to -0.85 ‰ accompanied by increasing Fe concentration and Si loss, whereas at the paleo-water table, a shift to the highest Fe concentrations is accompanied by the heaviest $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ composition of +0.36 ‰. Above the paleo-water table the isotopic composition returns to ^{53}Cr -depletion (BB-7) and, in the uppermost and most Cr-enriched samples (BB-8 and BB-9), to values closer to the range of unaltered igneous rocks (**Figure 3b**).

5. Discussion

The major and trace element systematics of both profiles, and their relationship to the different weathering intensities and critical zone processes, have been described in earlier studies (Babechuk et al., 2014; Kısakürek et al., 2004; Wimpenny et al., 2007). Therefore, only those data pertinent to understand the new Si and Cr isotopic systematics are considered here. These together with the new Si and Cr isotope data are presented in **Table 1, Figure 2 a,b, Figure 3 a,b** for the Chhindwara and Bidar profiles, respectively.

5.1 Weathering progression and elemental characteristics of the profiles

The Chhindwara profile displays considerable variation in CIA values from 36 to 80, with the lowest values preserved in the centre of the upper flow between a depth of 90 to 310 cm. A gradual increase in CIA values to about ~70-80 occurs below a depth of 310 cm towards the contact zone between upper and lower flow. The two samples within and immediately below the soil surface of the upper flow also exhibit higher CIA values (57-58). Compared to these significant changes in the CIA, near-constant Fe/Ti ratios of 7.3 ± 1.2 (2SD) characterise the upper flow, with only a small change towards lower Fe/Ti ratios at the transition between the two flows (~16 % variability within 2SD range). This clearly demonstrates low mobility of iron throughout much of this profile (**Figure 2 a,b**) that is related to its progressive oxidation with increasing weathering intensity, which crosses the contact zone of both flows. The progression in oxidation, expressed as the Fe^{2+}/Fe_T ratio (where $Fe_T = Fe^{2+} + Fe^{3+}$) is discussed in detail in Babechuk et al. (2014). Accompanying this change in iron oxidation and CIA_T is also a loss of Si, with SiO₂ and Si/Ti ratios ranging from 48.7 wt % to 40.9 wt % and 17.0 to 9.4 (**Figure 2 a,b**). For most of the samples, and especially those of the lower flow, the SiO₂ abundances are lower than in the protolith basalt, as well as other basalts from the Chhindwara area (Ganguly et al., 2014). These trends are comparable to those documented in other kaolinised basalt weathering profiles elsewhere (Nesbitt et al., 1980). Nevertheless, since the Si/Ti ratios do not depart substantially from that of the protolith, weathering reactions within this profile (and concomitant clay mineral formation) can only be supplying low to moderate amounts of Si to rivers and oceans (**Figure 2b**). The variability in Cr/Ti ratios of the Chhindwara profile, encompassing the data from both flows is limited, ranging from 30.6 to 53.5, with a mean of 42.6 ± 11.5 (2SD) amounting to 27 % variability. However, unlike the Si/Ti and Fe/Ti ratios, there is no distinct offset in Cr/Ti ratio between the upper and lower flow, although the latter flow exhibits a larger degree of internal Cr/Ti variability.

The Bidar laterite profile is thicker and its upper levels significantly more altered. Here, the lowermost and least weathered samples, BB-2 and BB-3, are comparable in alteration intensity to that of the entire variation observed in the Chhindwara saprolite. Above these samples, alteration of much greater intensity is encountered. The mobile major cations are so heavily

depleted and the CIA become insensitive for accurately tracking the further stages of weathering intensity (Babechuk et al., 2014). Instead, the chemical changes are dominated by the loss of Al and Si relative to Fe and the weathering intensity is better represented with the 'index of lateritisation' (IOL), which ranges from 34.9 to 93.7 (Babechuk et al., 2014) (**Figure 3a**). Compared to the Chhindwara profile, much larger variability of 200 % and 217 % (2SD) in Cr/Ti and Fe/Ti ratios are found, which is expressed through an upward increase from 72 to 987 and from 5.3 to 71, respectively (**Table 1, Figure 3b**). Furthermore, increasing Cr/Ti ratios show a systematic coupling to increasing Fe/Ti ratios upwards in the profile (**Figure 3b, Figure 6a**) with the exception of the saprolitic section of the Bidar profile (between 13 to 35 m depth), where Cr/Ti and Fe/Ti ratios are lower than the protolith BB-1. While Cr/Ti and Fe/Ti ratios show a positive covariation, Si/Ti ratios steadily decreasing along the Bidar profile opposing the trend defined by Cr and Fe. SiO₂ concentrations and Si/Ti ratios range from 6.1 to 50.1 wt% and 17.7 to 3.4, respectively, with a Si/Ti variability of 118 % based on 2SD variability around the mean (**Figure 3a,b**).

