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Oxidative mafic rock weathering through geological time

PhD Thesis

2015

Michael G. Babechuk



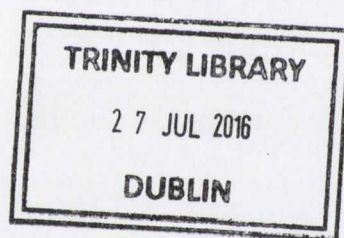
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Oxidative mafic rock weathering through geological time

Abstract

Oxidative chemical weathering requires the presence of free oxygen in the Earth's atmosphere. Reconstructing the terrestrial oxidation history in the ancient rock record has helped to detect the intrinsic links between atmospheric composition and biological evolution of oxygenic photosynthesis. This thesis contributes to this theme via the study of oxidative chemical weathering at different stages of Earth's history and at different weathering intensities. It presents detailed geochemical investigations of three profiles developed on mafic rock. Laterite (Bidar) and saprolite (Chhindwara) profiles hosted on Deccan Traps basalt (India) capture weathering in the Phanerozoic, while the ca. 1.85 Ga Flin Flon paleosol (Canada) hosted on greenstone captures weathering after the Great Oxidation Event (GOE, ca. 2.4-2.3 Ga). The new mafic index of alteration (MIA) is proposed to quantify the chemical progression of weathering both under the reducing conditions prior to the GOE and the oxidising conditions that have dominated after. The application of modern, high-quality trace element and Nd isotope analysis to the two Phanerozoic profiles aided in unravelling variations in the protolith chemistry, assessing aeolian input, and identified the Y/Ho ratio as a novel tracer of weathering.

Paleosols developed before 2.4 Ga show evidence for Fe loss or redistribution as Fe(II), whereas those younger than this age show evidence for Fe(II) oxidation to Fe(III) similar to modern profiles. This thesis confirms the Flin Flon paleosol as one of the oldest mafic weathering profiles showing near-complete oxidation of Fe. The oxidation state of Precambrian paleosols inferred from conventional Fe speciation, however, has recently been contradicted by the novel proxy of Cr isotopes, which suggests that atmospheric oxygenation events occurred as far back as the Mesoarchean. The combined application of the two proxies to the Phanerozoic saprolite profile and Flin Flon paleosol provides new insights into the behaviour of Cr isotopes during oxidative weathering. The saprolite profile shows that numerous elements (Fe, Mn, Ce, U) may leave strong fingerprint of oxidation even when Cr isotopes do not. The Flin Flon paleosol shows a Cr isotope signature that is opposite to that expected for oxidation of Cr(III) to Cr(VI) and suggests that mobilisation of Cr(III) without oxidation may fractionate the isotopes of Cr. Consequently, Cr isotopes alone may not be sufficient to fingerprint atmospheric oxygen and claims of Mesoarchean oxygenation from Cr isotope data may need to be revisited.

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Oxidative mafic rock weathering through geological time

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Chapter 1: Introduction to the thesis

1. Context of the thesis

The origin of Earth's oxygen-rich atmosphere has been an active area of research for many decades (Holland, 2011; Lyons et al., 2014). Because the production of atmospheric O₂ is a biological innovation only capable after the evolution of oxygenic photosynthesis, detecting evidence for the first appearance of O₂ in the geological record is of utmost importance in establishing when this occurred.

Many lines of geological and geochemical evidence from the sedimentary rock record converge in support of a transition from a reducing to oxidising atmosphere between ca. 2.4 and 2.3 Ga (summarised in the reviews of Holland, 1994; 2006; Farquhar et al., 2011; Pufahl and Hiatt, 2012), known as the Great Oxidation Event (GOE; Holland, 2002). This "oxyatmoverison" (Roscoe, 1973) is recorded by secular changes in the surficial cycles of many redox-sensitive elements (e.g., S, Fe, C, P, U, Mo, Cr, Ce) and the minerals that bear them, providing direct or indirect evidence for oxidative terrestrial weathering. These lines of evidence include:

- 1) the destabilisation of reduced minerals such as pyrite and uraninite at the Earth's surface leading to their disappearance as detrital clasts in fluvial deposits (Rasmussen and Buick, 1999; England et al., 2002);
- 2) the first substantial accumulation of oxyanion-forming elements (e.g., S, Mo, U, Re) in the oceans (e.g., Canfield, 1998; Collerson and Kamber, 1999; Scott et al., 2008; Guo et al., 2009); and,
- 3) the oxidation of Fe in soils and the first formation of red beds (Cloud, 1968; Rye and Holland, 1998; Prasad and Roscoe, 1996).

The disappearance of mass-independently fractionated (MIF) S isotope signature in sedimentary sulphides and sulphates (Farquhar et al., 2000; Pavlov and Kasting, 2002; Bekker et al., 2004; Papineau et al., 2007) coincides with these signatures of terrestrial oxidative weathering and is now cited as one of the strongest lines of evidence for the GOE.

The accumulation of free atmospheric O₂ at the GOE requires that the supply of oxygen overwhelmed the capacity of its sinks (e.g., reactions with reduced species like Fe²⁺), but does not necessarily pinpoint its first production by cyanobacteria. How early first production occurred prior

to the GOE remains uncertain (Farquhar et al., 2011 and the references therein). Authigenic enrichments of redox-sensitive elements have been detected in marine sedimentary rocks deposited throughout the Archean and as far back as ca. 2.96 Ga (Anbar et al., 2007; Wille et al., 2007; Frei et al., 2009; Reinhard et al., 2009; Crowe et al., 2013). These enrichments are similar to those associated with the GOE, albeit more subdued, and have accordingly been interpreted as episodes of element release from land induced by oxidative weathering. If authentic, these signatures require a very early evolution of cyanobacteria (ie., up to 600 Ma before the GOE) as opposed to closer to the GOE (Kirschvink and Kopp, 2008; Rasmussen et al., 2008). They also necessitate revised O_2 sink vs. source models that can explain the lag-time between first production and the GOE (e.g., Kump and Barley, 2007; Konhauser et al., 2009; Zahnle et al., 2013; Swanner et al., 2015). Based on these inorganic geochemical signatures (and some equivocal organic biomarker signatures: Brocks et al., 1999; Brocks, 2011) in marine sedimentary rocks, the once established picture of a singular, unidirectional rise of O_2 at the GOE is being replaced by one with O_2 accumulation as a series of complex and protracted events with significant fluctuations (e.g., Frei et al., 2009; Partin et al., 2013) preceded by transient episodes of O_2 pulses amidst a backdrop of widespread atmospheric anoxia.

One crucial yet poorly established assumption (explicit or often implicit) of putative Archean oxygenation events is that they truly record the accumulation of O_2 over the continents and not just in restricted marine environments. In this context, it is important that paleosols are direct archives of terrestrial weathering and have great historical significance for the discovery of the GOE through a transition in their Fe redox geochemistry (Rye and Holland, 1998). Paleosols clearly play a crucial role in testing the authenticity of the Archean oxygenation events inferred from marine sedimentary rocks. However, they have received little attention during the last 10 years of research that have concentrated on the marine realm and its record of (Archean) oxygenation events. This neglect is due in part to their scarcity in the geological record compared to marine sedimentary rocks and the complexities of their preservation that make extracting paleoatmospheric information more challenging. Nevertheless, there is a rapidly advancing arsenal of geochemical redox proxies waiting to be applied to paleosols with enormous potential to yield new information. To date, the only terrestrial evidence for Archean oxidative weathering is from a Cr isotope excursion in a ca. 2.96 Ga paleosol (Crowe et al., 2013), but it must be stressed that the final interpretation of these preliminary Cr isotope data hinges on a more complete understanding of the surficial Precambrian Cr cycle and Cr isotope fractionation (Konhauser et al., 2011; Planavsky et al., 2014). Apart from the controversial views of Ohmoto (1996), no other studies to date have provided irrefutable evidence for oxidative weathering reactions in paleosols >2.45 Ga in age.

Ignoring the complications associated with the burial and preservation of paleosols, weathering profiles are intricate systems developed at the intersection between the lithosphere, hydrosphere, atmosphere, and biosphere. Investigations of weathering profiles require careful consideration of the characteristics of the protolith and element losses and gains associated with internal chemical weathering reactions and the introduction of allochthonous materials, all within the context of the climate, regional topography, and biology. Any attempt at extracting paleoatmospheric information from Precambrian paleosols needs to be based on the foundation of insight from well-established Phanerozoic weathering profiles where the aforementioned variables can be better constrained. When attempting to fingerprint oxidative chemical weathering reactions as far back as the Archean, it is therefore logical to build a more robust picture of modern and post-GOE oxidative weathering.

For this thesis, detailed geochemical investigation was undertaken on three mafic oxidative weathering profiles – a Quaternary saprolite profile, a Paleogene laterite profile, and the Paleoproterozoic (ca. 1.85 Ga) Flin Flon paleosol – to contribute to the understanding of mafic rock weathering at present and in the deep geological past. Despite the sparse record of Precambrian paleosols, detailed studies of weathering profiles such as in this thesis are crucial in taking further steps in unifying (or decoupling) the marine and terrestrial archives of atmospheric oxygenation. The emphasis on mafic weathering profiles arises from the abundance of redox-sensitive and bioessential transition metals in mafic rocks, the importance of their chemical weathering in driving global climatic shifts, and their documented presence across all of the key transitions in Earth's atmospheric oxygen evolution (spanning the 2.96 to 0.45 Ga period). The application of high-density sampling and high-precision analytical techniques in this thesis are shown to provide new insights into weathering profile development, such as unravelling the nature of the protolith, constraining the addition of allochthonous components, and identifying new tracers of chemical weathering intensity.

The two Phanerozoic weathering profiles are from the Deccan Traps in India, representing different stages of oxidative basalt weathering. The Quaternary saprolite profile (Chhindwara) is described in this thesis for the first time and is of importance in constraining the geochemical progression associated with the initial stages of basalt weathering. The Paleogene laterite profile (Bidar) is studied here with new geochemical data building upon previous research (Borger and Widdowson, 2001; Kısakürek et al., 2004; Wimpenny et al., 2007), providing further insight into the long-term evolution of weathering profiles at extreme stages of alteration. The Precambrian profile, Flin Flon paleosol (Holland et al., 1989; Pan and Stauffer, 2000), is one of the oldest oxidised paleosols known to date and is thus essential for drawing comparisons between

Phanerozoic and Paleoproterozoic oxidative weathering and a highly promising paleosol upon which to apply new geochemical paleo-redox proxies. Due to its recognised status of scientific importance, the original outcrops are now under strict protection. The site of original research (Holland et al., 1989) was revisited for this thesis and a new profile was excavated permitting the extraction of a continuous high-resolution section.

2. Layout and themes of the thesis

The basic narrative of this thesis follows basalt weathering temporally, from modern to ancient, beginning with studies of the Quaternary saprolite profile (Chhindwara, India) and the Paleogene basaltic laterite (Bidar, India), followed by those of the ca. 1.85 Ga Flin Flon paleosol (Flin Flon, Canada).

Chapters 2 and 3 provide an overview of the importance of basalt weathering in the Earth system and introduce the geochemistry of the Bidar laterite and the Chhindwara profiles. Two new geochemical weathering indices are proposed to quantify mafic rock weathering trends under moderate (saprolitic) and extreme (lateritic) weathering conditions – the mafic index of alteration (MIA) and the index of lateritisation (IOL). High-precision trace element and isotope data are used to understand different aspects of basalt weathering, including the fractionation of the REE (Ce/Ce*, Sm/Nd, Eu/Eu*, Y/Ho) and the use of the high field strength elements and Nd isotopes to identify changes in the protolith chemistry and introduction of dust into a weathering profile.

Chapter 4 provides the transition between the Phanerozoic weathering profiles and ancient paleosols. Here, the criteria for paleosol identification and the key features of paleosol geochemical and mineralogical evolution are reviewed. A list of all of the definite mafic paleosols that are suitable for extracting paleo-atmospheric information is also supplied. These data are used for comparisons with those of the new weathering profiles from this thesis.

Chapter 5 presents a comprehensive geological and basic geochemical study of the new profile of the Flin Flon paleosol. It focuses on the physical, mineralogical, and major element evolution of the profile. The significance of the Fe-redox chemistry of this profile was previously under debate, but this study confirms that the Flin Flon paleosol is one of the oldest examples of near-complete Fe retention due to Fe³⁺-oxide formation during weathering.

Chapter 6 is a review of the available paleo-redox information from paleosols that places the Flin Flon paleosol in a more global context, draws attention to several outstanding issues and

unanswered questions regarding paleosol redox evolution, and provides an overview of current knowledge regarding Cr isotopes as a paleo-redox tracer.

Chapter 7 is a Cr isotope study of the saprolitic Chhindwara profile and the Flin Flin paleosol that provides new insight into the cycling of Cr during oxidative weathering that is relevant to the interpretation of other ancient paleosols and the interpretation of transient oxygen pulses in the Archean from Cr isotope data.

Chapter 8 is a synthesis of the main contributions of the thesis and the wider implications of the new findings to the study of chemical weathering and the evolution paleo-atmospheric oxygen.

Many chapters of this thesis constitute individual research contributions that were published as journal articles or reports during the duration of the thesis. These chapters are identified as such and their content is presented as available from the publisher, but formatted for the thesis. Chapter-specific tables, figures, and references are found at the end of each chapter. One exception is a copy of a Manitoba Geological Survey report that covered additional field work on the Flin Flon paleosol and is presented in Appendix A as it was published.

3. Co-author statement

The work of several co-authors (Balz Kamber, Mike Widdowson, Michael Murphy, Ronny Schoenberg, Ilka Kleinmanns) contributed to the publications derived from the thesis, through guidance and discussion, sample provision, analytical assistance or measurement, and manuscript editing. Mike Widdowson provided the samples and field context of the Bidar and Chhindwara samples, as well as editorial comments on chapters involving these samples (Chapters 2, 3, 7). Michael Murphy provided laboratory expertise and assistance with the Nd isotope measurements of Chapter 3. Ronny Schoenberg and Ilka Kleinmanns were involved in the Cr isotope aspect of this thesis by providing guidance throughout the stages of sample preparation, analysis, and data reduction at the University of Tübingen, as well as editorial comments and assistance with writing the methods section of Chapter 7. Balz Kamber provided guidance throughout all stages of the thesis, funding for field work and geochemical analysis, and editorial comments on all chapters. As first author on all publications, I prepared samples for analysis, wholly or partly analysed new data for the thesis, interpreted data, prepared all manuscripts, and addressed reviewer and editor comments. As such, I am responsible for any inaccuracies in the thesis and publications.

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Chapter 2: Quantifying chemical weathering intensity and trace element release from two contrasting basalt profiles, Deccan Traps, India

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Abstract

Weathering profiles developed on basalt substrate contain information relevant to climate, atmospheric composition and evolution, nutrient release into the hydrosphere, and understanding Martian regolith. In this study, the chemical compositions of two profiles developed on Deccan Trap basalt are examined. One is sub-Recent and has only progressed to a moderate degree of alteration (Chhindwara profile), whereas the other is ancient (Paleocene) and the degree of alteration is extreme (Bidar laterite). In an attempt to better quantify the chemical changes during incipient to intermediate weathering of mafic substrates, a new index is proposed: the mafic index of alteration (MIA). Similar to the chemical index of alteration (CIA), the MIA quantifies the net loss of the mobile major elements (Ca, Mg, Na, K $\pm$ Fe) relative to the immobile major elements (Al $\pm$ Fe). The redox-dependent weathering behaviour of Fe is factored into two separate arrangements of the MIA that apply to oxidative [MIA_(O)] or reduced [MIA_(R)] weathering. The MIA can be visualised in a variety of ternary diagrams in the Al–Fe–Mg–Ca–Na–K system. To chemically quantify the stages of advanced to extreme weathering, at which the MIA and CIA are ineffective, the SiO₂ to (Al₂O₃+Fe₂O₃) mass ratio, based on the established Si–Al–Fe (SAF) ‘laterite’ ternary diagram, is used; we propose that this ratio be referred to as the ‘index of lateritisation’ (IOL).

Major element chemical variations, as expressed by weathering indices, are used to relate the extent of weathering with the behaviour of trace elements (alkali, alkaline earth, rare earth, and Nb) in the profiles. During the early stages of basalt weathering, the mobile trace elements (Sr, Be, Li) are anti-correlated with the chemical weathering indices and thus released during these stages. By contrast, the monovalent elements (K, Rb, Cs, Tl), excluding Na and Li, appear to be associated with the pedogenetic clay minerals. Of these elements, those with the most similar ionic radii are closely related in their weathering behaviour. Fractionation of the REE (Sm/Nd, Eu/Eu*, Ce/Ce*) is evident during weathering of the basalt. The loss of Eu is linked with that of Sr, Ca, and Na and thus associated with

plagioclase dissolution during the stages of incipient to intermediate weathering. The fractionation of Sm/Nd suggests that basaltic weathering products may not always preserve their parent rock ratio and, consequently, their Nd isotope composition over time.

Finally, weathering in the sub-Recent profile is shown to have progressed across two lava flows, whose morphology initially controlled the extent of weathering. Certain compositional variations in the original flows (e.g., immobile element ratios) are preserved through the effects of chemical weathering and have the potential to influence mass balance calculations across the entire profile.

1. Introduction

Chemical breakdown of thermodynamically unstable minerals at the Earth's surface by weathering agents is a fundamental part of global elemental cycles. It is responsible for the long-term regulation of global atmospheric CO₂ concentrations and for generating clastic sediment and dissolved elements for delivery to fluvial and marine reservoirs. Therefore, in view of this critical role, it is perhaps not surprising that several geochemical indices have been introduced for the purpose of understanding and quantifying the processes of weathering (e.g., Parker, 1970; Kronberg and Nesbitt, 1981; Nesbitt and Young, 1982; Harnois, 1988; Maynard, 1992; Fedo et al., 1995; Retallack, 2001 and references therein; Ohta and Arai, 2007; Sheldon and Tabor, 2009; Nordt and Driese, 2010). Such quantification of the degree of weathering in soils/paleosols or clastic sedimentary sequences has proven important from the scale of an individual weathering profile up to that of global mass balance. At the scale of an individual weathering profile, the most useful weathering indices are those with elemental components that can be determined routinely and examined graphically to provide further insight into the weathering and/or post-weathering processes. One of the most widely used examples is the chemical index of alteration (CIA: Nesbitt and Young, 1982, 1984, 1989) and the accompanying A–CN–K diagram (Nesbitt and Young, 1984; Fedo et al., 1995).

In this study, a new chemical weathering index modelled after the CIA is introduced: the mafic index of alteration (MIA). The MIA adds the elements Fe and Mg to the Al–Ca–Na–K system, allowing the mafic mineral component of rock weathering to be quantified. The MIA is most suitable for, but not restricted to, studying mafic rock weathering. The study of chemical weathering of mafic substrates, compared to felsic substrates, provides many advantages from a geological and chemical perspective: a) the parent rock is often fine-grained and typically quite homogeneous; b) the substrate is rich in redox-sensitive elements, such as the transition metals; c) basalt or its metamorphosed/altered equivalent are ubiquitous throughout the known geological record, and d) it is of increasing importance for interpreting Martian substrate alteration. Silicate weathering is perhaps the most important removal mechanism of CO₂ from the atmosphere, with the weathering of mafic substrates often being cited as especially important in the regulation of global climatic changes (Louvat and Allègre, 1997; Schwarz, 1997; Gaillardet et al., 1999; Taylor and Lasaga, 1999; Dessert et al., 2001; Das et al., 2005; Navarre-Sitchler and Brantley, 2007).

Although the major elements closely reflect the mineralogical transformations during weathering, understanding the cycling of certain minor and trace elements has potential to provide further insight

into pedogenetic processes, such as biological activity or the oxidation state of a profile. Linking the release or retention of these elements to specific stages of chemical weathering can be accomplished through the combined use of major element weathering indices and trace element mass balance. In this study, this is demonstrated for the alkali, alkaline earth, and rare earth elements during different stages of alteration of the Deccan Traps basalt.