5.2 Silicon isotopes

Quaternary age weathered volcanic ash displays isotopically light Si due to preferential adsorption on Fe-oxides (Opfergelt et al., 2009). The degree of weathering, as well as the abundance and mineralogy of the Fe-oxides, apparently exert control on the magnitude of isotopic fractionation (Opfergelt et al., 2009). Isotopically light Si compared to primary magmatic host rock is a typical signature of secondary aluminous clay minerals (Bern et al., 2010; Georg et al., 2006; Georg et al., 2007; Opfergelt and Delmelle, 2012; Ziegler et al., 2005b). The adsorption of Si from solution onto precipitated Al-hydroxides is associated with a large kinetic isotopic fractionation favouring the adsorption of isotopically light Si (Oelze et al., 2014; Ziegler et al., 2005a; Ziegler et al., 2005b). However, re-equilibration between adsorbed and dissolved Si occurs if the transformation from Al-hydroxides into minerals with higher degree of order does not proceed fast enough. In such a case, no significant $\Delta^{30/28}\text{Si}$ difference is expected between both Si reservoirs (Oelze et al., 2014). Therefore, re-

equilibration conditions may thus explain the relatively homogeneous Si isotopic composition of the Chhindwara profile where the Si isotopic composition broadly matches the range of unweathered basalts (Savage et al., 2010), although changing Si/Ti ratios indicate significant Si mobility and loss of primary Si especially from the lower flow that appears to be accompanied with the formation of kaolinite. However, the use of whole rock powders, rather than mineral separates, might add to the limited variance in Si isotopic values due to the superposition of primary and secondary Si isotopic signatures. A localised signature of isotopically light Si was measured near the transition between the upper and lower flows, coinciding with the higher abundance of pedogenic clays, zeolite minerals, and Fe-oxides. This shift towards lighter Si isotopic values at the contact zone might therefore record increased incorporation of isotopically light Si within secondary clay minerals caused by higher weathering kinetics at this contact zone and/or adsorption of dissolved isotopically light Si onto secondary Fe-oxides. Qualitatively, it is difficult to untangle which, if any, of the known Si isotopic fractionation mechanisms is exerting the dominant control on the storage of isotopically light Si in this zone. A weak negative co-variation between Si isotopes and Al_2O_3 content (as indicator for clay fraction), Mn/Ti and Fe^{2+}/Fe_T ratios (as indicators for pedogenic oxide formation) within the profile is insufficient to permit a clear distinction of mechanisms.

By contrast, the Bidar profile samples record a higher magnitude of Si isotope fractionation and there is strong evidence that the formation of Fe-oxides exerted the primary control on the Si isotopic composition, especially in the most aggressively altered laterite horizons. The increase of Fe coincides with a decrease in Si concentration leading to co-variation between Fe/Ti and Si/Ti ratios (**Figure 6b**). Therefore, the extreme decrease in SiO_2 content down to 6 wt. % in samples BB-6 to BB-9 was caused by a combination of Si loss and Fe oxide precipitation, whereas Si concentration and Si/Ti ratios within samples BB-3 to BB-5 are controlled by Si loss (**Figure 6b**) without accompanying precipitation of Fe-oxides. Although the formation of abundant Fe-oxyhydroxides within samples BB-6 to BB-9 is not accompanied by an observable Si gain, the adsorption of isotopically light Si on the Fe-oxyhydroxides likely overwhelmed the Si signatures of secondary clay minerals and remnant primary silicates. This

is shown by a significant co-variation between Fe/Ti and $\delta^{30/28}\text{Si}_{\text{NBS28}}$ in these sections (**Figure 6c**). In the less altered horizons of the profile (between 35 and 15 m in depth; BB-2 to BB-5), phyllosilicates dominate the neo-formed pedogenic mineralogy, but only BB-3 shows a distinct light Si isotopic composition relative to the unweathered basalt, whereas BB-2 and BB-4 are, within error, identical to BB-1. Similar to the low Si isotopic variability of the Chhindwara profile, $\delta^{30/28}\text{Si}_{\text{NBS28}}$ signatures of samples BB-4 and BB-5 are not very different from the unweathered protolith BB-1, despite showing a high loss of Si and high degree of kaolinisation. Similar to the Chhindwara profile, equilibrium conditions between the Si dissolved in pore water and Si adsorbed on Al-hydroxides (Oelze et al., 2014) might explain these unfractionated Si signatures. Superimposed on this, the contribution of primary, unweathered silicates could have also shifted Si isotopic values of BB-4 and BB-5 closer to BB-1.

Previous studies identified significant element re-deposition in the horizon represented by BB-3 that must have been derived from leaching of minerals higher in the profile, as indicated by heavily HREE enriched pattern, superchondritic Y/Ho ratios and significantly less radiogenic Nd isotope ratios than the BB-1 protolith (Babechuk et al., 2014; Babechuk et al., 2015). Such element redistributions into depth are common in laterite profiles (Patino et al., 2003; Viers and Wasserburg, 2004) and presumably triggered by pore-waters meeting a sharp permeability and/or pH boundary that drives element deposition into neo-formed minerals (e.g., phosphates). Although low Si/Ti ratios indicate an overall loss of Si from sample BB-3, the formation of secondary Si minerals capturing remobilised Si simultaneously with the REE cannot be discounted. The precipitation of small amounts of secondary Si phases in the form of siliceous cements or opaline silica from pore water favour the lighter isotopes of Si (André et al., 2006; Basile-Doelsch et al., 2005) and could explain the shift in Si isotopic composition of sample BB-3 to lighter values relative to BB-4 and BB-2.

5.3 Chromium isotopes

The Cr isotope composition of several weathering profiles has been investigated previously, including two highly ferruginous modern profiles developed on tonalite in a tropical region and

basalt in a sub-tropical region (Berger and Frei, 2014; D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015). Consequently, two models have been proposed for the within profiles Cr variations. In the first scenario, Cr loss may reflect leaching and small-scale redistribution of Cr(III) under low Eh and pH conditions with no evidence of isotopic fractionation. In the second scenario, partial oxidation of Cr(III) to Cr(VI) at comparatively higher Eh and pH conditions led to loss of soluble and isotopically heavy Cr(VI) species (Berger and Frei, 2014). This implies that the elemental mobility of Cr as Cr(III) is promoted by acidic conditions without isotopic fractionation, while the partial oxidation of Cr(III) to Cr(VI) subsequently triggers isotopic fractionation that can be stored within the weathering profile. The presence of Mn(III)/(IV)-oxides as a catalyst is likely required to induce redox reactions (Ball, 2004; Landrot et al., 2010; Tang et al., 2014) and isotopic fractionation between Cr(III) and Cr(VI), which is 6-7 ‰ at equilibrium at 24.85 °C obtained by theoretical calculations (Schauble et al., 2004). The separation of isotopically heavy Cr(VI) as a soluble anionic species to be transported within a profile with subsequent reduction or escape to the hydrosphere is then viewed as the means of preserving variable but often isotopically light Cr isotope signatures in weathering profiles. Accordingly, the overall behaviour of Cr is driven by the complex interplay between Eh and pH conditions. Given that deep, lateritic weathering profiles reach pH and Eh extremes beyond those found in stratigraphically thinner and less altered weathering profiles, new constraints can be placed on the Cr isotope systematics under oxidative weathering conditions by comparing the geochemistry of the contrasting Chhindwara saprolite and Bidar laterite.