2. Basalt chemical weathering and lateritisation

2.1. Incipient to intermediate weathering

For typical basaltic rocks, the susceptibility of minerals to chemical weathering follows the order of glass $\approx$ olivine $>$ plagioclase $\approx$ pyroxene $>$ Fe-Ti oxide (e.g., Eggleton et al., 1987; Nesbitt and Wilson, 1992), although some exceptions related to particular textural characteristics or the weathering environment have been reported (e.g., Craig and Loughnan, 1964). Ultimately, pedogenetic phyllosilicates (e.g., kaolinite and the smectite group minerals) and Fe and Mn oxides or oxyhydroxides form from the primary basaltic constituents during weathering. The exact pedogenetic mineralogy and order of mineral formation depend on the parent rock composition, climate, biology, redox state, and drainage of the profile (e.g., Prudêncio et al., 2002; Rasmussen et al., 2010). During the incipient to early stages of basalt weathering, 2:1 layer phyllosilicates typically form and significant hydration occurs. As weathering progresses to intermediate and advanced stages, 1:1 layer clays such as kaolinite or halloysite are typical stable end-products. Therefore, this realm of chemical weathering is sometimes referred to as 'kaolinitisation'.

During the early stages of basalt weathering, a general net loss of the mobile elements (Mg, Ca, Na, $\pm$ K) accompanies the mineralogical transformations (e.g., Nesbitt et al., 1980; Chesworth et al., 1981; Kronberg and Nesbitt, 1981). By contrast, Al, Fe, and Si are predominantly retained. Therefore, quantification of weathering intensity during these stages typically assumes conservation of Al and measures the loss of the mobile elements (Ca, Na, K, Mg). The weathering behaviour of Fe, however, may be more complicated and dependent on the redox and drainage conditions of the profile (e.g., Driese, 2004).

2.2. Advanced to extreme weathering and lateritisation

The term 'laterite' comes with a history of debate and disagreement related to the origin of duricrusts (for recent discussion see Ollier and Galloway, 1990; Bourman, 1993; Bourman and Ollier 2002, 2003; Schellmann, 2003). We prefer to adopt the genetic distinction between ferricrete and laterite (e.g., Aleva, 1994; Widdowson, 2007); in this study, 'lateritisation' will refer to the progressive, *in situ* alteration of rock. By contrast, ferricretes are alteration profiles that are largely generated by the allochthonous input and accumulation of ferruginous cement within existing subaerial substrates. In practice, the distinction between laterite and ferricrete cannot always be readily made in the field, and may require very detailed characterisation of duricrusts (e.g., Beauvais, 1999). Genetic distinctions are further complicated on a smaller scale since even *in situ* weathering profiles are subject to some lateral element transfer and the incorporation of aeolian sediment (Figure 1).

Lateritisation is generally associated with intense and prolonged leaching conditions in sufficiently hot and humid climates. During advanced to extreme weathering that is associated with lateritisation, the stage of pedogenetic phyllosilicate accumulation is exceeded and Fe- and Al-oxyhydroxides and sesquioxides (e.g., gibbsite, goethite, hematite) begin to dominate the weathering profile mineralogy. The Si largely retained in the phyllosilicates during earlier stages of weathering is lost (e.g., Widdowson and Gunnell, 1999; Hill et al., 2000) and desilication becomes the dominant process modifying the chemistry of the weathering profile. In this respect, the classic chemical definition of 'laterite' by Schellmann (1981, 1982, 1986) based on the SiO_2 to $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ ratio becomes useful in accompanying field observations of lateritic profiles. This ratio and the accompanying SiO_2 - Al_2O_3 - Fe_2O_3 (SAF) ternary plot provide a quantifiable chemical criterion to examine highly altered substrates, although they are not applicable to allochthonous duricrusts (i.e., ferricretes). The full progression of chemical weathering must be recorded within a single 'laterite profile' that is characterised by a gradual alteration of parent rock to saprolite near the base and grading into a pallid zone, followed by a mottled zone, and finally an indurated, Fe-rich duricrust at the top (i.e., the 'textbook' laterite profile). Caution should be exercised where an *in situ* progressive weathering profile cannot be unequivocally identified or where the parent rock is unavailable or unknown.

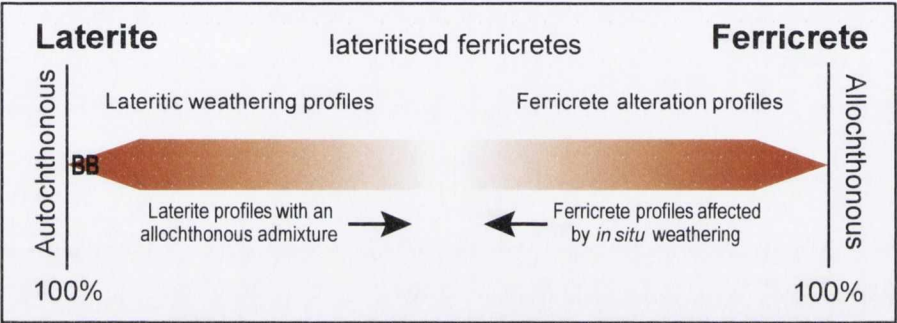


Figure 1: Illustration showing the transitional relationship from end-member autochthonous to allochthonous duricrusts (i.e., laterite to ferricrete), modified from Widdowson (2007). The Bidar (BB) laterite profile is an autochthonous profile formed from *in situ* weathering.

3. Geology

3.1 Geological and geochemical context of the Deccan Volcanic Province

The Deccan Volcanic Province (DVP), located in western peninsular India, is the remnant of an extensive, continental flood basalt emplaced during a tholeiitic eruptive acme between ca. 67 and 65 Ma (e.g., Duncan and Pyle, 1988; Gallet et al., 1989; Widdowson et al., 2000; Hofmann et al., 2000; Chenet et al., 2007; Hooper et al., 2010) at the Cretaceous-Paleogene Boundary (KPgB). Immediately following the eruption of the Deccan Traps flood basalt, the neo-formed lava fields were exposed to intense tropical weathering due to the equatorial location of the DVP around the KPgB. Accordingly, deep (lateritised) weathering profiles developed uninterrupted throughout the Paleocene. The weathering intensity is likely to have waned in the Eocene following continental uplift resulting from the collision of the Indian and Asian plates and/or denudational uplift of the rifted margin of Western India (65-50 Ma; Beck et al., 1995; Widdowson, 1997); this, together with climate changes resulting from the closure of the Tethyan seaway and later uplift of the Himalayas, and associated profound alteration of Indian continental drainage patterns, are likely to have resulted in changes in Indian weathering regimes (e.g., Kerrick and Caldeira, 1993).

Remnants of Paleocene and Miocene duricrusts are found located at topographical highs in the Western Ghats and across the low-lying Konkan coastal plain, respectively (Widdowson and Cox, 1996; Widdowson, 1997). The high-level duricrusts are interpreted as remnants of the once extensive weathering residuum that had developed on the top of the DVP lava flow package after eruptions had ceased (ca. 60 Ma), while the low-lying examples of the Konkan plain represent alteration of a piedmont-like paleosurface developed at the foot of the Western Ghats escarpment in the upper Tertiary (e.g., Widdowson and Gunnell, 1999; Widdowson, 2007).

Differential weathering and erosion of the flat-lying basaltic flows (c. 4-10 m thick) has produced spurs, ridges and mesas that are separated by flat-floored valleys often containing meandering rivers. East of the Ghats escarpment these rivers drain eastward and southward eventually discharging into the Bay of Bengal, while those that drain the escarpment and Konkan plain flow westward into the Arabian Sea. Increased aridity during the LGM resulted in reduced stream flow magnitudes in the rivers of south and SE Asia, while the glacially-induced eustatic low extended river courses across exposed coastal plains. As wetter (monsoon) conditions returned in the early Holocene, the rivers in peninsular India responded by deepening and enlarging their channels to accommodate increased discharge leading to widespread erosion and development of river terraces (e.g., Clift et al., 2002,

Kale, 2002; Figure 2). In most areas, these fluvial processes stripped the deeply lateritised Paleocene duricrust and exposed fresh basalt in topographical lows to Holocene weathering. Therefore, most of the current outcrop of the DVP (> 90%) consists of basalt variably weathered to 1 to 10 m in a stepped mesa-like topography that is largely the result of Quaternary (Pleistocene-Holocene) fluvial processes of valley incision and widening in the wake of the last glacial maximum (LGM).

The DVP provides an ideal natural laboratory to study the various stages of chemical weathering of compositionally similar tholeiitic basalt. The thick, near horizontal geometry of the DVP flows and the mesa topography of the area has ensured that the current chemical state of the weathering profiles has been isolated from interaction with ground or surface waters. Further, given the massive areal extent of the DVP flows, the study sites are remote from other basement lithology and only minor aeolian input could possibly interfere with the DVP's excellent potential for investigating basaltic chemical weathering (Kisakürek et al., 2004; Wimpenny et al., 2007).

In the present study, two weathering profiles from the eastern DVP, representing very different stages of basalt alteration, are examined. The first is an ancient (Paleocene), highly advanced (lateritic) weathering profile developed in the Bidar area (BB sample series). The second is a post-Pleistocene (sub-Recent) weathering profile located in a roadside quarry near Chhindwara (ChQ sample series) in the Madhya Pradesh district. This profile is substantially less advanced in its degree of alteration, lacking any duricrust development. The geology and sampling strategies of these two chemically different weathering profiles are summarised next and illustrated in Figure 3.

3.2. Bidar profile

The Bidar laterite profile is well exposed at a hillside edge of a mesa near Bidar, Madhya Pradesh, India (17°54.87' N, 77°32.39' E; Figure 2). This site is where Newbold (1844, 1846) first suggested laterite to be the consequence of *in situ* rock weathering. The Bidar laterite, sampled in 1998, is interpreted as a deep (~50 m) weathering profile with upwardly increasing alteration and concomitant Fe-enrichment (Borger and Widdowson, 2001; Kisakürek et al., 2004). Between the top and bottom of the profile there is a typical lateritic weathering progression, including a mottled zone, and an indurated duricrust cap (Figure 3a). The unweathered basalt (at a profile depth of > 40 m) gradationally gives way to a corestone-rich horizon and saprolite matrix between a depth of 35 and 30 m. This depth range is characterised by the typical depletion of mobile alkali and alkaline earth elements that is associated with incipient weathering. Between 30 and 25 m, saprolite with Fe-rich mottles and segregations becomes dominant. Above this point, primary silicates have been completely removed

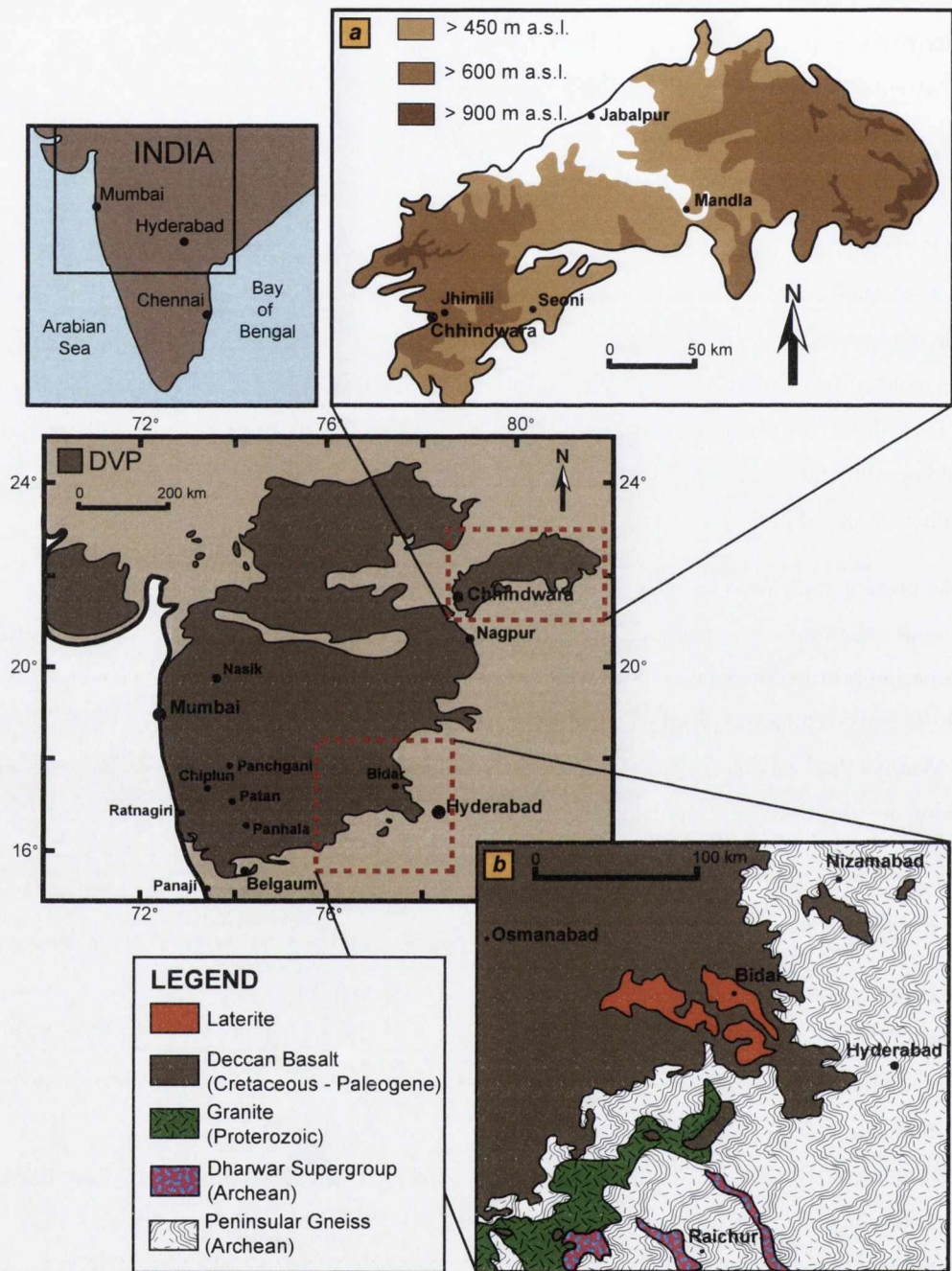


Figure 2: Simplified geological map showing the extent of the Deccan Volcanic Province (DVP) within peninsular India and the geomorphology of the weathered basaltic terrane. Inset maps show (a) the mesa topography near Chhindwara in the Madya Pradesh district and (b) the more detailed geology of the SE lobe of the DVP, including the extent of the thick laterite that hosts the Bidar profile. DVP geology maps modified from Borger and Widdowson (2001) and Kisakürek et al. (2004).

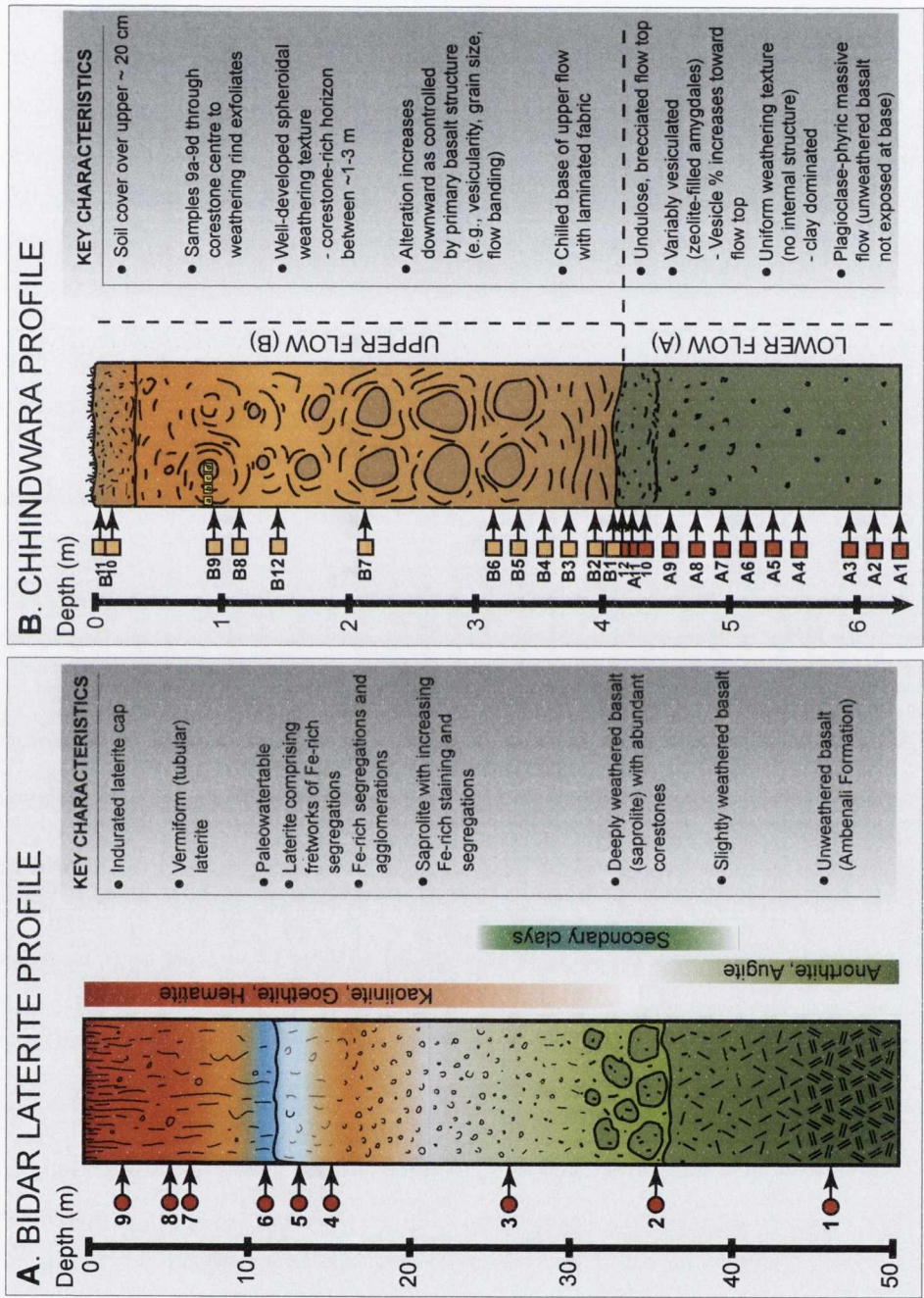


Figure 3: Geological sketch section of the: a) Bidar laterite (modified from Kisakirek et al., 2004 and Widdowson, 2007) and b) Chhindwara weathering profile. Highlights of the key features in the weathering progression accompany the schematic of each profile. Note the different scales of depth. The Chhindwara weathering profile is developed across two identifiable basalt flows (A – lower flow and B – upper flow). The sample identification and locations are also provided.

from the profile and Si and Al concentrations decrease relative to Fe. This is associated with an increase in the abundance of irregular Fe-rich agglomerations and a reddening of the saprolite colour upward between ~25 and 15 m. An unexpected return to bluish-grey saprolite between ~15 and 10 m marks the only apparent discontinuity in the upward weathering progression. Based on higher than expected Fe concentrations and trace metal accumulation, Kisakürek et al. (2004) argued that this horizon represents the position of a stable paleo-water table. At the highest, and most advanced part of the weathering profile, tabular, semi-indurated laterite at ~10-4 m grades into an indurated laterite cap (4 m and up). Further details of the profile geology are described in Borger and Widdowson (2001) and Widdowson (2007).