Limited Cr mobility is indicated by the relatively homogeneous Cr/Ti ratios and the absence of stable Cr isotope fractionation of the Chhindwara profile (**Figure 2b**). Thus, despite the weathering intensity and magnitude of Fe oxidation, any Cr isotope signatures generated through pedogenic processes are likely masked by the comparatively larger isotopic pool of unfractionated igneous Cr(III) in the bulk rock measurements. If correct, neither the Quaternary weathering nor the vegetative conditions triggered a sufficient aqueous mobility of Cr within the soil profile to imprint Cr isotopic differences caused by isotopic fractionation through interaction with neoformed pedogenic oxides (D'Arcy et al., 2016). This exemplifies that

oxidative weathering under modern atmospheric conditions does not necessarily imprint changing Cr isotopic signatures within soils and that soil Cr isotopic signatures are not necessarily indicative of oxidative atmospheric conditions. Interestingly, the coupled offset in Cr/Ti ratios and $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ at the flow boundary matches that of other immobile element ratios (Babechuk et al., 2015) and may instead record a very subtle primary isotopic difference between the lava flows. In a recent study by Schoenberg et al. (2016), small isotopic heterogeneities within (ultra-)mafic magmatic rocks have been shown that are correlated with geochemical indices like Mg# that possibly could explain the observed difference in $\delta^{53/52}\text{Cr}_{\text{NBS979}}$.

The behaviour of Cr is significantly different in the deep and highly altered Bidar laterite. Lateritic weathering can occur under variable but very low pH conditions (Widdowson, 2008). For instance, the solubility of Al only rises significantly below a pH of 4, and pH conditions are modelled to reach as low as 2 in order to induce the ligand-mediated mobilisation of platinum group elements (PGE) and gold and silver (Bowles, 1986; Mann, 1984; Wimpenny et al., 2007). Low pH conditions develop through oxidation of Fe^{2+} that produces excess H^+ (Mann, 1984). Therefore, the lowest pH values were likely present around the paleo-water table where dissolved Fe^{2+} was oxidised and removed as Fe-oxyhydroxides from pore water under increasingly oxidising conditions. Weathering under acidic conditions can lead to large Cr depletion within the weathered rock due to increased Cr(III) mobilisation. Such a scenario has been proposed for extreme Cr depletion of up to 90% reported from a lateritic profile developed on tonalitic bedrock (Berger and Frei, 2014). Such an extreme Cr depletion is not seen within the Bidar lateritic profile. Rather, samples from near and above the paleo-water table which have been exposed to low pH pore waters show a significant increase in Cr concentration and Cr/Ti ratios associated with a highly variable $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ isotopic signature (**Figure 3a,b, 6d**). The positive covariation between Cr and Fe concentrations show that these Cr enrichments were likely caused by Fe oxidation and precipitation from pore waters.

Although it is difficult to attribute a single mode of weathering to be responsible for the Cr isotopic signature within the Bidar profile, dissolution of sulphides and silicate minerals deep within the profile under variable pH, Eh conditions might have liberated Fe(II) and Cr(III) into pore solution without significant isotopic fractionation. The mobility of Cr(III) across different pH ranges in association with ligands (organic or inorganic) is scientifically recognised (Cao et al., 2011; Duckworth et al., 2014; McClain and Maher, 2016), yet not widely regarded to induce an isotopic effect in the stable Cr isotope distribution in weathering profiles. An important observation is that the Fe and Cr concentrations are highly correlated, which concludes that Fe oxides and hydroxides incorporated Cr after its mobilisation. Chromium is structurally incorporated into many pedogenic Fe minerals as Cr(III) (Schwertmann et al., 1989; Schwertmann and Pfab, 1996). Lower Cr/Ti ratios in samples BB-2 to BB-5 compared to the protolith BB-1 indicate that Cr was mobilised in the lower parts of the profile (**Figure 3b**). As a result, Cr enriched pore fluids may have migrated upwards in the weathering profile to the paleo-water table where increasing Eh conditions in combination with the oxidation of Fe(II) led to the precipitation of ferric iron and co-precipitation in Fe(III)-oxides. Although isotopic fractionation during co-precipitation of Cr(III) with iron-oxides or -hydroxides has not been investigated so far, preferential adsorption of isotopically light Cr, might have shifted the isotopic composition of the remaining dissolved Cr reservoir to heavier values. Such a local transport of mobilised Cr from deeper parts of the profile and Cr accumulation by reduction and adsorption has been interpreted to be the reason for light $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ of top soils from a Central Madagascar lateritic profile (Berger and Frei, 2014). Therefore, migration of dissolved Cr upwards the profile coupled with precipitation of Fe hydroxides could have caused open system Rayleigh type characteristics in $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ of the evolving dissolved Cr reservoir. This might explain the isotopic pattern from light to heavy $\delta^{53/52}\text{Cr}$ seen in samples BB-4 to BB-6 and again BB-7 to BB-9 (**Figure 3b, 6d**). It must be noted that the oxidation of Cr(III) to Cr(VI) may also be triggered by the formation of manganese oxides and the partial removal and adsorption of Cr(VI) could also have led to some isotopic variability. This may also have contributed to the dissolved Cr pore water pool, especially in the upper part of the profile with

increasing Eh conditions. The reduction and co-precipitation of Cr(VI) with Fe oxides is known to favour the light Cr isotope and might have led to similar isotopic pattern as described above (Døssing et al., 2011; Ellis et al., 2002; Izbicki et al., 2008; Zink et al., 2010).

At present, a more conclusive evaluation of fractionation factors is not possible since whole rock Cr signatures are a combination of re-absorbed Cr(III) on Fe hydroxides superimposed by primary Cr(III) within the soil. The modal abundances of both phases are not known. However, the good correlation between $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ and $\delta^{30/28}\text{Si}_{\text{NBS28}}$ (**Figure 7**) (except for sample BB-3, see discussion above) indicates that the cycling and redistribution of iron within the profile had a strong influence on the isotopic composition of Cr and Si. The preferred model to explain the Cr distribution and isotopic characteristics involves mobilisation and sequestration of Cr predominantly in its Cr(III) state with a subordinate, but non-negligible role of Cr(VI). However, more robust Cr reconstruction is hindered by a lack of Cr(III)/Cr(VI) speciation and an unconfirmed role of Cr(III) processes (dissolution, complexation, and adsorption) in stable isotopic fractionation. The latter has been suspected to cause significant isotopic fractionation in other studied paleosols (Babechuk et al. 2017).

5.4 Sources of allochthonous Chromium, Iron and Silicon

Previous studies of the Bidar laterite profile have used a mass balance calculation and isotopic constraints to investigate the role of allochthonous input. Although the low sampling density throughout the Bidar profile hinders an accurate mass balance determination, previous studies demonstrate that changing ratios of immobile element ratios and radiogenic isotope patterns cannot be explained without dust input (Babechuk et al., 2015; Kısakürek et al., 2004; Wimpenny et al., 2007). However, dust input alone is insufficient to explain the excess of the elemental budgets in certain horizons, notably that of the paleo-water table. Therefore, lateral and open-system addition of elements from groundwater have been invoked to explain particularly elevated concentrations at a postulated paleo-water table level within the profiles. Groundwater transport was likely to have been active concurrently with dust accretion to the profile.

Given these documented complexities, and their detailed treatment in previous studies, similar mass balance calculations are attempted here for Cr and Fe to investigate the influence of dust on excess Fe and Cr within the upper Bidar profile. For this reason, an absolute mass change of an element per unit volume of material is determined to test whether a vertical redistribution can account for Cr and Fe enrichment within the profile (see Supplemental Materials for the model details). This model illustrates that lateral redistribution of Cr and Fe from bottom upwards can only account for their enrichments up to the position of the paleo-water table. For instance, nearly twice to three times more Cr and Fe is deposited within the top of the profile than released from the lower parts (**Figure 8**). Therefore, it seems likely that Cr and Fe enrichment in the top samples of the Bidar profile is partly derived from lateral groundwater transport of dissolved Cr and, in the upper parts of the profile, by atmospheric deposition as indicated by strong enrichments of Th/Nb ratios coupled with less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Babechuk et al., 2015). However, the fact that the concentration weighted average $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ of all measured Bidar samples is -0.1 ‰ and therefore close to the protolith BB-1 shows that any possible source for excess Cr, and possibly also Fe, was likely unfractionated compared to the average isotopic composition of the continental crust. The most likely sources for such dust input would likely be either the surrounding exposed basaltic terrain, or else the cratonic basement that surrounds it.