Nine samples (BB1-BB9) were collected from the Bidar laterite for previous studies (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2007), each representative of zones of key textural change. The focus during the sampling was on the uppermost transition from saprolite to laterite and on representing the various mineralogical and textural changes in the upper, most highly weathered part of the profile. Approximately 1-3 kg of material was taken for each sample to minimise the vertical and horizontal heterogeneity that is common in deeply weathered laterite profiles. The same samples were used for the present study (Figure 3a).

3.3. Chhindwara profile

The Chhindwara District is situated on a 600-750 m elevation basaltic plateau that extends approximately 200 km NE from the Seoni-Chhindwara area toward Jabalpur (Figure 2). Throughout the area, terraced hillsides or low mesas of 50-100 m elevation are separated by flat-floored valleys containing ephemeral rivers draining eastward and southward. The higher elevation duricrust cap common to the Bidar area is absent. A transect through the Quaternary weathering front, located in a recently abandoned road stone quarry, 7 km east of Chhindwara (22° 04.213' N; 79° 01.393' E; Figure 2) was sampled in 2009; see field photographs (Figure 4).

Located at 741 m elevation, the weathering profile extends to a total exposed depth of >6 m across two clearly identifiable massive lava flows exposed in the face of the quarry (Figure 4a). Stratigraphically and geochemically, the two flows appear to belong to the Poladpur-Ambenali formation transition zone (Mitchell and Widdowson, 1991). In general, the flow-banded and higher vesicularity areas of both flows are more altered than the thicker, massive regions. This implies that the primary flow morphology has had a strong control on fluid penetration, chemical attack, and, consequently, chemical weathering intensity.

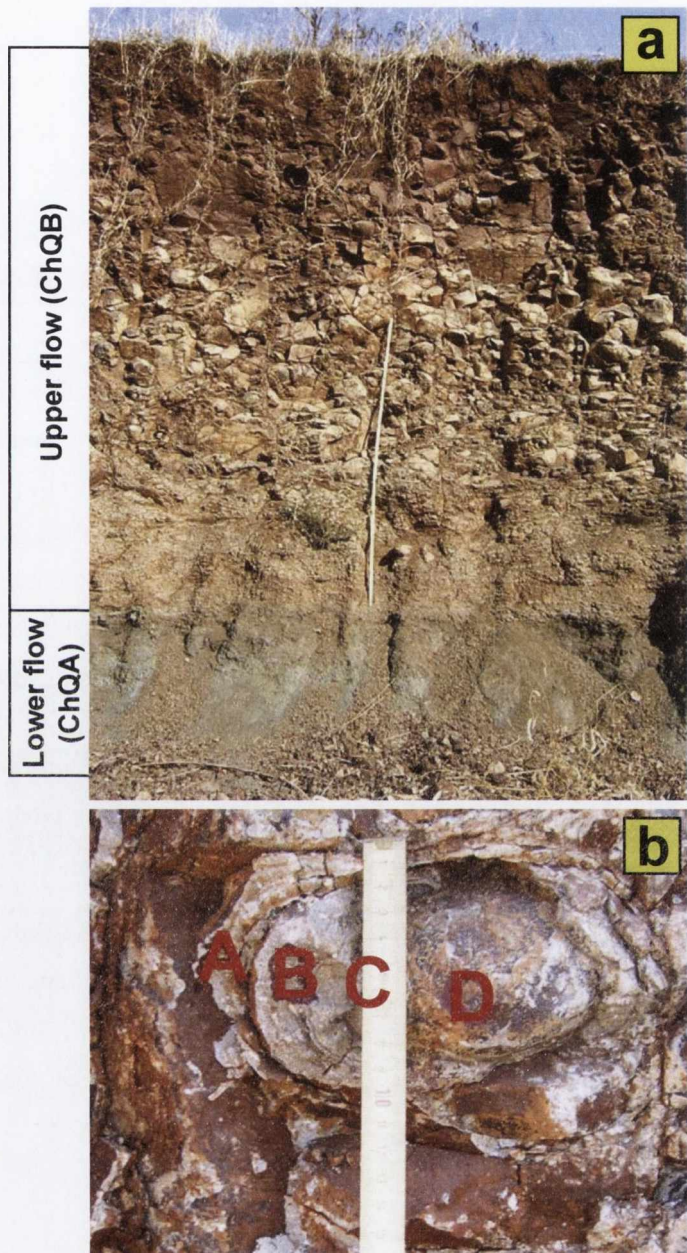


Figure 4: Field photographs of the Chhindwara weathering profile. (a) The entirety of the sampled weathering profile exposed in a road side quarry. Note the colour change marking the transition from the upper flow (ChQB) to the lower flow (ChQA). (b) Corestone within the upper flow at a depth of 90 cm from the surface that was divided into four sub-samples (ChQBa-d) for geochemical analysis.

The fully exposed (~4 m) upper flow (ChQB) has weathered to a rust red colour with spheroidal weathering features present throughout and is capped by a thin (~20 cm) soil horizon at the present day surface (Figure 4). The more massive, homogeneous basalt that constitutes most of the flow grades into a zone of weak 'banding' at the base (lower 80 cm), which may relate to rheological effects during emplacement and/or minor mineralogical variation. The weathering intensity in the flow, as indicated by the clay content, follows the aforementioned morphology transition, with a sharp increase in phyllosilicates near the base that is coincident with the appearance of the banded texture.

The transition from the upper to lower flow unit is clearly identifiable by the grayish colour of the latter. The colour is presumably a result of the higher abundance of pedogenetic clays and zeolite minerals. In this flow, vesicularity, made evident from zeolite-infilled amygdules, increases towards the flow top and terminates with a brecciated and highly vesicular flow top (~ 20 cm). The base of the lower flow is not exposed beyond the quarry floor. The colour and clay mineralogy are relatively consistent throughout the exposed portion (215 cm) of the lower flow, and suggests a higher (relative to the upper flow) but relatively consistent intensity of weathering. The difference in colour (from the rust red to brown to the greenish-gray) between the upper and lower flows could also indicate that the latter records an earlier weathering history. That is, it may represent a bole bed that formed during a period of volcanic quiescence in the DVP emplacement history (Ghosh et al., 2006; Sayyed and Hundekari, 2006) prior to the eruption of the upper flow. In addition, the presence of zeolite minerals in Deccan basalt is thought to have some control on the chemical weathering progression by retaining elements and inhibiting complete kaolinitisation (Bhattacharyya et al., 1999).

From the Chhindwara profile, a total of 27 samples were collected. The upper flow (ChQB1-B12) and lower flow (ChQA1-A12) are represented by 12 samples each and the remaining samples are from a horizontal profile through a corestone at a depth of 90 cm from the upper flow surface (ChQB9a,b,c,d; Figure 4b). The least-weathered samples of the profile, ChQB12 and ChQB9d, are located in the upper flow at a depth of 140 cm and within the corestone centre, respectively. The sample locations are indicated on a schematic log (Figure 3).

4. Methodology and analysis

Samples for the Chhindwara profile were pulverised in an agate mill to minimise metal contamination, whereas the powders for the Bidar profile were prepared in a tungsten carbide mill. The major element

composition for both profiles was determined by X-ray fluorescence (XRF) following loss on ignition (LOI) measurement; the Bidar XRF data were obtained at the Open University (UK) and reported previously (Kisakürek et al., 2004; Widdowson, 2007), while the Chhindwara samples were analysed at the Geoscience Laboratories (Sudbury, Ontario). Ferrous iron measurements were also obtained on Chhindwara samples at the Geoscience Laboratories via potentiometric titration with potassium permanganate.

All trace element data were obtained in the Department of Earth Sciences at Laurentian University. A 100 mg powder aliquot was digested in thoroughly cleaned 29 mL PFA screw-top beakers using a 2.5 ml HF plus 0.5 ml HNO₃ acid mixture. After a 72 h digestion period at 160°C, samples were dried down at 110°C to drive off SiF₄. The fluoride residue was attacked twice with 0.5 mL 6 N HCl to reduce organic components before double conversion with HNO₃. The converted residue was taken up in 10 g of 20% HNO₃ to yield a nominal 1:100 parts total dissolved solids stock solution. This was transferred to a clear polystyrene test tube and centrifuged to inspect for insoluble fluorides, which were not encountered.

For the trace element analysis, 0.2 g (i.e., 2%) of the stock solution was gravimetrically diluted to 6 g 2% HNO₃ together with a mixture of internal standards (10.6 ppb ⁶Li, 4.4 ppb each Rh, Re and Bi and 1.5 ppb ²³⁵U). A total of 46 trace elements were analysed by quadrupole ICP-MS (Thermo XSeriesII) using the methodology of Eggins et al. (1997) with some modifications (Kamber et al., 2003; Kamber, 2009). Calibration of analyses was performed using the USGS standard W-2 digested under the same conditions as the experiment unknowns. The preferred values for W-2 used for calibration have been reported previously (e.g., Babechuk et al., 2010). Long-term reproducibilities for most elements with this method are between 1 and 2% (e.g., Kamber, 2009; Babechuk et al., 2010; Marx and Kamber, 2010). The major element and trace element data set relevant to the present study is reported for the Bidar profile in Table 1 and the Chhindwara profile in Table 2.

5. Results and discussion – Part I

Major elements, loss on ignition, and quantification of the extent of weathering

In the following sections, the bulk major element trends of the Bidar and Chhindwara weathering profiles are interpreted using the widely recognised chemical index of alteration (Section 5.1), as well as the new mafic index of alteration and index of lateritisation (Sections 5.2 and 5.3). A useable

Table 1: Major^a (wt. %) and trace element (ppb) data for the Bidar (BB) laterite profile

	BB1	BB2	BB3	BB4	BB5	BB6	BB7	BB8	BB9
Depth (cm)	4700	3500	2600	1500	1300	1100	600	500	200
SiO ₂	48.90	50.06	38.59	38.78	30.61	6.12	36.68	31.35	9.59
TiO ₂	2.16	2.29	5.11	4.78	5.76	1.40	2.44	2.33	2.03
Al ₂ O ₃	13.72	14.15	31.54	31.95	25.83	6.97	31.3	27.22	9.85
Fe ₂ O _{3(T)}	13.40	12.63	24.10	21.64	36.95	84.81	27.70	38.37	77.53
MgO	6.93	5.99	0.40	0.38	0.23	0.14	0.26	0.10	0.16
MnO	0.19	0.22	0.11	0.06	0.06	0.03	0.33	0.07	0.23
CaO	10.99	11.45	0.19	1.91	0.07	0.00	0.05	0.00	0.04
Na ₂ O	2.46	2.78	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K ₂ O	0.16	0.25	0.02	0.01	0.02	0.00	0.03	0.07	0.03
P ₂ O ₅	0.16	0.19	0.18	0.03	0.08	0.33	0.07	0.08	0.12
LOI	0.60	0.72	11.7	12.4	11.1	11.1	11.4	11.1	7.31
Total	99.07	100.01	100.24	99.54	99.61	99.8	98.86	99.59	99.58
CIA	36.5	36.0	99.9	90.4	99.9	100.0	99.9	99.7	99.7
MIA _(O)	35.0	35.5	97.8	91.3	98.8	99.4	98.6	99.4	99.3
IOL	35.7	34.9	59.0	58.0	67.2	93.7	61.7	67.7	90.1
Nb	9262	10200	18940	18600	23480	5646	14490	16900	14030
Li	4466	5159	7019	3736	4271	1202	13230	19960	7304
Rb	956	5678	1165	335	811	321	1524	3996	1332
Cs	8.3	221	114	68	102	37	142	407	98
Tl	3	24	8	16	29	7	272	43	140
Be	606	632	2435	1289	1319	3814	859	1080	718
Sr	208500	227600	13750	23690	6022	46070	15490	9748	9974
Ba	50840	92870	59310	10600	16260	24810	398600	17800	153400
La	8587	10310	31320	4642	9357	35770	26390	13080	6333
Ce	21800	24700	25510	15510	21650	119200	285000	27490	53920
Pr	3250	3729	16140	1724	4044	8776	4007	2590	1569
Nd	15510	17760	74510	7240	17300	32630	11510	8986	5757
Sm	4448	5035	28320	1717	4166	7276	1901	1885	1264
Eu	1592	1786	12010	490	1134	1832	464	490	320
Gd	5264	6039	62890	1657	3688	5340	1444	1627	1009
Tb	850	968	12620	288	620	860	274	297	181
Dy	5083	5758	91420	1791	3642	4878	1516	1856	1091
Ho	1028	1170	21860	365	712	926	300	385	220
Er	2688	3047	63010	1022	1956	2614	848	1137	627
Tm	379	425	9016	162	310	440	137	189	103
Yb	2290	2556	53590	1087	2003	3089	933	1297	707
Lu	321	360	8079	155	280	425	131	188	99

^a Major element data has been recalculated without the LOI as reported in Borger and Widdowson (2001) and Kisakürek et al. (2004)

Table 2: Major (wt. %) and trace element (ppb) data for the Chhindwara (ChQ) weathering profile

	ChOA1	ChOA2	ChOA3	ChOA4	ChOA5	ChOA6	ChOA7	ChOA8	ChOA9	ChOA10	ChOA11	ChOA12	ChOB1	ChOB2	ChOB3	ChOB4	ChOB5
Depth (cm)	630	610	590	550	530	510	490	470	450	430	420	410	405	390	370	350	330
SiO ₂	40.91	41.70	41.02	42.00	41.99	41.38	41.23	41.72	41.98	45.44	46.92	45.14	41.76	41.43	41.29	42.14	43.69
TiO ₂	2.97	3.03	3.10	3.03	3.10	2.92	2.91	2.91	3.04	2.52	2.43	2.27	2.58	2.72	2.59	2.67	2.55
Al ₂ O ₃	13.19	12.46	12.50	12.28	12.66	12.87	13.08	12.86	13.23	11.53	11.72	12.44	15.16	15.85	14.99	15.14	14.48
Fe ₂ O _{3(T)}	17.18	18.21	18.39	17.59	17.65	16.97	16.50	17.04	16.59	16.57	15.91	16.23	16.40	16.74	17.97	17.14	16.82
FeO	1.71	1.51	1.81	1.71	1.64	1.47	1.24	1.37	1.38	0.92	0.85	0.82	0.47	0.60	1.18	1.10	2.42
MgO	2.30	2.45	2.43	2.69	2.68	2.72	2.94	2.94	3.01	3.72	3.30	3.43	2.61	2.74	2.28	2.14	2.97
MnO	0.21	0.25	0.26	0.21	0.15	0.22	0.27	0.22	0.25	0.18	0.22	0.20	0.39	0.38	0.31	0.31	0.26
CaO	2.62	2.47	2.20	2.23	1.91	1.97	2.05	1.90	1.88	1.53	1.39	1.40	1.97	1.92	2.92	3.29	5.39
Na ₂ O	0.55	0.43	0.26	0.22	0.02	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.30	0.26	0.84	1.04	1.59
K ₂ O	0.27	0.36	0.41	0.43	0.58	0.42	0.25	0.32	0.33	1.79	1.82	1.69	0.64	0.48	0.31	0.29	0.26
P ₂ O ₅	0.25	0.26	0.24	0.24	0.21	0.19	0.23	0.16	0.17	0.08	0.05	0.03	0.17	0.14	0.20	0.22	0.21
LOI	18.41	17.00	17.90	17.85	17.90	18.95	19.12	18.58	18.07	15.90	15.87	16.47	17.42	16.68	15.01	14.83	10.86
Total	98.86	98.61	98.71	98.78	98.86	98.59	98.57	98.58	98.56	98.80	99.55	99.24	99.40	99.33	98.69	99.20	99.10
ClA	71	72	74	74	78	78	79	79	80	72	73	74	78	79	70	67	54
MI(A ₀)	68	68	70	68	70	69	68	69	68	63	63	64	70	71	68	67	56
IOI	43	42	43	42	42	42	42	42	42	38	37	39	43	44	44	43	42
Nb	13180	13900	14130	14050	13920	13350	13100	13620	13910	11940	11310	10320	10170	10620	10120	10280	9728
Li	5704	6372	6893	8006	6533	5848	5279	5899	5066	10430	10340	8789	6570	6290	5076	5351	5167
Rb	10860	12050	15800	15730	22800	16430	9251	13770	13240	80360	75650	70450	10460	8058	5368	4333	3551
Cs	267	263	357	274	485	321	130	111	281	1963	1528	1377	111	150	236	188	145
Tl	27	32	38	40	41	48	41	43	47	130	128	107	95	66	39	37	25
Be	775	855	856	1013	966	901	820	818	803	803	809	839	846	807	803	796	700
Sr	94860	87130	71690	81900	55070	65040	58590	50270	42330	36120	34680	36640	61940	57760	102000	113400	151900
Ba	59970	59280	56570	64120	43630	67110	65600	44470	34010	76710	84040	64760	172400	91070	89130	93010	94790
La	13550	17020	15250	16040	14300	13480	17270	14070	13160	11540	10260	10100	13730	11770	15300	13710	12560
Ce	34980	38790	37270	37430	33820	38470	45310	39900	56790	33210	28960	23080	32290	35070	32620	32290	29130
Pr	4998	6149	5290	5747	5107	4893	6398	5074	4803	3803	3305	3338	5150	4507	5556	4901	4488
Nd	22620	27900	23880	26050	22890	22200	28810	22700	21390	16530	14440	14970	23770	20550	26090	22960	20970
Sm	6081	7479	6395	6966	6075	5961	7656	6039	5648	4371	3844	4095	6450	5697	7083	6283	5732
Eu	1969	2404	1958	2200	1717	1694	2082	1628	1451	1238	1173	1353	1956	1745	2367	2116	1984
Gd	6750	8345	7248	7737	6520	6412	8106	6401	5907	4553	4161	4652	7109	6210	8054	7185	6593
Tb	1092	1333	1158	1234	1043	1043	1290	1031	947	745	691	763	1144	1036	1274	1130	1046
Dy	6525	7847	6916	7167	6100	6083	7476	6074	5550	4387	4133	4635	6789	6297	7569	6657	6226
Ho	1313	1559	1391	1413	1204	1208	1473	1216	1097	867	834	939	1364	1272	1518	1334	1243
Er	3516	4085	3666	3666	3180	3193	3884	3260	2911	2287	2236	2543	3652	3441	3992	3510	3250
Tm	502	574	517	513	448	459	531	476	422	331	324	368	524	500	564	489	456
Yb	3112	3503	3168	3088	2783	2870	3395	3024	2702	2068	2078	2356	3241	3138	3433	2970	2769
Lu	427	476	437	417	378	393	464	424	374	286	291	337	453	441	478	413	389

ChOB6	ChOB7	ChOB8	ChOB9a	ChOB9b	ChOB9c	ChOB9d	ChOB10	ChOB11	ChOB12
310	210	110	90	90	90	90	10	0	140
46.95	46.35	47.34	45.12	47.58	48.16	48.75	41.28	39.98	48.72
2.32	2.23	2.35	2.33	2.31	2.24	2.36	2.78	3.32	2.23
13.39	13.7	12.98	13.22	13.11	13.03	13.69	14.92	15.17	12.93
15.40	15.73	15.60	17.20	15.42	15.23	13.36	18.16	19.92	15.07
6.17	6.18	7.00	4.71	6.58	7.20	6.55	4.97	5.20	9.75
4.71	4.75	4.92	3.88	4.87	5.09	5.03	3.95	3.62	5.46
0.21	0.22	0.23	0.25	0.23	0.22	0.20	0.24	0.30	0.23
9.06	8.43	9.48	6.88	9.38	9.90	10.16	5.43	5.57	10.55
2.11	1.81	2.26	1.57	2.25	2.33	2.49	0.68	0.91	2.43
0.31	0.18	0.22	0.19	0.22	0.23	0.23	0.12	0.29	0.28
0.21	0.19	0.21	0.20	0.20	0.20	0.21	0.20	0.16	0.20
4.93	6.01	3.55	8.57	4.31	3.40	3.33	10.78	10.04	1.51
99.59	99.59	99.12	99.42	99.87	100.04	99.79	98.53	99.27	99.61
40	43	39	47	39	38	38	58	57	36
42	44	41	50	41	40	39	56	57	38
38	39	38	40	37	37	36	44	47	36
8956	8279	9195	8880	8575	8566	8821	10670	12220	8554
5583	6094	5933	5178	5330	5526	5360	7695	11970	5713
3287	1853	1644	1802	1477	1447	1231	2008	13700	5226
82	79	79	85	60	51	30	74	509	89
12	14	17	33	21	11	8	34	63	46
773	629	726	750	630	681	573	890	908	686
185500	166500	195500	145900	191000	198000	210200	125600	112000	201500
99950	86700	113600	92080	95020	99650	110400	182400	165200	83570
12660	10520	12460	11180	11440	11130	11520	19250	12450	10800
26220	24890	27970	27310	26540	26810	27650	28900	32240	26790
4549	3880	4442	4071	4029	3936	4032	6346	4344	3876
21560	18520	20980	19230	19000	18620	18700	29780	19770	18270
6133	5258	5960	5408	5397	5290	5296	8280	5483	5137
2209	1906	2113	1870	1917	1846	1898	2839	1849	1809
7475	6212	7105	6284	6547	6383	6369	10170	6305	6103
1201	1006	1159	1014	1072	1036	1044	1623	1041	994
7396	6090	7100	6101	6573	6389	6402	9809	6271	6058
1505	1229	1440	1228	1342	1319	1319	2013	1286	1246
4005	3283	3857	3293	3599	3560	3527	5302	3448	3319
568	466	547	471	509	504	501	741	497	473
3453	2842	3328	2880	3115	3070	3020	4442	3080	2901
481	398	468	405	441	441	426	626	434	413

spreadsheet that demonstrates the weathering index calculations can be found in the supplementary materials. Each weathering index is also discussed on accompanying ternary diagrams that allow for the graphical interpretation of the proportional chemical changes. Included in ternary plots for comparison is a data compilation of published sub-Recent basaltic weathering profiles and Tertiary basaltic laterite and bauxite profiles (Chesworth et al., 1981; Eggleton et al., 1987; Marsh, 1991; Price et al., 1991; Nesbitt and Wilson, 1992; Karrat et al., 1998; Rudnick et al., 2004; Retallack, 2008; Oh and Richter, 2005; Hausrath et al., 2011; Sanematsu et al., 2011; Liu et al., 2013). In Section 5.4, correlations of the weathering indices with the loss on ignition further demonstrate the mineralogical transformations that dictate the chemical weathering trends.