Although an addition of Fe and Cr via dust or groundwater transport to the upper part of the Bidar profile is likely, only ~ 2% Cr would need to be incorporated in order to account for the overall Cr content of the unweathered profile. Further this modest input seems to have not affected: a) the isotopic covariation between Cr and Si; b) the Si isotopic covariation with Fe within these samples; c) the overall, concentration weighted Cr isotopic composition of all Bidar samples (the latter remains close to the unweathered sample BB-1). Importantly, dust input to the top of the profile must have occurred concurrently with the process of lateritisation to explain our isotopic observations. If this interpretation is correct, then the dust input itself will also have been affected by the internal chemical weathering reactions and element remobilisation. Therefore, we conclude that the Cr isotopic signatures of the Bidar profile

developed through the vertical redistribution of autochthonous and allochthonous Cr and Fe and changing Eh and pH conditions.

The Si elemental mass balance and isotopic systematics of the Bidar profile samples also provide evidence that dust input to the Bidar site must have been contemporaneous with laterite formation. Up to 50% dust input with average UCC element concentrations (Rudnick and Gao, 2003) to the top samples BB-8 and BB-9 have been calculated using Nb/Th ratios (Babechuk et al., 2015). For sample BB-9, such a contribution of dust after laterisation would have raised its SiO₂ concentration far beyond the 9.6 wt %. Again, this simple mass balance calculation shows that although the Si input by dust cannot be neglected, the $\delta^{30/28}\text{Si}_{\text{NBS28}}$ vs. Fe/Ti and $\delta^{30/28}\text{Si}_{\text{NBS28}}$ vs. $\delta^{53/52}\text{Cr}_{\text{NBS979}}$ co-variations of the Bidar profile samples BB-8 and BB-9 follow the same trend as the deeper samples that experienced minor dust input. This indicates that the Si isotopic composition is not significantly altered by dust. Possibly, the dust input in the topmost levels was similarly exposed to intense weathering and consequently changed the elemental composition. This might explain why the dust input is not imprinted within the Si and Cr isotopic composition of the weathering profiles.

We acknowledge that the topmost samples in both profiles could also be influenced by biotic fractionation processes (Opfergelt and Delmelle, 2012). However, given the behaviour of $\delta^{30/28}\text{Si}_{\text{NBS28}}$ vs. Fe/Ti and $\delta^{30/28}\text{Si}_{\text{NBS28}}$ vs. $\delta^{53/52}\text{Cr}$ throughout the samples of the Bidar profile, it appears unlikely that plant uptake or biogenic silicia (phytoliths) (Opfergelt and Delmelle, 2012) have significantly altered the Si isotopic signature defined by Fe oxide adsorption processes.

The Si and Cr isotopic information of the profile to the total loss and gain of the respective elements and may be summarised as follows:

- 1) Cr shows a largest isotopic variability within the Bidar lateritic soil profile, and is largely attributable to fractionation and redistribution processes operating within the weathering profile. However, regardless of its strong fractionation in such lateritic profiles, the primary

impact of this behaviour upon the dissolved Cr flux to the oceans is likely to be small. This is because most of the liberated Cr rapidly becomes incorporated into neo-formed iron oxides and because the overall weighted isotopic composition of the entire profile thus remains close to that of unweathered basalt. However, the aeolian transportation of iron oxides in mineral dust particles might supply isotopically fractionated Cr into the ocean.

2) With consideration to the calculated Si loss of ca. 60% from the Bidar laterite profile, and by using the concentration, the overall weighted average $\delta^{30/28}\text{Si}_{\text{NBS28}}$ of -3.74 ‰, the isotopic composition of mobilised Si would be -0.05 ‰ $\delta^{30/28}\text{Si}_{\text{NBS28}}$. Although this weighted average is consistent with the Si isotopic range of river waters (-0.70 to 4.66 ‰ $\delta^{30/28}\text{Si}_{\text{NBS28}}$), the predicted light isotopic composition is somewhat lighter to predominantly heavy $\delta^{30/28}\text{Si}_{\text{NBS28}}$ values of dissolved Si in rivers (Poitrasson, 2017), but perhaps more comparable to $\delta^{30/28}\text{Si}_{\text{NBS28}}$ values of $+0.02 \pm 0.15$ ‰ in of the Congo and Amazon Basin rivers which are known to drain large areas affected by laterisation (Cardinal et al., 2010; Hughes et al., 2013). Hence, the isotopic light Si fingerprint in rivers is likely to indicate that they are, in part, sourced from areas where lateritic profiles are forming, or are being actively eroded, and not simply from currently active weathering zones which are only progressing to the saprolitic stage (i.e., where primary minerals are broken down).