5.1. The chemical index of alteration (CIA)

5.1.1 Quantifying the intensity of weathering with the CIA

Most igneous rocks of varying composition will plot between a CIA value of 35 and 50, with mafic rocks occupying the lower values. Similar to other basalts, the least-weathered (parent rock) samples of both the Chhindwara and Bidar profiles yield a CIA value of ~35.

During chemical weathering, the values of weathering indices increase due to the loss of mobile elements relative to an element assumed to be immobile. The CIA predominantly tracks feldspar dissolution and the concomitant release of Ca, Na, and K relative to Al, since the latter is typically retained within pedogenetic clays. This is evident in the clear separation of the CIA values of primary minerals (e.g., plagioclase, pyroxene: 50 and under) from those of pedogenetic minerals such as smectites, illite (70-85), and kaolinite (100).

In the Chhindwara profile, the samples extend from the unweathered CIA value of 35 to a maximum of 80 in their most altered state. This indicates that the most weathered samples of the Chhindwara profile have not yet reached complete 'kaolinitisation' and still retain a detectable amount of the labile elements (Ca, Na, and minor K), possibly due to the presence of zeolite minerals (Bhattacharyya et al., 1999). By contrast, the altered samples of the Bidar laterite profile have CIA values of 90 or greater. These high CIA values indicate the near-complete removal of the labile major elements. The CIA is ineffective at quantifying or differentiating elemental changes during the advanced stages of weathering since the dominant process occurring during lateritisation is desilication and Si is not factored into the CIA.

5.1.2 The A–CN–K diagram

The greatest strength of the CIA as a chemical weathering proxy is the utility of the accompanying A–CN–K diagram, which has empirically and kinetically predictable weathering vectors for various minerals and rock types (e.g., Nesbitt and Young, 1984; Nesbitt, 1992). The overall weathering vector for feldspar destruction in various different parent rocks is parallel or sub-parallel to the A–CN axis (e.g., Figure 5a). The precise vector direction is a function of the relative proportion of plagioclase and K-feldspar, their congruent or incongruent dissolution, and the rate of conservation of aluminous weathering products. As predicted for basalt weathering (Nesbitt and Wilson, 1992), the majority of the Chhindwara samples follow a weathering trend that is adjacent to the A–CN join (Figure 5a). Should the degree of weathering continue, the vector is predicted to continue along the A–CN join until it reaches the A apex and Ca, Na, and K are completely removed (complete ‘kaolinitisation’). Further chemical weathering trends cannot be represented in the A–CN–K plot, as demonstrated by the Bidar laterite samples, which cluster around the A apex (Figure 5a).

5.1.3. K enrichment

A further utility of the A–CN–K plot is identifying and unravelling the effects of potassium enrichment in weathering profiles (Fedo et al., 1995). Enrichment of K results in a trend away from the weathering vector towards the K apex. This is evident in three samples located near the contact of the lower flow (ChQA) in the Chhindwara profile (K concentration of 1.7–1.8 wt.%). The position of these samples deviates from the main weathering trend in the A–CN–K plot defined by the remainder of the profile (Figure 5a). The significance of these samples is discussed further in Section 6.2.3.

5.2. The mafic index of alteration (MIA)

5.2.1 Introduction to the MIA

The mafic index of alteration (MIA) is proposed here as a chemical weathering index that extends the equation of the CIA to include the mafic elements Mg and Fe. Many of the mafic minerals (pyroxene, olivine) are susceptible to chemical weathering, resulting in the loss of Mg from weathering profiles. The loss of Mg can be monitored independently using the Mg index (MgI; Maynard, 1992). By contrast to Mg, the fate of Fe during the weathering of most mafic minerals is redox-dependent. In reducing environments, ferrous iron [Fe^{2+}] can be mobile and leached along with Mg during mafic mineral weathering. In oxidative weathering environments, however, Fe is usually retained by the

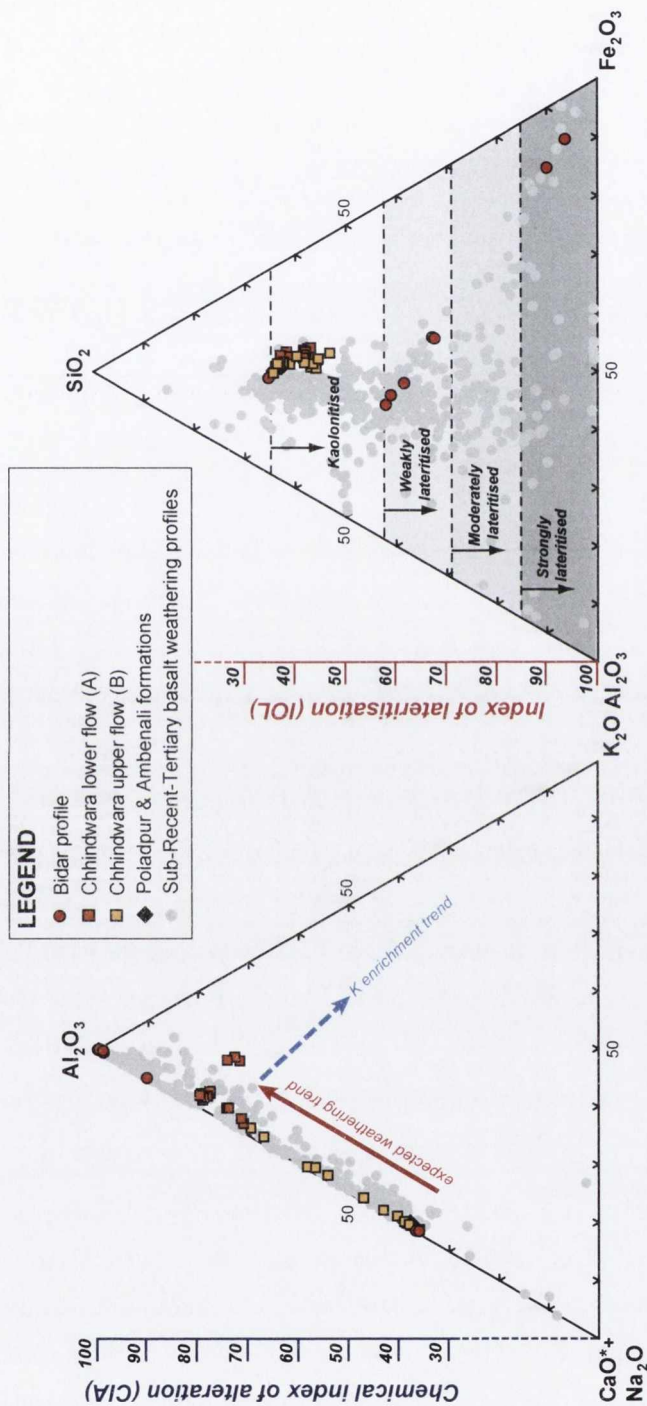


Figure 5: (a) Molar Al_2O_3 - CaO^*+Na_2O - K_2O (A-CN-K) and (b) mass SiO_2 - Al_2O_3 - Fe_2O_3 (T) (SAF) ternary plots illustrating the different degrees of alteration experienced between the Chhindwara (solid squares) and Bidar (solid circles) weathering profiles. The figure symbols for the Bidar and Chhindwara samples and the data compilation are consistent throughout all subsequent figures unless specified otherwise. In both figures, a data compilation of sub-Recent mafic weathering profiles and Tertiary basaltic laterite a and bauxite profiles is plotted as shaded circles (see text for references). The chemical index of alteration (CIA) and the index of lateritisation (IOL) may be integrated into both the A-CN-K and SAF ternary plots, respectively, as shown. In the SAF plot, the kaolinitisation and lateritisation boundaries are calculated from the chemistry of BB1 (parent rock of the Bidar profile).

formation of highly insoluble ferric iron $[\text{Fe}^{3+}]$ oxides or oxyhydroxides (e.g., Driese, 2004) and thus enriched along with Al. Due to this dichotomous redox behaviour of Fe, an arrangement of the MIA is proposed for each of the end-member weathering environments.

When the alteration environment is oxidising and Fe is retained, total Fe is considered an immobile element along with Al (Al_2O_3) and the MIA calculation is:

$$\text{Eq. 1: } \text{MIA}_{(\text{O})} = 100 \times [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})}) / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})} + \text{MgO} + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})]$$

When the alteration environment is reducing and Fe is leached along with Mg, total Fe is considered a mobile element along with Mg, Ca, and K and the MIA calculation is:

$$\text{Eq. 2: } \text{MIA}_{(\text{R})} = 100 \times [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})} + \text{MgO} + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})]$$

In both arrangements of the MIA [$\text{MIA}_{(\text{O})}$ or $\text{MIA}_{(\text{R})}$], increasing index values represent progressively more altered rock, as is the case with the CIA. A value of 100 indicates complete removal of the mobile elements. As with the CIA, the MIA uses the molar ratios of the major element oxides by converting the wt. % concentrations into moles (see Table 3). The molar CaO is corrected for the presence of carbonate and apatite as for the CIA (e.g., Fedo et al., 1995) to consider only the silicate-bound Ca (CaO^*).

In addition to the index value, the proportional changes of the elements in the MIA can be studied graphically with ternary plots in the Al–Fe–Mg–Ca–Na–K system (e.g., Nesbitt and Young, 1989; Nesbitt and Wilson, 1992) whereby both versions of the MIA are arranged into the plots in the same manner as the CIA with the A–CN–K diagram. The $\text{MIA}_{(\text{R})}$ arranges into the Al_2O_3 –($\text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}$)–($\text{Fe}_2\text{O}_{3(\text{T})} + \text{MgO}$) (A–CNK–FM) plot (Nesbitt and Young, 1989), while the $\text{MIA}_{(\text{O})}$ arranges into the Al_2O_3 –($\text{MgO} + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}$)– $\text{Fe}_2\text{O}_{3(\text{T})}$ (A–L–F) plot (Nesbitt and Wilson, 1992) as well as the newly proposed $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})})$ –($\text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}$)–MgO (AF–CNK–M) plot. The details of these plots are presented in Sections 5.2.3–5.2.5.

It needs to be cautioned that the MIA calculation values and the trends in ternary plots will vary slightly depending on the use of FeO or Fe_2O_3 for total Fe due to the cation mole difference. The factor for converting between FeO wt. % and Fe_2O_3 wt. % is shown in Table 3. Either oxide can be applied in the MIA, but consistency should be used between the weathering index calculations and the ternary plots and when comparing separate data sets. In this study, the moles of Fe are calculated using the total Fe as Fe_2O_3 . All literature values used were recast to total Fe expressed as Fe_2O_3 and all of the

Table 3: Mole conversions for weathering index calculations

$$\begin{aligned} \text{moles Al}_2\text{O}_3 &= \text{wt \% Al}_2\text{O}_3 \div 101.96 \\ \text{moles Fe}_2\text{O}_3 &= \text{wt \% *Fe}_2\text{O}_3 \div 159.69 \\ \text{moles FeO} &= \text{wt \% FeO} \div 71.84 \\ \text{moles MgO} &= \text{wt \% MgO} \div 40.30 \\ \text{moles CaO} &= \text{wt \% CaO} \div 56.08 \\ \text{moles Na}_2\text{O} &= \text{wt \% Na}_2\text{O} \div 61.98 \\ \text{moles K}_2\text{O} &= \text{wt \% K}_2\text{O} \div 94.20 \\ \text{moles P}_2\text{O}_5 &= \text{wt \% P}_2\text{O}_5 \div 141.94 \\ \text{moles CO}_2 &= \text{wt \% CO}_2 \div 44.01 \end{aligned}$$

$$\text{CaO}^* = \text{moles CaO} - \text{moles CO}_2_{(\text{calcite})} - (0.5 \times \text{moles CO}_2)_{(\text{dolomite})} - [(10/3) \times \text{moles P}_2\text{O}_5]_{(\text{apatite})}$$

$$\text{*wt \% Fe}_2\text{O}_3 = \text{wt \% FeO wt} \div 0.8998$$

major element oxides subsequently normalised to 100% on an anhydrous basis to allow for accurate comparison.

The application of the MIA and associated ternary plots to studying weathering profiles is best accompanied with independent knowledge of the redox-related behaviour of Fe. This can be accomplished with independent tests of iron immobility or the determination of the Fe^{2+} content. For example, a ternary plot of Al_2O_3 – MgO – $\text{Fe}_2\text{O}_{3(\text{T})}$ (A–M–F) or a cross-plot of the CIA vs. $\text{Fe}_2\text{O}_{3(\text{T})}$ can be used to examine the net behaviour of iron (i.e., retention or loss) in a weathering profile relative to Al, as demonstrated by Young (2013). Plots of total Fe vs. Ti or Al have also been used to test for iron mobility (e.g., Rye and Holland, 1998).

5.2.2 Comparison of the MIA and CIA

There is an inherent range in MIA and CIA values for unweathered igneous protoliths reflecting bulk composition (see supplementary information). For the purpose of this study, discussion is limited to mafic compositions and their weathered products. The weathering index values of several mafic USGS standards and parent rock samples from the Bidar and Chhindwara profiles are summarised in Table 4. In all cases, the $\text{MIA}_{(\text{O})}$ values are low (less than 45) and close to the calculated CIA values. The CIA vs. $\text{MIA}_{(\text{O})}$ values from the Bidar and Chhindwara profiles are plotted in Figure 6a along with the compilation of sub-Recent mafic and Tertiary laterite/bauxite profiles. Overall, the $\text{MIA}_{(\text{O})}$ is only slightly lower than the CIA for the majority of samples and the data are very well correlated ($r^2=0.900$), confirming the similar bulk weathering behaviour of Mg, Ca, and Na. The overall correlation between the two indices is poorest between a CIA value of 60 and 85, which could indicate a slightly different behaviour of Mg from Ca and Na during pedogenetic clay formation in the intermediate weathering stages.

When examined in greater detail, it is evident that the $\text{MIA}_{(\text{O})}$ and CIA are nearly linearly correlated in the upper flow of the Chhindwara profile ($r^2=0.978$; up to a CIA and MIA value of approximately 70), but decoupled in the lower flow. In the latter, the CIA continues to increase to a value of 80 while the $\text{MIA}_{(\text{O})}$ remains relatively static between 68 and 70, suggesting a divergence in the behaviour of Mg and/or Fe from Ca and Na. The concentrations of Fe and Ti are correlated and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreases from 2.56 to 0.03 with increasing CIA values (Figure 6b) in the entire profile, suggesting complete Fe retention via oxidative weathering. Therefore, it appears that the CIA- $\text{MIA}_{(\text{O})}$ decoupling is most likely related to minor Mg retention in the samples from which Ca and Na are more heavily

Table 4: Weathering index values for mafic standards and parent rock samples

<i>Sample</i>			
<i>USGS^a</i>	CIA	MIA_(O)	IOL
BIR-1	36.3	30.5	35.8
BHVO-2	35.7	33.4	34.1
BCR-2	41.2	44.1	33.5
W-2	39.5	36.0	33.3
DNC-1	43.2	33.2	37.5
<i>Parent rocks</i>			
BB-1	36.5	35.0	35.7
ChQB12	36.0	38.0	36.5
ChQB9d (corestone centre)	38.0	38.8	35.7
<i>Deccan Traps (Widdowson et al., 2000)</i>			
average Poladpur formation	37.8	37.1	35.9
average Ambenali formation	37.2	37.4	37.2

^aweathering index values were calculated using the accepted values for the USGS standards

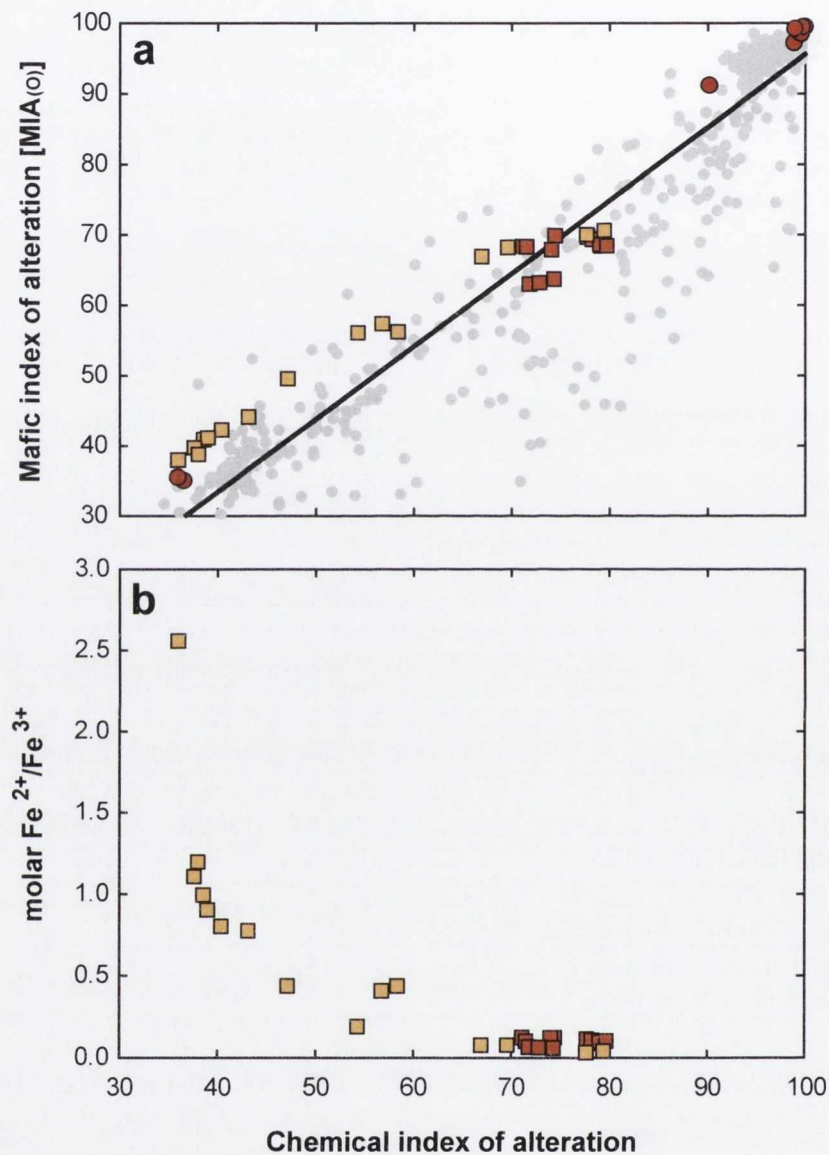


Figure 6: (a) Comparison of the $\text{MIA}_{(\text{O})}$ and CIA weathering indices for the Chhindwara and Bidar profiles, as well as the data compilation from Figure 5. (b) Plot of $\text{Fe}^{2+}/\text{Fe}^{3+}$ vs. CIA for the Chhindwara profile demonstrating the progressive conversion of Fe^{2+} to Fe^{3+} in the basalt with increasing weathering intensity.

depleted, perhaps in a smectite group mineral or zeolite. Consequently, the MIA is less sensitive to the chemical changes that occur in the lower flow of the profile.