6. Conclusions and broader Implications

We report Si and Cr isotopic data of two weathering profiles of different ages and degrees of alteration. These data are compared to compositional changes in major and trace element abundances relative to the unweathered protolith in order to investigate the mobility and adsorption processes of Si and Cr within different weathering regimes and intensities.

The Si isotopic compositions within the moderately weathered, Quaternary Chhindwara profile show a modest shift towards lighter $\delta^{30/28}\text{Si}_{\text{NBS28}}$ in those levels which contain higher abundances of pedogenic clays, zeolite minerals, and Fe-oxides. Accordingly, we conclude that this Si isotopic signature is related to the incorporation of isotopically light Si into secondary

clays, or else to adsorption of isotopically light Si onto secondary Fe-oxides. The absence of any Cr isotopic shift beyond that of the parent substrate, together with the homogeneous Cr/Ti ratios, indicates that oxic alteration in this profile was insufficient to allow the degree of aqueous mobility of Cr required to deliver Cr isotopic fractionation to the neo-formed pedogenic oxides.

By contrast, the more extreme weathering regime, displayed by the lateritic Bidar weathering profile, results in much greater variation in Si and Cr abundances, and a larger variability of Si and Cr isotopic values relative to unweathered parent basalt. This indicates a much greater mobility of both elements within this weathering regime. Further, the strong co-variation of Fe with enrichment as well as the Si and Cr isotopic composition, strongly indicates that within profile Fe mobility and oxidation of iron is a dominant factor for isotopic variability.

Although mass balance calculations reveal autochthonous or allochthonous Cr and Fe inputs to the profile, the vertical redistribution of Fe, Cr and Si during chemical weathering under changing pH-Eh conditions remain the most plausible explanation for the observed isotopic behaviour. The importance of Fe-oxide formation upon both Si and Cr isotopes illustrates that redox-dependent transformation and the redistribution of iron during weathering have a significant influence on the overall aqueous mobility of Cr and the isotopic signatures of Si and Cr in meteoric waters.

Intense chemical weathering during lateritisation favours significant removal of Si. The formation of Fe-oxides during lateritisation is accompanied by Si isotopic fractionation in response to Si adsorption. However, its effect on the net Si isotopic removal is likely to be relatively small. Therefore, rivers draining areas of dominantly lateritic terrains are likely to display slightly lighter Si isotopic values, but will remain close to that of the initial parent lithology, (e.g., as observed in rivers of the Congo Basin by Cardinal et al., 2010).

It has been reported that Cr can be mobilised in pore waters under low pH and Eh conditions during lateritisation (Berger and Frei, 2014). Here, reductive loss of Fe and Cr from the profile is likely associated with a limited isotopic fractionation such that the overall Cr removal has an

isotopic composition close to that of the magmatic range. This is consistent with Fe isotope investigations in modern lateritic profiles which display little or no Fe isotopic variation within laterites (Li et al., 2017; Poitrasson et al., 2008). However, by contrast to Fe, significant Cr isotopic fractionation is observed in those horizons where liberated Cr is effectively scavenged by the formation of Fe-oxides. Such a process will decrease the dissolved Cr output from the soil horizon and, accordingly, its overall influence upon the global budget. However, on a local scale the input of lateritic dust by aeolian transportation into marine basins or the open ocean might have a strong influence on dissolved Cr isotopic composition in marine surface waters.

Lateritisation processes affect large areas of continents located at low latitudes, where precipitation rates are high. Chemical reactions and element mobilities during laterite formation have considerable influence on the ocean element budgets. Long-term increase in laterite formation and associated elemental fluxes and isotopic fractionation processes would coincide with those periods when tectonic processes have preferentially assembled landmasses at low, tropical latitudes. Short-term increases would be coeval with times of climatic global warming and high precipitation rates coupled with elevated atmospheric CO₂, ocean anoxia and mass extinction events (Retallack, 2010). An increased Si flux to the oceans coupled with a lighter, continental isotopic signature in the marine sedimentary record should, therefore, reflect those times when extensive continental areas, and/or 'greenhouse' climate conditions became prevalent.