In the Bidar profile, the $MIA_{(O)}$ values are high and relatively invariable (from 91 to 99), similar to the CIA, showing that the MIA suffers from the same inability to quantify the advanced to extreme stages of weathering.

5.2.3 The A–CNK–FM diagram

The A–CNK–FM ternary diagram was proposed by Nesbitt and Young (1989) in order to consider the mafic mineral component in rock weathering. In this plot (Figure 7a), the feldspar (felsic) weathering vector should follow a direction approximately away from the CNK apex through the position of the unweathered sample. The exact magnitude and direction is largely influenced by the rate of feldspar weathering and the type of secondary weathering product. The loss of Fe and Mg from the mafic minerals should result in a weathering vector that emanates away from the FM apex through the unweathered sample. During oxidative weathering, however, Fe is not typically lost from the system. This complicates the mafic weathering trends and contributes to the difficulty in predicting the overall rock weathering vectors (Nesbitt and Young, 1989; Nesbitt, 1992). Regardless, empirical data for Phanerozoic basalt weathering (e.g., Nesbitt and Wilson, 1992) show that progressive alteration of basalt results in a trend away from the CNK apex. Such a trend is evident in the Chhindwara weathering profile (Figure 7a). Taken alone, a net weathering vector emanating away from the CNK apex suggests a greater relative mobility and more extensive leaching of Ca, Na, and K compared to Mg. This may be misleading, however, since Mg is known to exhibit a similar bulk weathering behaviour to Ca and Na (Nesbitt and Wilson, 1992). Therefore, it appears that the behaviours of Fe and Mg are not accurately represented in the plot due to their contrasting behaviour in most (oxidative) weathering environments. It is not until Ca, Na, and K are depleted and the stages of advanced weathering are reached that change in the relative proportion of Mg, Fe and Al are recorded on the A–CNK–FM plot (Nesbitt and Young, 1989). This is demonstrated by the lateritised Bidar samples in Figure 7a, which fall on the A–FM axis and are a function of the relative proportion of aluminous (e.g., gibbsite, kaolinite) and ferruginous (e.g., hematite, goethite) pedogenetic products.

Our analyses suggest that the A–CNK–FM diagram is most applicable to weathering environments in which Fe^{2+} is mobile and behaves like Mg during chemical weathering (i.e., in reduced geochemical environments, such as recorded in Archean and early Proterozoic weathering profiles). In these environments, loss of Mg and Fe is summative and results in a mafic mineral weathering vector away

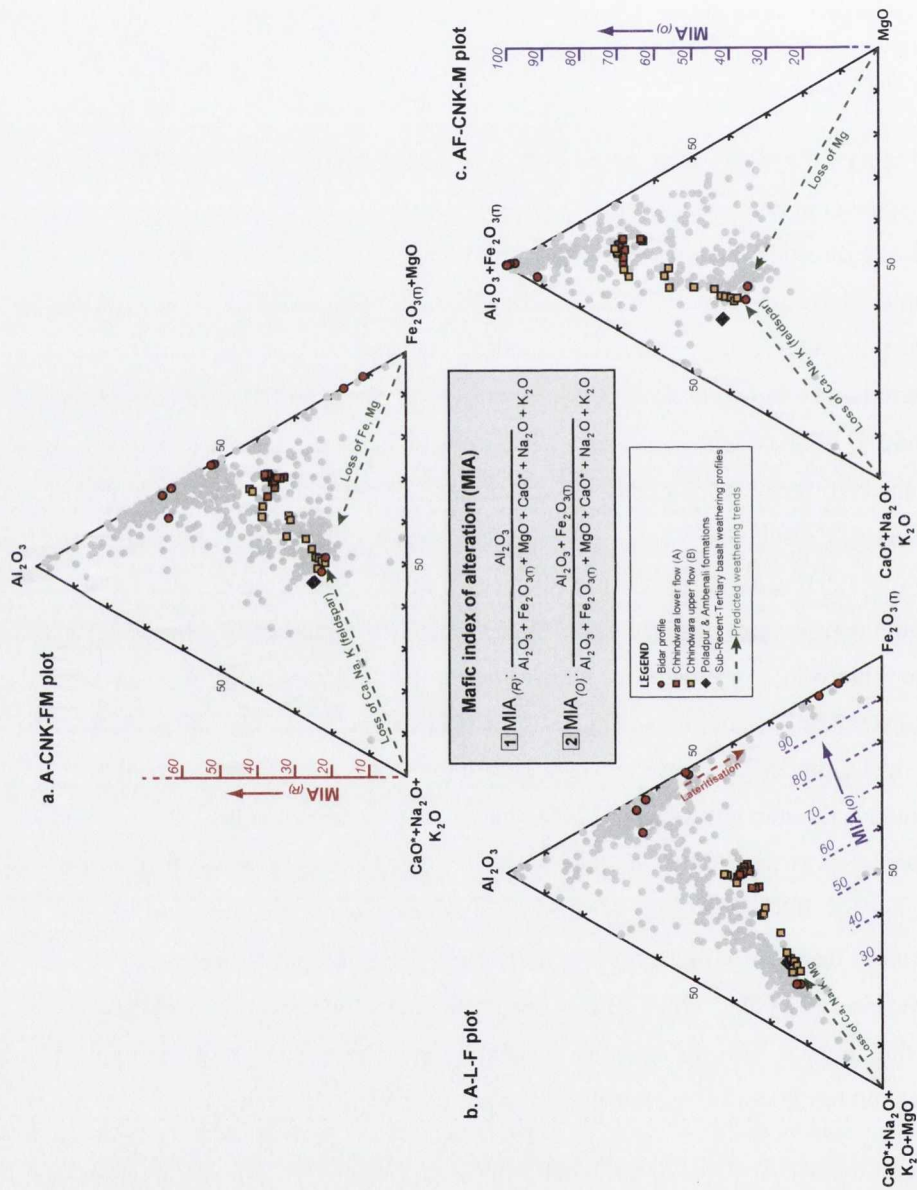


Figure 7: Molar ternary plots in Al-Fe-Mg-Ca-Na-K (AFMCK) space. See Table 3 for molar oxide conversions. The (a) A-CN-K-FM and (b) A-CN-K-M-F (A-L-F) plots were proposed by Nesbitt and Young (1989) and Nesbitt and Wilson (1992), respectively, while the (c) AF-CN-K-M plot (shaded) is proposed in the present study. These diagrams expose the contribution of the mafic and felsic mineral components to rock weathering. The integration of the new mafic index of alteration (MIA) into AFMCK space is illustrated; the A-CN-K-FM plot, most suitable for studying weathering in reducing environments, is integrated with the MIA_(R), while the A-L-F and AF-CN-K-M plots are integrated with the MIA_(O) for studying oxidative weathering trends. In addition to the Chhindwara and Bidar samples, the data compilation from Figure 5 is plotted as well.

from FM apex. Ultimately, this would result in a net weathering vector that is directed away from the CNK–FM axis towards the A apex. In this scenario, the $MIA_{(R)}$ can be projected into the diagram and is equivalent to the tie-line between the A–CNK and A–FM axes, as shown in Figure 7a. In oxidative weathering environments, one of the two following ternary re-arrangements is more useful.

5.2.4 The A–L–F diagram

One solution to the competing Fe and Mg vectors of the A–CNK–FM diagram, is the A–L–F diagram of Nesbitt and Wilson (1992), where Mg is moved to the same apex as Ca, Na, and K (Figure 7b). These four elements comprise the total labile (L) cation content. The upper apex is Al and the remaining axis becomes total Fe. In this plot, the net rock weathering vector is predicted to emanate away from the L apex through the position of the unweathered sample as Ca, Na, K, and Mg are lost. The magnitude of this vector represents the degree of element loss during weathering. This trend is demonstrated with the Chhindwara profile and the literature compilation in Figure 7b. Minor differences in the starting modal mineralogy and the exact pedogenetic weathering products, however, appears to result in slightly different slopes in the empirical weathering vectors. Complete loss of these elements would result in the trend reaching the A–F axis. Accordingly, the $MIA_{(O)}$ value in the A–L–F plot is equivalent to the tie line joining the L–A and L–F axes, with values increasing towards the A–F tie axis (MIA value of 100).

Although $MIA_{(O)}$ values reach a maximum at the A–F axis, one advantage of the A–L–F plot is that advanced weathering trends can be graphically visualised by trends moving towards the Fe apex (lateritisation) or the Al apex (bauxitisation). The proportion of the aluminous and ferruginous minerals in the advanced weathering residue can be extracted from the plot based on the sample position trend along the A–F axis (Nesbitt and Wilson, 1992). For example, the Bidar samples plot along the A–F axis moving towards the F apex, demonstrating the Fe enrichment in the profile (Figure 7b). Therefore, the plot is also useful for assessing the net behaviour of Fe (i.e., enrichment or loss) during weathering in modern and ancient weathering profiles, similar to the A–M–F plot (Young, 2013).

5.2.5 The AF–CNK–M diagram

For further assessing (oxidative) mafic weathering trends, another complementary ternary plot is proposed: the AF–CNK–M ternary plot (Figure 7c). This ternary diagram is generated by a simple rearrangement of Fe to the upper apex along with Al, leaving Mg to its own apex. As such, the plot

allows the immobile behaviour of Fe in oxidised weathering environments to be separated from the typically mobile behaviour of Mg. The main advantage of this arrangement of the apices is that the relative contribution of CNK (feldspar) dissolution to the overall weathering vector can be compared to that of Mg loss. The net weathering vector is the summation of the two independent vectors emanating away from the CNK and M apices towards the AF apex. This is demonstrated with the literature compilation in the plot (Figure 7c). On the scale of an individual weathering profile, the starting position and exact vector direction is influenced by the proportion of mafic minerals to feldspar and the rate at which they weather relative to each other. In the AF–CNK–M plot, the MIA is equivalent to the tie line between the CNK and M apices, increasing upwards toward the AF apex (MIA value of 100).

The samples from the Chhindwara profile on the AF–CNK–M plot illustrate that plagioclase weathering (loss of Ca, Na) has exceeded mafic mineral weathering (loss of Mg), resulting in an empirical trend that is directed slightly towards the AF–M join. However, by comparison with the A–CNK–FM plot, the AF–CNK–M plot confirms that Mg does contribute significantly to the weathering vector, since the empirical trend is not directed purely away from the CNK apex. Furthermore, the AF–CNK–M emphasises the change in weathering behaviour of Mg in the lower flow of the Chhindwara profile compared to the upper flow (Section 5.2.2); in the lower flow samples, the loss of Mg appears to slow while minor Ca and Na loss continues as indicated by the change to a horizontal vector in the diagram (Figure 7c).

In the AF–CNK–M plot, advanced weathering trends converge towards the AF apex and the enrichment of an Al vs. Fe cannot be diagrammatically visualised as it can in the A–L–F plot. Therefore, all of the Bidar laterite profile samples plot at or near the AF apex at $MIA_{(O)}$ values greater than 90.

5.2.6 Extended application and limitations of the MIA

The focus of the present study is to highlight the applicability of the MIA to quantifying weathering intensity and associated chemical changes in mafic substrates. Apart from this application, the use of the MIA may extend to studying intermediate and felsic rock weathering, sediments and sedimentary rocks, or different types of alteration. It needs to be strictly noted, however, that unweathered igneous rocks of different composition will have varying initial $MIA_{(O)}$ and $MIA_{(R)}$ values (Supplementary information). Therefore, a singular MIA value should not be used to infer the extent of weathering unless some knowledge of the parent rock to a weathering profile or sediment is known.

One of the unique applications of the MIA is for quantifying chemical weathering trends in the ancient paleosol record, since the $MIA_{(R)}$ can be applied to paleosols in which Fe is lost (anoxic paleosols), while the $MIA_{(O)}$ can be used for those in which Fe is retained (oxygenated paleosols). Similar to modern weathering environments, most Precambrian paleosols and clastic sedimentary rocks are significantly depleted in Ca and Mg and, thus, the MIA may be useful in the modelling of global chemical weathering fluxes in both the modern environments and the ancient rock record (e.g., Kramers, 2002). Additionally, both versions of the MIA can be calculated without K ($MIA-K$), in a manner analogous to the CIA, to counter the effects of K metasomatism (e.g., Fedo et al., 1995; Maynard, 1992). Caution must be used when inferring chemical weathering intensity in rocks that have experienced post-weathering Fe and/or Mg mobility.

5.3 The index of lateritisation (IOL)

It is clear that the $MIA_{(O)}$ and CIA are incapable of adequately quantifying the stages of advanced chemical weathering. A different approach is required that is suited to the chemical changes in laterite or bauxite profiles. During lateritisation, dissolution of quartz and kaolinite (congruent or incongruent) and the enrichment of Fe oxides are the dominant processes, resulting primarily in a loss of Si relative to Al and Fe in the weathered residue (e.g., Widdowson and Gunnell, 1999; Hill et al., 2000).

Schellmann (1981, 1982, 1986) proposed a chemical classification of laterites based on the $SiO_2/(Al_2O_3+Fe_2O_3)$ ratio and the $SiO_2-Al_2O_3-Fe_2O_3(T)$ (SAF) ternary plot to distinguish between kaolinitised, lateritised, and bauxitised weathering residues. First, a notional 'limit of kaolinitisation' for the early to intermediate stages of weathering can be calculated, which is associated with relatively minor Si loss. Desilication begins to dominate beyond this limit and a quantitative tripartite progression of the 'degrees' (i.e., weakly, moderately, and strongly) of lateritisation or bauxitisation can be made. This chemical classification, however, is not unanimously accepted (e.g., Bourman and Ollier, 2002; 2003) primarily because accurate representation of the alteration progression is premised upon the autochthony of a weathering profile (Figure 1) and there is a necessity to identify the protolith in order to complete the calculation. Therefore, there is potential of its inappropriate use without this type of thorough geological contextualisation. However, where applied in combination with careful geomorphological and geological interpretation, this method of chemical classification does offer significant insight into the alteration progression in a weathering profile (Schellmann, 2003; Widdowson, 2007). Accordingly, we promote use of the $SiO_2/(Al_2O_3+Fe_2O_3)$ ratio and here suggest that it should be referred to as the 'index of lateritisation' (IOL) or the 'index of bauxitisation' (IOB).

To be consistent with the chemical classification of laterite and the SAF plot, we define the IOL using the *mass* (wt. %) ratio of SiO_2 , $\text{Fe}_2\text{O}_{3(\text{T})}$, and Al_2O_3 , as shown in equation 4.

$$\text{Eq. 3: IOL} = 100 \times [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(\text{T})})]$$

The IOL value is designed to directly accompany the SAF diagram, similar to the approach of Hill et al. (2000). Unweathered mafic rocks have IOL values that are generally less than 40, as demonstrated by the mafic USGS rock standards and the least-weathered samples in this study (Table 4); for instance, unweathered Deccan basalt (BB1) gives an IOL value of 35.7. In a similar fashion to the CIA and MIA, higher IOL values correspond to more intensely weathered samples; accordingly, the calculated IOL values for increasingly weathered samples progressively fall within the divisions of kaolinitisation, weak, moderate, and strong lateritisation, as determined from the composition of the protolith. The aforementioned divisions are calculated based on the amount of Si necessary to convert Al in the protolith into kaolin (see Widdowson, 2007, and the method given in the supplementary materials). The limit of kaolinitisation for the Deccan basalt, calculated from sample BB1, is 43% SiO_2 (Figure 5). In terms of the IOL, this division between kaolinitisation and lateritisation occurs at an IOL value of 57; for reference, both BB3 and BB4 lie near this boundary (i.e., IOL value of 59 and 58, respectively).

In the Chhindwara profile, samples are restricted to IOL values of ~35-50, consistent with the modest loss of SiO_2 relative to Al_2O_3 and Fe_2O_3 during kaolinitisation. The Bidar laterite, however, extends across the kaolinitisation-lateritisation boundary and defines a clear trend towards the F apex with IOL values ranging from 57 to 94 (Figure 5b; Borger and Widdowson, 2001, Widdowson, 2007). The more extreme range in the IOL values is consistent with the upward increase in modal abundance of Fe oxides in the Bidar profile. As discussed previously, however, the samples BB5 and BB6 do not conform to the upward Fe-enrichment trend held by the remaining profile. These samples (~10-15 m depth; Figure 3), interpreted to represent a paleo-water table (e.g., Kisakürek et al., 2004; Widdowson, 2007), contain significantly higher Fe (and other metal) concentrations than would be expected at their stratigraphic position. Therefore, comparing the stratigraphy with the IOL may help to identify samples that do not meet the criteria for strict *in situ* formation.

5.4 Loss on ignition

The volatile content of a sample measured by the loss on ignition is considered proportional to the amount of hydrated minerals, in addition to carbonate, organic carbon, sulphur, less any mass gain

from oxidation of elements during analysis. The LOI value of a fresh basalt is typically less than 3 wt. %. During chemical weathering, as the primary and largely anhydrous magmatic minerals are replaced by hydrated pedogenetic phyllosilicates (e.g., smectites, illite, kaolinite), the LOI is expected to increase. Previous studies have shown that the LOI can be a useful parameter for assessing the degree of weathering (e.g., Duzgoren-Aydin and Aydin, 2003), although the specific pedogenetic mineralogy ultimately controls the degree of hydration (Duzgoren-Aydin et al., 2002). Plotting the CIA, $MIA_{(O)}$, or IOL weathering indices of the Chhindwara and Bidar profiles against the LOI provides further insight into the pedogenetic mineralogical transformations (Figure 8).

A distinct positive correlation between the LOI (~1 to 18 wt. %) and the $MIA_{(O)}$ or CIA weathering indices is exhibited by the Chhindwara samples (Figure 8a). By contrast, the more intensely weathered samples of the Bidar profile are removed from the correlation and are less hydrated, with LOI values ranging from ~7 to 12 wt.%. Whereas this may seem counter-intuitive, the lateritised samples are dominated by gibbsite, goethite, and hematite (Kisakürek et al., 2004) which are less hydrous than the intermediate weathering products (kaolinite, smectites). The replacement of the hydrated phyllosilicates by sesquioxides of Fe and Al during lateritisation results in an inverse correlation with the LOI (Figure 8b). In effect, this observation provides mineralogical corroboration of the SAF plot since the change in weathering vector in Figure 5b effectively represents the notional ‘limit of kaolinitisation’ determined for the parent basalt.

6. Results and discussion – Part II

Mass gains and losses of the alkali and alkaline earth elements

The following sections discuss the geochemical behaviour of the alkaline earth (Section 6.1) and alkali elements (Section 6.2) during basalt weathering. The analysis employs a combination of mass balance values, element-element ratios, and the major element chemical weathering indices. Combining the independently calculated mass changes with the chemical weathering indices has the power of linking high-precision trace element data with specific stages of basalt alteration. The discussion will only consider the Chhindwara weathering profile since the elemental systematics of the Bidar laterite have previously been analysed (e.g., Kisakürek et al. 2004) and have been complicated by ancient paleo-water table changes and aeolian input (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2007). The K-enriched samples in the lower flow of the Chhindwara profile (Section 5.1.3) are

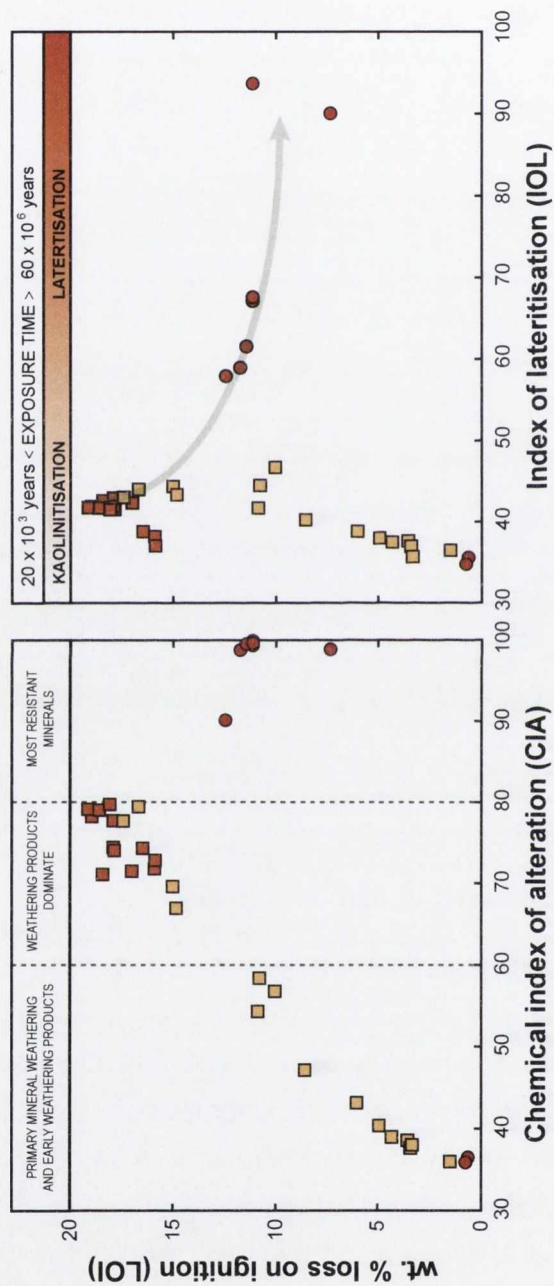


Figure 8: Co-variation of the loss on ignition (wt. %) with the (a) chemical index of alteration and (b) index of lateritisation. The calculated kaolinitisation and lateritisation boundaries from Figure 5b are shown on the latter. Strong correlations of the weathering indices with the loss on ignition during incipient to intermediate weathering (Chhindwara weathering profile) confirm the transformation of relatively anhydrous pyroxene and plagioclase to hydrous phyllosilicates (i.e., smectites and kaolinite). Over the much longer time scales of advanced weathering, Si is lost as these phyllosilicates are progressively altered to sesquioxides of Al and Fe. This trend is defined by a decreasing loss on ignition as the index of lateritisation increases.

discussed separately from the remaining samples in Section 6.2.2. The release or retention of elements in the profile is linked when possible with the Deccan Traps river water (Das et al., 2005) and sediment (Das and Krishnaswami, 2006, 2007) chemistry that is sourced from the DVP basaltic terrane.

For mass balance calculations, the tau (τ) mass transport model (Brimhall and Dietrich 1987; Anderson et al., 2002) is used. In this model, the concentrations (C) of elements (j) in the parent rock (p), relative to that of an immobile index element (i), are used as a normalisation to establish the mass changes in the progressively altered rock (w):

$$\text{Eq. 4: } \tau_{ij} = \{[(C_{j,w}) / (C_{j,p})] / [(C_{i,w}) / (C_{i,p})]\} - 1$$

The sample representing the parent rock of the Chhindwara weathering profile is ChQB12 (depth of 140 cm) based on its low degree of chemical alteration (CIA: 36, $MIA_{(O)}$: 38) and Nb is used the immobile index element (Widdowson and Cox, 1996). The $\tau_{Nb,j}$ values are plotted vs. depth in Figure 9. It should here be remembered that the Chhindwara profile is developed across two independent lava flows. Each flow can be fingerprinted chemically using immobile element ratios such as Al_2O_3/TiO_2 ; the upper flow has a mean ratio of 5.74 ± 0.35 whereby the lower flow is distinct with a mean ratio of 4.27 ± 0.19 . Normalisation using the immobile element composition of the parent material in the upper flow results in minor mass balance offsets ($\tau_{Nb,j}$ values) for elements in the lower flow that are unrelated to pedogenesis. This does not significantly influence the interpretation of the mass balance changes, but a slight inaccuracy in the reported mass gains and losses is expected as a result.

6.1 Alkaline earth elements (+ Na)

The elements of the alkaline earth group are the most mobile during continental weathering (e.g., Nesbitt et al., 1980), being hosted in mineral phases most susceptible to chemical attack, highly soluble, and, in general, incompatible in pedogenetic clays. In Figure 10, the $\tau_{Nb,j}$ values of the alkaline earth elements are plotted against the CIA and an anti-correlation exists for nearly all of the elements. The degree of element depletion (represented by the steepness of the slope) differs as a function of how closely related the behaviour of the element in question is to Na and Ca.

Within a 'stratigraphic' context, the degree of alkaline earth element (+ Na) depletion in the Chhindwara flows follows the visible extent of basalt alteration (Section 3.3); the $\tau_{Nb,j}$ values for the alkali elements change only minimally in the centre of the upper flow, but decrease near the modern

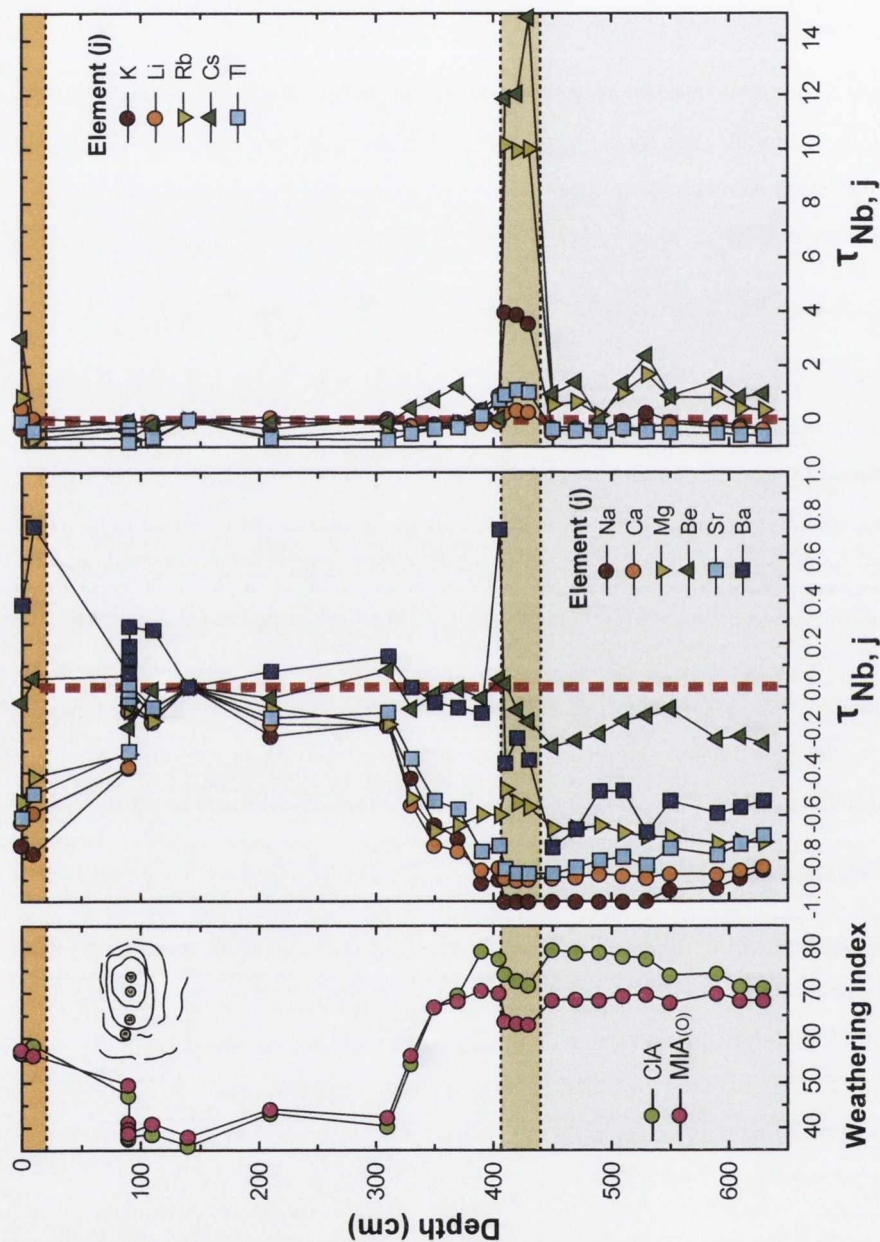


Figure 9: Stratigraphic variation of the weathering indices (MIA_(O) and CIA) (a) and mass balance (τ mass transport function) profiles of the alkaline earth (b) and alkali elements (c) for the Chhindwara weathering profile. The depth of the modern soil surface and the two individual lava flows are indicated. Mass balance calculations use Nb as the immobile index element and sample ChQB12 (depth of 140 cm) for the parent rock. Values less than 0 indicate a mass loss relative to the parent rock (up to 100 % or -1) while values greater than 0 are mass gains. Note the extreme enrichment in the alkali elements at the top of the lower flow (darker shading).

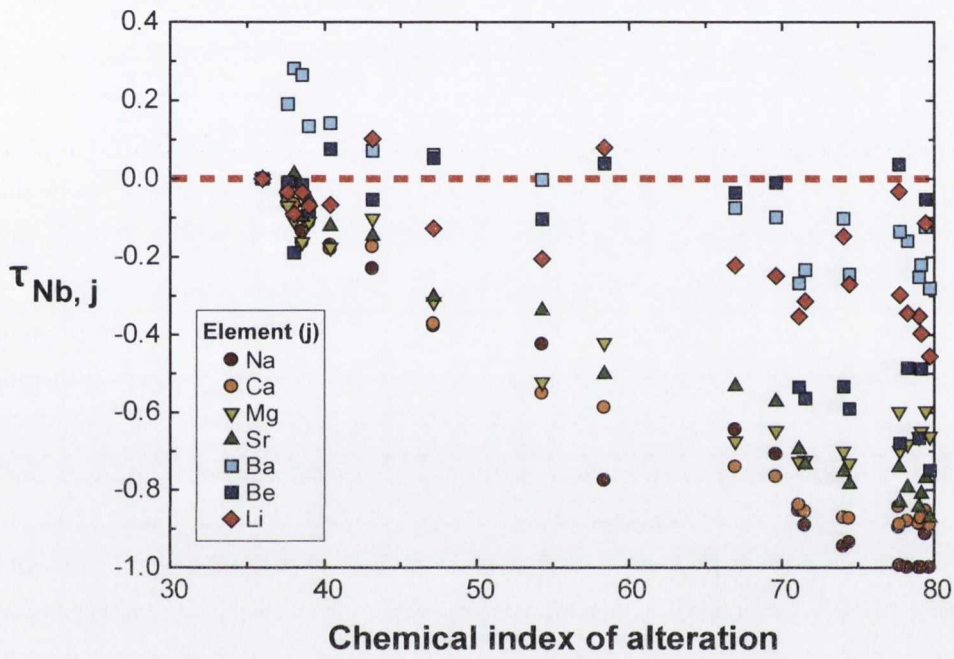


Figure 10: $\tau_{Nb,j}$ values vs. the CIA for the alkaline earth elements (plus Na and Li). Note that values below 0 (dotted line) represent a mass loss up to -1 (100 % depletion). The $\tau_{Nb,j}$ value of most elements is anti-correlated with the CIA indicating that they are mobile during the incipient to intermediate stages of weathering.

soil surface and at the flow-banded area at the base (Figure 9). Within the lower flow, the degree of depletion and CIA values are higher and increase from the deepest sample (ChQA1) towards the flow contact (ChQA10-12) in parallel with the vesicle (amygdale) abundance. The overall weathering behaviour of the alkaline earth elements (+ Na), assessed using the τ mass transport model and molar element ratios, suggests an order of susceptibility of $\text{Na} \approx \text{Ca} \approx \text{Sr} > \text{Mg} > \text{Ba} > \text{Be}$. This order of mobility during weathering, with the exception of Mg, is consistent with the data from work on the river sediments and water of the drainage basins in the Deccan Traps (Das et al., 2005; Das and Krishnaswami, 2006, 2007), as discussed further in the following sections.

6.1.1 Na, Ca, Sr

The behaviour of Ca, Na, and Sr is strongly linked in the profile. For example, the Sr concentration is highly correlated with the CIA ($r^2=0.977$) and the $\tau_{\text{Nb,Sr}}$ values with $\tau_{\text{Nb,Ca}}$ ($r^2=0.973$). These elements exhibit the greatest net depletion based on the $\tau_{\text{Nb,j}}$ values (Na: 100%, assuming a concentration of 0 for analyses below the detection limit of the XRF; Ca: 90%; Sr: 87%). They are hosted predominantly in plagioclase, which is highly susceptible to chemical weathering. The average molar Ca/Na ratio of the least-weathered basalt samples ($\text{CIA} \leq 40$: ChQB12, ChQB9b-d) in the Chhindwara profile is 2.26 ± 0.06 ($n=4$), which is near the average of the Poladpur and Ambenali formations (2.45-2.53; Subbarao et al., 2000; Widdowson et al., 2000). The Ca/Na is relatively constant in the remainder of the profile, with two exceptions. First, slightly lower Ca/Na ratios are present in three samples at the base of the upper flow (ChQB3-ChQB5; Ca/Na: 1.60-1.75), possibly indicating enhanced Ca removal. Second, the Ca/Na ratios approach infinity for the samples in which Na is below the detection limit of the XRF. This observation, coupled with the near constant molar Ca/Na ratios in Deccan river sediments (Das and Krishnaswami, 2007) and river waters (Das et al., 2005) suggests that Ca and Na are removed congruently from the Deccan basalt during chemical weathering.

6.1.2 Mg

A strong depletion of Mg follows the other alkaline earth elements at the base of the upper flow, as indicated by the correlation of $\tau_{\text{Nb,Mg}}$ with $\tau_{\text{Nb,Ca}}$ ($r^2=0.952$) and the relatively invariable molar Ca/Mg ratio. The latter ratio is similar to the least-weathered basalt samples (constant at 1.37 ± 0.03 , $n=4$) and the range exhibited by unweathered Deccan basalt (Subbarao et al., 2000; Widdowson et al., 2000). The change in weathering behaviour of Mg in the lower flow (Section 5.2.2) is expressed by lower Ca/Mg ratios, which range from 0.29 to 0.72. Although the spread in $\tau_{\text{Nb,Mg}}$ values in the lower flow is small (65-73% depletion), the minor variations appear to be anti-correlated with Ca, Na, and Sr loss.

This change in Mg weathering behaviour is unlikely to be important to the overall flux of Mg to the hydrosphere from the weathering of the Deccan basalt province. Near-constant Mg/Sr and Ca/Mg ratios of the Deccan river sediments suggest a similar and congruent weathering behaviour of Mg to these other alkaline earth elements (Das and Krishnaswami, 2007). However, the river water data do exhibit notable scatter in the Ca/Mg ratio (Das et al., 2005) and this may indicate that preferential leaching of Ca relative to Mg is important locally, consistent with the observations of Mg in the lower flow of the Chhindwara profile.

6.1.3 Ba

The $\tau_{Nb,Ba}$ values, although reaching up to 68% depletion, indicate a higher retention for Ba than most other alkaline earth elements and the values are less correlated with the CIA. There are some areas of local Ba enrichment (~75 %), such as near the soil surface. By comparison, the ionic radius of Ba^{2+} is larger and much closer to that of K^+ , suggesting a stronger association with pedogenetic phyllosilicates. Although Ba and K are not directly correlated in the Chhindwara profile, they are in the river sediments of the Deccan Traps (Das and Krishnaswami, 2007), indicating a broadly similar retention in sediments derived from the Deccan Traps.

Barium has long been known to exhibit a different weathering behaviour than the other, more mobile alkaline earth elements (e.g., Nesbitt et al., 1980; Buggle et al., 2011). It is often contrasted with Sr since the Ba^{2+} and Sr^{2+} ionic radii differ by roughly 12-13% in the same coordination, leading to the disparity in their mobility. Accordingly, the Ba/Sr ratio has been applied as an index of the degree of alkaline earth element depletion or leaching during hydrolysis (e.g., Retallack, 1994; Gallet et al., 1996). The Ambenali and Poladpur formations have average molar Ba/Sr ratios that range from 0.24 to 0.38 (Widdowson et al., 2000). The Ba/Sr ratio of the Chhindwara profile evolves from a similar ratio of ~0.3 in the least-weathered samples to a maximum of 0.7 (if the horizons of Ba enrichment are excluded). Collectively, the Ba geochemistry of Deccan Traps river waters and sediments confirm its less mobile behaviour during basalt weathering. The mean ratios of Ba to other alkaline earth elements (Sr, Mg, Ca) in Deccan rivers are typically 2-3 times lower than the Deccan basalt (Das and Krishnaswami, 2006) and the river sediment Ba/Sr ratios are highly variable, ranging from 0.3 to 3.2, with a mean value of 1.1 (Das and Krishnaswami, 2007). The sediment samples with the highest Ba/Sr appear to be heavily influenced by the sediments of the Krishna tributaries, which may have a greater input of lateritised products that experienced greater degrees of leaching.

6.1.4 Be

In the Chhindwara weathering profile, the $\tau_{\text{Nb,Be}}$ values are the highest of all of the alkaline earth elements, suggesting that it is the least mobile of the group. The best correlation of $\tau_{\text{Nb,Be}}$ is found with $\tau_{\text{Nb,Ba}}$ and $\tau_{\text{Nb,Li}}$. Despite its slight depletion, it appears that the small ionic radius of Be^{2+} results in a less mobile behaviour, possibly due to the greater potential of the cation to form insoluble hydrolysates.

6.2 Alkali elements (+thallium)

The alkali elements, with their lower ionic potential compared to the alkaline earths, are more strongly associated with the phyllosilicates, substituting into interlayer sites or adsorbing to clay mineral surfaces. Despite the high solubility of many of the alkali elements, this factor tends to lead to a lower mobility during weathering (Nesbitt et al., 1980). This is evident by the $\tau_{\text{Nb,j}}$ values for the alkali elements (see Figure 9 for values and trends with depth), which exhibit minimal to no positive or negative correlation with the CIA, indicating a strong decoupling from the mobile alkaline earth elements. When the $\tau_{\text{Nb,j}}$ values of several alkali elements are plotted against each other, two separate correlations normally result, suggesting that the mass balance calculations are more greatly influenced by the different parent flow chemistry. Included with the alkali elements is thallium (Tl) due to its similar geochemical properties, namely a commonly monovalent charge and similar ionic radius (Shannon, 1976). The behaviour of Li is largely decoupled from the remaining alkali elements and is discussed separately in Section 6.2.1.