Figures:

Figure 1: Simplified geological map, adapted from Babechuk et al. (2014) after Kisakurek et al. (2004), showing the extent of the Deccan Volcanic Province (DVP) within peninsular India and the location of the two studied weathering profiles.

Figure 2: a) Element, oxide concentration and CIA index values for the Chhindwara profile (Babechuk et al., 2014); dashed line and grey shaded areas indicate average and range of

element concentration data of unweathered basalts from different flows of the Chhindwara area (Ganguly et al., 2014). **b)** Titanium (Ti) normalised element ratios and Si and Cr isotopic data; dashed line and grey shaded areas either indicate average and range of unweathered basalts from different flows at the Chhindwara area for Ti normalised concentration data (Ganguly et al., 2014) or Si and Cr isotopic range of unaltered mafic rocks (Savage et al., 2010; Schoenberg et al., 2008).

Figure 3: a) Element, oxide concentration and CIA index values for the Bidar profile (Babechuk et al., 2014); dashed line represents the element, oxide concentration and IOL index of protolith BB-1 **b)** Titanium (Ti) normalised element ratios and Si and Cr isotopic data; dashed line of unweathered basalt BB-1 and Si and Cr isotopic range of unaltered mafic rocks. **b)** Titanium (Ti) normalised element ratios and Si and Cr isotopic data; dashed line and grey shaded areas either indicate average and range of unweathered basalt BB-1 or Si and Cr isotopic range of unaltered mafic rocks (Savage et al., 2010; Schoenberg et al., 2008).

Figure 4: Trace element maps of the Chhindwara profile samples **a)** Photomicrograph under plane polarised light (ppl) of Fe-Mg rich clinopyroxene (cpx), volcanic glass (vg), plagioclase (plg), primary Fe-Ti oxide (opq = opaque) and titanite (tit). Volcanic glass occurs as inclusions in all silicate minerals and the matrix. The pink frame delineates the area that was laser ablated. **b)** Semi-quantitative LA-ICP-MS compositional maps of Cr.

Figure 5: Photomicrograph under ppl of the **a)** nodular cap (hem = hematite; feh = iron-hydroxide), **b)** paleo water-table (gt = goethite), **c)** bedrock (cpx = clinopyroxene; vg = volcanic glass; plg = plagioclase; opg = opaque primary Fe-Ti oxide) of the Bidar laterite profile with semi-quantitative LA-ICP-MS compositional maps of Fe, and Cr. The red frame in each photomicrograph delineates the area that has been laser ablated. **a)** In the centre, a vein composed of iron hydroxide, goethite and hematite is visible that is enriched in Fe and Cr. Particularly, below the vein lower but still high concentrations of Fe are visible, whereas only in places moderately to high concentrations of Cr are evident. This indicates the relationship between iron oxides and Cr. **b)** In the photomicrograph, mainly goethite is visible and enriched

in Fe and Cr and both concentrations derived from an extraneous source. **c)** The trace element maps of the protolith indicate that Cr is mainly hosted in pyroxene.

Figure 6: **a)** Titanium normalised Fe concentrations (Fe/Ti) vs. Titanium normalised Cr concentrations (Cr/Ti) **b)** Titanium normalised Fe concentrations (Fe/Ti) vs Titanium normalised Si concentrations Si/Ti **c)** Titanium normalised Fe concentrations (Fe/Ti) vs Si isotopic composition ($\delta^{30}\text{Si}$) **d)** Titanium normalised Fe concentrations (Fe/Ti) vs Cr isotopic composition ($\delta^{53}\text{Cr}$) of Bidar profile samples.

Figure 7: $\delta^{30}\text{Si}$ vs. $\delta^{53}\text{Cr}$ of Bidar profile samples

Figure 8: Depth integrated fluxes of Cr and Fe per cm^2 based on mass balance reference to the unweathered basalt protolith (sample BB-1). Negative values indicate loss from the profile, positive values indicate excess allochthonous Cr and Fe input to the profile.

Tables:

Table 1: Major, trace element concentration; * (Babechuk et al., 2014); # (Babechuk et al., 2015) and Si and Cr isotopic data of the Chhindwara and Bidar weathering profile. Different Run # represent Si isotope replicates of different sample powder aliquots.

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