Overall, the alkali elements closest in ionic radius exhibit the most similar behaviour and the correlations between the element concentrations and mass balance values decrease. For example, strong correlations exist between $\tau_{\text{Nb,K}}$ and $\tau_{\text{Nb,Rb}}$ within the separate flows in the Chhindwara profile ($r^2=0.832$ in the upper and $r^2=0.939$ in the lower). Using similar relative relationships, the behaviour of Cs is most closely associated with Rb, and the behaviour of Tl is closely related with Rb. In the latter case, a similar weathering behaviour can also be inferred from the strong correlation of these elements in alluvial sediment (Kamber et al., 2005).

6.2.1 Li

A more significant anti-correlation, similar to the alkaline earth elements, is found between the $\tau_{\text{Nb,Li}}$ values and the CIA (Figure 10). As an expected consequence, the $\tau_{\text{Nb,Li}}$ values correlate better with

those of Na, Ca, and Sr and less with the other alkali elements (i.e., Rb, K, Cs). The behaviour of lithium during continental weathering is reasonably well understood and the subject of more detailed focus due to stable isotope fractionation during pedogenesis (Huh et al., 2001; Rudnick et al., 2004). In general, Li is expected to be more mobile during weathering than the other alkali elements (excluding Na), but has a stronger affinity for phyllosilicates, likely as a result of coupled substitution with Mg^{2+} for Al^{3+} in the octahedral sites (Ronov et al., 1970; Anderson et al., 1989; Huh et al., 2004).

6.2.2 Alkali element enrichment

Excluded from the previous discussion were three samples from the lower flow of the Chhindwara profile that appear to have experienced K addition (Section 5.1.3). Based on the τ_{NbJ} values, this K enrichment is up to 400 % of the parent rock concentration. This enrichment extends to the other elements in the alkali group (Figure 9), with the most extreme enrichment exhibited by Cs (~1500 %), followed by Rb (~1000 %) and Tl (~110 %). In many Phanerozoic to modern weathering profiles, K enrichment is attributed to preferential uptake in plants and/or the addition of an allochthonous, K-rich material such as aeolian dust (Sheldon, 2003).

Stratigraphically, these samples constitute the vesicular and brecciated flow top. Accordingly, input of allochthonous material (dust or sediment) to the lava flow during or after emplacement is a likely explanation for the enrichment (e.g., Ghosh et al., 2006). Since the alkali elements are depleted in the mantle source of most basalt and highly enriched in the continental crust, only minor degrees of allochthonous addition could generate significant chemical enrichments. Further work, such as high-precision Nd isotope analysis could substantiate this hypothesis (Mason et al., 2000). The alternative explanation, biological enrichment of K (e.g., Sheldon, 2003), remains less favourable since the enrichment extends to the other alkali elements and it is localised to only the flow top zone.

7. Results and discussion – Part III

Behaviour of the rare earth elements during basalt weathering

The CI-chondrite normalised REE patterns of the three least-weathered samples from the Bidar (BB1) and Chhindwara (ChQB12 and ChQB9d) weathering profiles (Table 4) are nearly identical, differing only in absolute abundance. This justifies their use as parent rock values for normalising the progressively more weathered samples (Figure 11). This normalisation most readily exposes REE

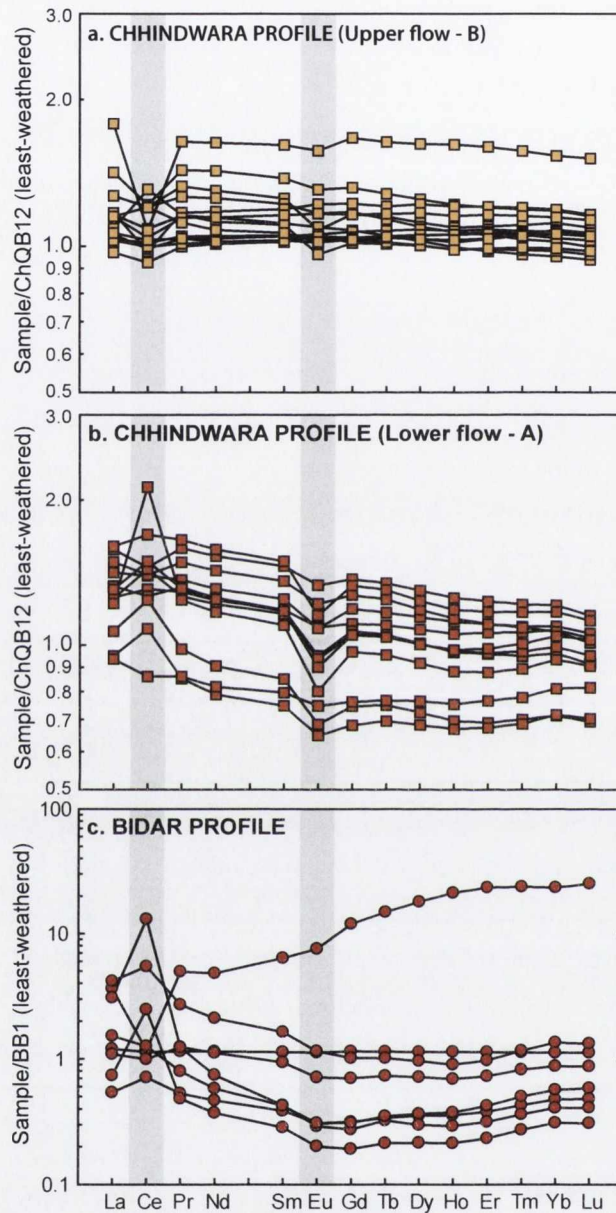


Figure 11: Normalised REE plots for the (a) upper and (b) lower flow of the Chhindwara profile and (c) the Bidar laterite. Note the change in scale between the two profiles. In each of the REE plots, the samples are normalised to the least-weathered (parent rock) samples (Table 4). Fractionation of the lanthanides is evident in the changes in the slope and the abundance relative to 1 (parent rock) in the plots. Highlighted for emphasis are Ce and Eu.

mobility (e.g., Laveuf et al., 2008). The REE are known to be variably mobile during weathering and fractionate during pedogenesis (e.g., Nesbitt, 1979; Duddy, 1980; Braun et al., 1993; Cotten et al., 1995; Laveuf and Cornu, 2009 and the references therein; Sanematsu et al., 2011), but there is still little consensus regarding the details of the behaviour.

7.1 Overall REE behaviour

Fractionation of the REE in the Chhindwara and Bidar weathering profiles is evident in the change in abundance and slope of the normalised REE patterns in Figure 11. In most of the Chhindwara samples, the REE are enriched relative to the parent rock (ChQB12) and the retention follows the general order of LREE>MREE>HREE during the weathering progression. This observation is consistent with previous studies regarding the mobility of the REE during pedogenesis (e.g., Laveuf and Cornu, 2009 and the references therein) whereby the LREE are less readily fluid-complexed than the HREE and become enriched in weathering products such as the phyllosilicates (e.g., Nesbitt, 1979; Mongelli, 1993).

The REE abundance of the samples in the Bidar laterite profile changes more significantly relative to the parent rock (Figure 11c). A more pronounced depletion is evident within the highly lateritised (upper 10 m) zone of the profile. If the REE are predominantly associated with clays in the early-forming weathering residue, the advanced stages of Si loss during lateritisation appears to release them from the profile. A higher retention of the LREE, however, is still present in the lateritised samples (Figure 11c). The MREE are more depleted than the LREE and HREE during the advanced stages of weathering. As an exception to the above samples, BB3 has a highly anomalous REE pattern and abundance. It is significantly enriched relative to the parent basalt and has an extremely high HREE/LREE slope. This sample may represent a horizon in which REE (and preferentially the HREE) leached from higher in the profile and accumulated at a site of contrasting pH and/or decreased permeability (e.g., Braun et al., 1998; Patino et al., 2003; Viers and Wasserburg, 2004; Kamgang Kabeyene Beyala et al., 2009), such as near the saprolite-protolith boundary. When studying deep, highly advanced weathering profiles, however, the addition of allochthonous material (e.g., dust) can also potentially influence the chemistry of the profile during long surface exposure times (e.g., Kisakürek et al., 2004; Wimpenny et al., 2007). Further, constraining the influence of dust addition to the REE chemistry of the Bidar laterite is also difficult without knowledge of the chronology of lava stacking and dust composition at the time of accumulation.

7.2 Sm/Nd fractionation

In addition to the obvious changes in the LREE/HREE abundance during pedogenesis, fractionations between some of the closely spaced REE are also detectable, as exemplified by the Sm/Nd ratio. If both flows are considered together, a decrease in Sm/Nd correlates with increasing weathering intensity ($r^2=0.813$; Figure 12). The parent basalt Sm/Nd ratio of the upper and lower flows appears to have differed slightly, which complicates the superimposed effects resulting from chemical weathering.

These observations suggest that Sm/Nd and, consequently, Nd isotope systematics of altered basalt and derived sediments are sensitive to pedogenetic fractionation. This would not alter the Nd isotope composition of modern profiles or sediments, but fractionation in Sm/Nd would manifest as variations in the Nd isotope composition in ancient weathering profiles. In this sense, the more weathered material would be less radiogenic as a result of the lower Sm/Nd generated during LREE enrichment. This has been exploited to crudely date the age of paleosols since an isochron develops that is proportional to the age of pedogenesis (e.g., Stafford, 2007; Frei and Polat, 2013). Using the Chhindwara profile as an example, the extent of Sm/Nd fractionation in the upper flow would translate to a one ϵ_{Nd} unit difference over a billion years. Note that this calculation assumes that all of the change in the $^{147}\text{Sm}/^{144}\text{Nd}$ is generated from pedogenesis (highest ratio in the parent basalt and the lowest in the most weathered material), the initial parent rock $^{143}\text{Nd}/^{144}\text{Nd}$ is constant, and that the isotope system remains closed after pedogenetic fractionation.

These findings contradict the conclusions of Nesbitt and Markovics (1997), where changes in Sm/Nd were undetectable in weathered granodiorite. Therefore, more extreme LREE fractionation may occur during basaltic weathering by comparison to more felsic and/or coarser grained rocks. At present, it is difficult to attribute this to a property of the parent rock (e.g., grain size, bulk composition, mineralogy), differences in the pedogenetic mineralogy, or the weathering environment (e.g., drainage, organic matter). Regardless, given the high erosion rates of basaltic terrain and their greater abundance on the early Earth, this is an important consideration for global weathering fluxes. Further, it seems that the Sm/Nd (or La/Ce) ratio may not always be an ideal provenance indicator, as advocated, for instance, by Sheldon and Tabor (2009). Tests of immobility should be made, if possible, prior to provenance interpretation.

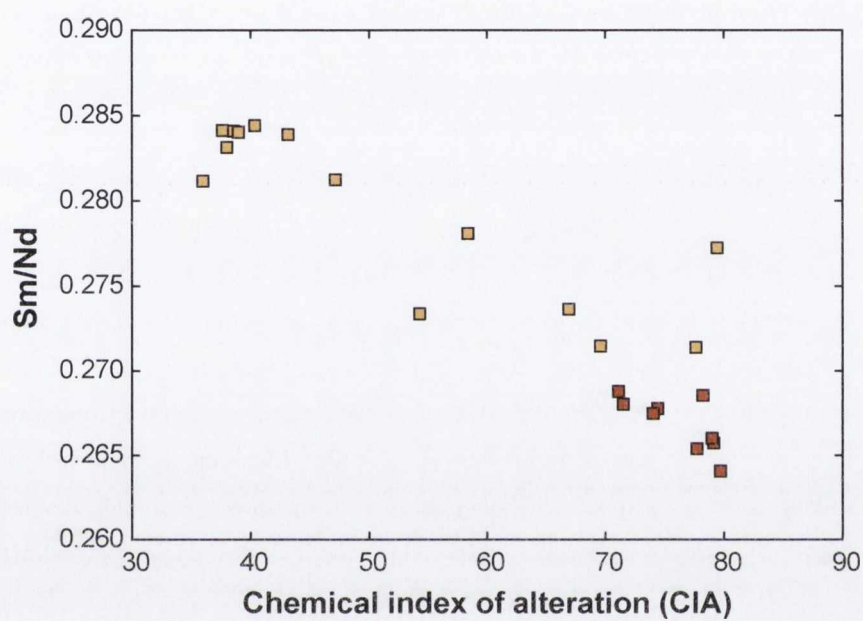


Figure 12: Fractionation of Sm/Nd ratio as a function of the CIA during the incipient and intermediate stages of Deccan Traps basalt weathering.

7.3 Europium anomaly (Eu/Eu*)

Europium is the only lanthanide that commonly occurs in a divalent oxidation state and whose behaviour is strongly influenced by plagioclase. This results in the potential for Eu to fractionate from the other lanthanides during weathering, since plagioclase is one of the most susceptible minerals to chemical dissolution. Fractionation of Eu can be tracked using the Eu anomaly $[Eu/Eu^* = Eu_n / (Sm_n \times Gd_n)^{1/2}]$. In the following discussion, the Eu/Eu* values are calculated using normalisation to the parent rock sample of the profile in question. Qualitatively, it is apparent that nearly all of the samples within both weathering profiles have a negative Eu anomaly (Figure 11).

The Eu/Eu* values in the Chhindwara profile decrease from 1 to ~0.75. Importantly, this variation in the Eu/Eu* value is inversely correlated with the CIA (Figure 13a). During the earliest stages of weathering recorded within the upper flow of the Chhindwara profile (CIA: 35-70), there is only a subtle change in the Eu anomaly (to as low as 0.90). Within the lower flow of the Chhindwara profile (CIA: 70-80), the slope of the CIA vs. Eu/Eu* anti-correlation steepens and Eu/Eu* reaches its lowest values. The same inverse correlation of the Eu/Eu* value with the CIA in the Chhindwara profile also exists with Sr concentration and the Rb/Sr ratio (Figure 13b), including the same inflection point at the transition from the upper to lower flow. Although these observations could indicate more aggressive Eu loss at higher degrees of weathering intensity in the lower flow, the minor variation in the primary chemistry of the two flows is probably the cause for the apparently different slope. Regardless, these observations confirm a strong relationship between Eu loss and plagioclase weathering. Similar reports of a declining negative Eu anomaly as a function of weathering intensity have been made previously (e.g., Condie et al., 1995; Huang and Gong, 2001; Ma et al., 2011). In the study of Ma et al. (2011), pore waters within the local weathering residuum possessed a positive Eu anomaly. Lawrence et al. (2006) noted that when river waters were normalised to the composition of their catchment geology, significant variation in the Eu anomaly remained that suggested a more complicated and possibly mineral-specific weathering contribution to the waters (such as preferential plagioclase dissolution).

In the Bidar laterite samples, the Eu/Eu* values are essentially constant between 0.85 and 0.90. The Eu/Eu* value does not change as a function of the weathering intensity in the Bidar samples (i.e., there is no obvious correlation between the IOL and Eu/Eu*). This confirms that the major loss of Eu occurs during the earlier stages of weathering. By the time all plagioclase has been removed from the weathering profile, the Eu/Eu* variability ceases and the remaining Eu changes only as a function of

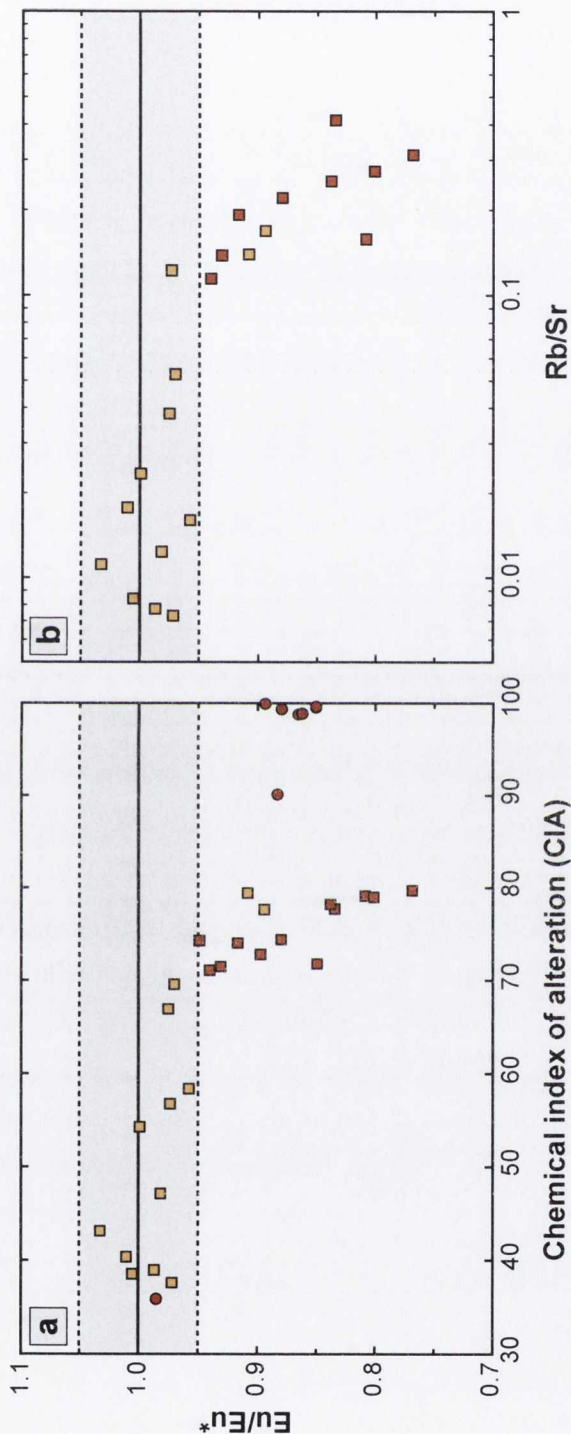


Figure 13: The fractionation of Eu from the trivalent REE, expressed as the Eu/Eu* ratio, is anti-correlated with the (a) CIA and the (b) Rb/Sr ratio, indicating the loss of Eu is strongly linked to that of Sr, Ca, and Na (i.e. plagioclase dissolution) during basalt weathering. The Eu/Eu* ratio is calculated following normalisation to the parent rock values (ChQB12 for Chhindwara profile and BB1 for Bidar profile). A Eu/Eu* value of 1 (dashed line) represents no Eu anomaly between Sm and Gd relative to the parent rock. The alkali element enriched samples from the Chhindwara profile (very high Rb/Sr) and the Bidar samples are not shown on the Rb/Sr plot.

the processes affecting the remaining trivalent lanthanides. The possibility needs to be considered that Eu/Eu* could also have been affected by dust introduction during weathering exposure.

7.4 Ce anomaly (Ce/Ce*)

Cerium can track redox-related transformations during pedogenesis in modern and ancient weathering profiles as a result of the potential oxidation of Ce³⁺ to Ce⁴⁺ (e.g., Middelburg et al., 1988; Braun et al., 1990; Mongelli, 1993; Gallet et al., 1996; Murakami et al., 2001; Patino et al., 2003). A positive Ce anomaly [$Ce/Ce^* = Ce_n / (La_n \times Pr_n)^{1/2}$] develops at sites of Ce enrichment, although there are often cases of weathered samples displaying distinct negative Ce anomalies, presumably generated by the cycling of REE away from areas of Ce enrichment (e.g., Nesbitt, 1979; Marsh, 1991; Fodor et al., 1992; Cotten et al., 1995). It is evident from the REY plots of the weathered Deccan basalt (Figure 11) that Ce is fractionated to varying degrees (relative to La and Pr) in nearly all samples, confirming its decoupling from the other LREE.

The Ce concentration increases during the incipient to intermediate weathering of the Chhindwara basalt along with the other LREE. There is, however, no obvious correlation between the Ce/Ce* value and the degree of weathering and several samples in the upper flow have negative anomalies. The presence of negative and positive Ce anomalies indicates that Ce oxidation is probably occurring at a smaller scale in the weathering front (e.g., Taunton et al., 2000). By contrast, within the lower and more highly weathered flow (CIA > 70), more samples have positive and higher Ce anomalies.

The Bidar laterite profile has much more extreme variation in Ce/Ce* with values ranging from 0.27 to 6.71. The Ce anomaly does not have any obvious correlations with the IOL, although the two highest Ce/Ce* values (BB7: 4.14 and BB9: 6.71) are within the upper, most highly lateritised portion of the weathering profile. This is consistent with the implied importance of specific oxides and secondary minerals (e.g., florencite; Sanematsua et al., 2011) in the fractionation of the REE. The REE-enriched sample deep in the profile (BB3), has the most negative Ce anomaly (0.27), indicating that the lanthanides transported from above were likely leached in the presence of Mn oxides from higher in the profile.

8. Conclusions

In this study, two weathering profiles located in the Deccan Traps, India, were studied to better quantify and understand different stages of basalt alteration. In basaltic weathering environments, lava flow morphology and texture (e.g., flow banding and vesicularity) are dominant controls on the penetration of weathering fluids and fluid-rock interaction. Mineralogical differences, such as the presence of zeolites, may also affect chemical weathering progression. Weathering profiles can develop across several basalt flows and some primary chemical variations from the original flows may survive overprinting by pedogenesis (e.g., HFSE ratios). From a geochemical perspective, this influences the accuracy of alteration mass balance calculations, especially where unweathered parent material is not available from different flows.

In order to better understand mafic substrate alteration, a new chemical weathering index, the mafic index of alteration (MIA), is proposed. The dichotomous, redox-related behaviour of Fe is factored into two separate MIA equations suitable for reducing [$MIA_{(R)}$] or oxidising [$MIA_{(O)}$] environments. The quantitative MIA value can be used in combination with ternary plots in the Al–Fe–Mg–Ca–Na–K system that display the proportional chemical changes. Like the majority of currently established weathering indices, the MIA is most suitable for understanding the early to intermediate stages of chemical weathering ('kaolinitisation'). Obtaining a quantitative handle on advanced chemical weathering requires a different approach. We propose using the index of lateritisation (IOL) as a quantitative expression of the Si–Al–Fe (SAF) ternary plot (Schellmann, 1981, 1982, 1986). Plotting chemical weathering indices against LOI values can provide additional insight into pedogenetic mineral transformations.

Chemical weathering studies should always start with the major element composition of the weathering profile prior to trace element or isotopic analysis. When used in combination, weathering indices and high-precision trace element analysis can provide insight into which stages of alteration the trace element loss or retention are associated with. In the present study, the focus is on the alkali, alkaline earth, and rare earth elements of the basaltic weathering profiles. The main observations and conclusions presented are:

- The alkali and alkaline earth element geochemistry in the Chhindwara profile conforms predominantly to the expected weathering behaviour. The alkaline earth elements (+Na) exhibit an order of depletion of $Na \approx Ca \approx Sr > Mg > Ba > Be$. By contrast, the alkali elements

exhibit a greater retention in the altered substrate. Notably, Tl appears to behave most closely to Rb and Li exhibits the greatest mobility of the alkali elements, apart from Na.

- Alkali element (K, Rb, Cs) and Tl enrichment at the paleo-flow top of the Chhindwara profile is best explained by the allochthonous addition of dust to the profile. The results show that the enrichment in K reported in other studies may similarly be accompanied by the other alkali elements. This may help constrain the mechanism of enrichment (e.g., metasomatism, plant uptake, dust).
- Rare earth element fractionation occurs during weathering of the Deccan basalt whereby the enrichment of the LREE is greater than the MREE and HREE in the weathering residue. Significant pedogenetic fractionation of the closely spaced LREE is also evident from variation in the Sm/Nd ratio. Consequently, this indicates that REE ratios should be treated with caution when used for assessing the provenance of weathered materials. Fractionation of Sm/Nd can manifest as a varying Nd isotope composition over time.
- The preferential loss of Eu, measured with the Eu anomaly (Eu/Eu^*) is highly correlated with Sr, Ca, and Na loss from plagioclase. Following the complete weathering of plagioclase, the Eu/Eu^* does not appear to change further as a function of weathering intensity.
- Cerium is fractionated from the trivalent lanthanides during pedogenesis but there is a lack of correlation of Ce/Ce^* with any of the weathering indices, consistent with fractionation being controlled by pedogenetic minerals that are not contributing to the calculation of the weathering indices.

The results presented here are relevant to ancient paleosol research and may be useful for studying Martian substrate alteration.

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Chapter 2 supplementary information

1. Introduction

The mafic index of alteration (MIA) is intended primarily as a quantification or gauge of alteration in mafic rocks. As such, it has wide application and importance given the abundance of basaltic products and their derivatives on Earth (and other terrestrial planets). It can be applied to other rocks types, but this must be done with caution because protolith composition influences the MIA value and placement on ternary plots, and then the subsequent range of MIA values that result from alteration. This behaviour is also true of the more established and familiar weathering indices, such as the chemical index of alteration (CIA). Principally, the MIA and CIA values of igneous rocks decrease with the felsic to mafic compositions due to the presence of Ca in non-feldspar silicate minerals and the increasing abundance of mafic minerals. Using a selection of igneous rocks, the effect of these bulk compositional variations upon the MIA and CIA values is demonstrated below. This compositionally controlled behaviour requires careful consideration before applying the MIA (and CIA) to weathering profiles and derived sedimentary products; in effect, the weathering index should only be used where some contextual knowledge of the parent rock or sediment source is known.

2. CIA and MIA values of average igneous rocks and common minerals

In general, more mafic rocks have progressively lower MIA values due to the increasing contribution of mafic minerals to the weathering index, whilst felsic and intermediate rocks have similar $MIA_{(O)}$ values. The calculated values for both the CIA and $MIA_{(O)}$ indices are similar for common igneous protoliths, excepting ultramafic rock compositions. The $MIA_{(R)}$ values, however, are consistently lower than the CIA values at all compositions and the degree of deviation increases more drastically in the most mafic rocks.

To illustrate this, the average igneous (volcanic and plutonic) rock compositions calculated by Nockolds (1954) are shown in Table S1 along with the corresponding CIA, $MIA_{(O)}$, and $MIA_{(R)}$ values. In Figure S1, the CIA is plotted against the $MIA_{(O)}$ and $MIA_{(R)}$, along with a reference line representing a 1:1 CIA to MIA ratio. Variations in the CIA and MIA related to composition are well correlated. As mentioned above, it is clear that felsic and intermediate rocks have nearly identical CIA and $MIA_{(O)}$ values, although the $MIA_{(R)}$ is consistently lower than the CIA at all

compositions. Progressively more mafic rocks have lower MIA values relative to the CIA, deviating from the 1:1 line with ultramafic rocks plotting to substantially lower MIA values.

The position of the average igneous rock compositions in the A–CN–K and A–C–N–K–F–M ternary plots is demonstrated in the following pages: A–CN–K (Figure S2), A–CNK–FM plot (Figure S3), A–CNKM(‘L’)–F plot (Figure S4), and AF–CNK–M plot (Figure S5). The CIA, $MIA_{(O)}$, or $MIA_{(R)}$ index values, where appropriate, are projected into the ternary plots for reference.

The positions of common igneous and pedogenetic minerals (Table S2) are also shown in the ternary plots. A significant degree of element substitution can occur in some minerals, most notably in the mafic minerals (pyroxenes, amphiboles) and pedogenetic phyllosilicates (smectite group minerals, illite), but a single composition is used in most cases to represent a mineral group. The molecular proportion assumed for these compositions is shown in Table S2. It should be recognised, however, that the position of some of the minerals can be highly variable in the ternary plots. Ideally, the bulk chemical composition in the plots would be accompanied by mineral chemistry for the sediment or weathering profile being studied.

Table S1: Major element (wt. %) composition of average igneous rocks (Nockolds, 1954) and calculated molar weathering index values

	Peridotite	Tholeiitic basalt	Gabbro	Andesite	Diorite	Granodiorite	Adamellite (Quartz Monzonite)	Tonalite	Alkali Granite	Calc- Alkali Granite	Alkali Rhyolite
Symbol	PER	BAS	GAB	AND	DIO	GRD	ADA	TON	GRA	GRA	RHY
# of analyses	23	137	160	49	50	137	121	58	48	72	21
SiO ₂	43.54	50.83	48.36	54.20	51.86	66.88	69.15	66.15	73.86	72.08	74.57
TiO ₂	0.81	2.03	1.32	1.31	1.50	0.57	0.56	0.62	0.20	0.37	0.17
Al ₂ O ₃	3.99	14.07	16.84	17.17	16.40	15.66	14.63	15.56	13.75	13.86	12.58
Fe ₂ O ₃	2.51	2.88	2.55	3.48	2.73	1.33	1.22	1.36	0.78	0.86	1.30
FeO	9.84	9.00	7.92	5.49	6.97	2.59	2.27	3.42	1.13	1.67	1.02
MgO	34.02	6.34	8.06	4.36	6.12	1.57	0.99	1.94	0.26	0.52	0.11
MnO	0.21	0.18	0.18	0.15	0.18	0.07	0.06	0.08	0.05	0.06	0.05
CaO	3.46	10.42	11.07	7.92	8.40	3.68	2.45	4.65	0.72	1.33	0.61
Na ₂ O	0.56	2.23	2.26	3.67	3.36	4.13	3.35	3.90	3.51	3.08	4.13
K ₂ O	0.25	0.82	0.55	1.11	1.33	3.01	4.58	1.42	5.13	5.46	4.73
P ₂ O ₅	0.05	0.23	0.24	0.28	0.35	0.17	0.20	0.21	0.14	0.18	0.07
H ₂ O ⁺	0.76	0.91	0.64	0.86	0.80	0.68	0.54	0.69	0.47	0.53	0.66
CIA	35	38	41	45	43	49	50	49	53	52	49
MIA _(O)	12	36	35	42	39	47	50	48	54	52	52
MIA _(R)	4	23	25	31	27	41	43	39	49	46	46

*Fe was converted to Fe₂O₃(T) and the major element oxides were normalised to 100% on an anhydrous basis prior to calculating weathering index values and plotting on ternary diagrams

Table S2: Select minerals and their molecular proportions in the A–CN–K and A–C–N–K–F–M ternary plots

Mineral	Symbol	Assumed molecular proportions (%)				
		A : CN : K (50 : 50 : 0)/(50 : 0 : 50)	A : CNK : FM 50 : 50 : 0	A : CNKM('L') : F 50 : 50 : 0	AF : CNK : M 50 : 50 : 0	
Feldspars (plagioclase/k-feldspar)	<i>fel(pla/ksp)</i>					
Muscovite	<i>mus</i>	75 : 0 : 25	75 : 25 : 0	75 : 25 : 0	75 : 25 : 0	
Biotite (phlogopite)	<i>bio</i>	50 : 0 : 50	13 : 12 : 75	12.5 : 87.5 : 0	12.5 : 12.5 : 75	
Diopside	<i>dio</i>	0 : 100 : 0	0 : 50 : 50	0 : 100 : 0	0 : 50 : 50	
Augite	<i>aug</i>	17 : 83 : 0	9 : 44 : 47	9 : 86 : 5	14 : 44 : 42	
Hypersthene	<i>hyp</i>	-	0 : 0 : 100	0 : 67 : 33	33 : 0 : 67	
Tremolite	<i>tre</i>	0 : 100 : 0	0 : 29 : 71	0 : 100 : 0	0 : 29 : 71	
Actinolite	<i>act</i>	10 : 90 : 0	4 : 31 : 65	4 : 86 : 10	14 : 31 : 55	
Ferrohornblende	<i>fho</i>	30 : 70 : 0	17 : 40 : 43	17.5 : 40 : 42.5	60 : 40 : 0	
Magnesiophornblende	<i>mho</i>	30 : 70 : 0	12 : 29 : 59	12 : 86 : 2	14 : 29 : 57	
Olivine	<i>oli</i>	-	0 : 0 : 100	0 : 94 : 6	6 : 0 : 94	
Chlorite (Clinochlore)	<i>chl</i>	100 : 0 : 0	19 : 0 : 81	18 : 70 : 12	30 : 0 : 70	
Smectite (Nonttronite)	<i>sme</i>	77 : 23 : 0	30 : 9 : 61	30 : 9 : 61	91 : 9 : 0	
Illite	<i>ill</i>	77 : 0 : 23	77 : 23 : 0	77 : 23 : 0	77 : 23 : 0	
Gibbsite	<i>gib</i>	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	
Halloysite	<i>hal</i>	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	
Kaolinite	<i>kao</i>	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	100 : 0 : 0	
Fe oxides	<i>fe-o</i>	-	0 : 0 : 100	0 : 0 : 100	100 : 0 : 0	

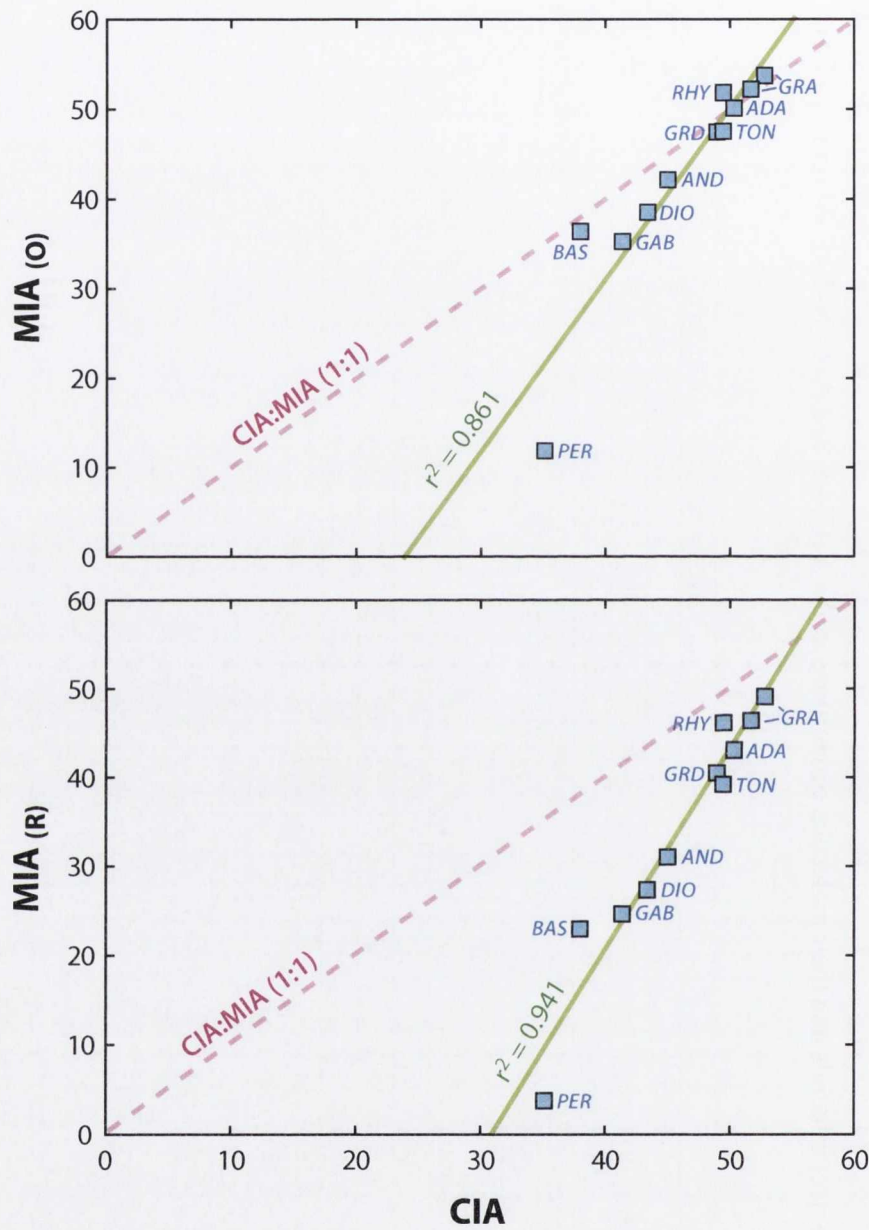


Figure S1: Plot of $MIA_{(O)}$ and $MIA_{(R)}$ vs. CIA for the average composition of several igneous rocks (Nockolds, 1954).

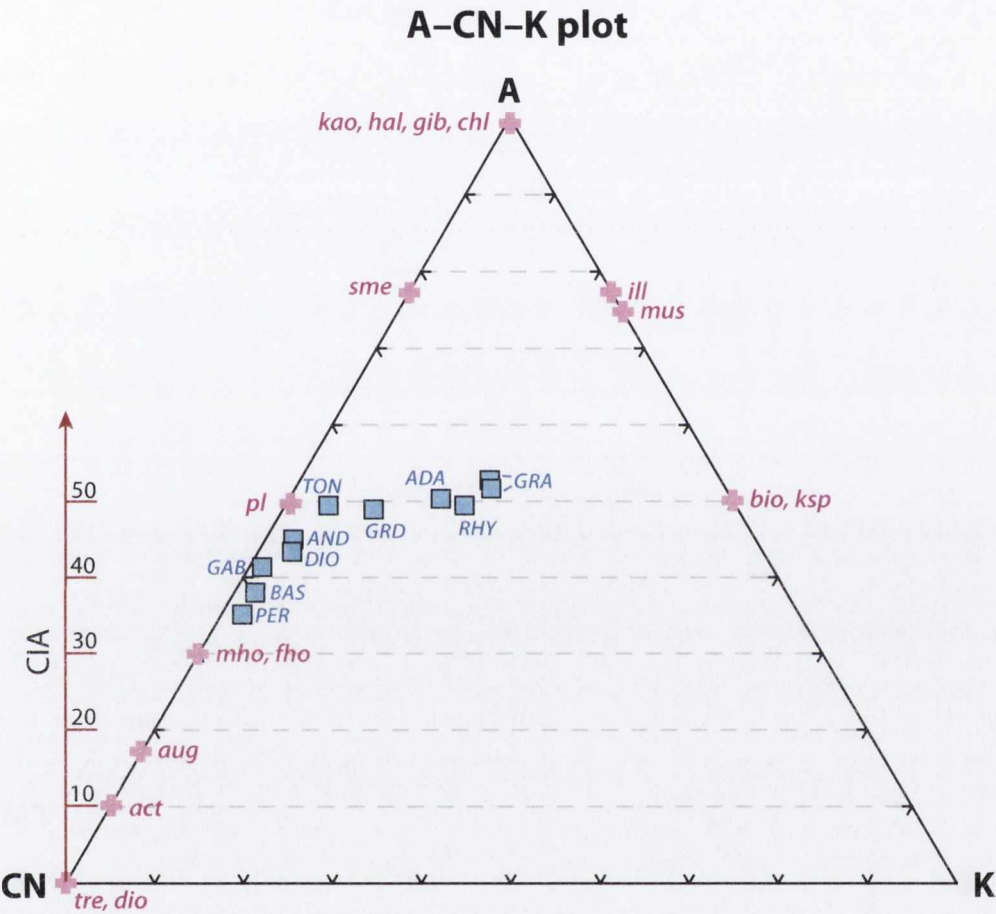


Figure S2: Average igneous rock compositions (Nockolds, 1954; Table S1) and selected minerals (Table S2) within the A-CN-K plot showing the projection of the CIA values.

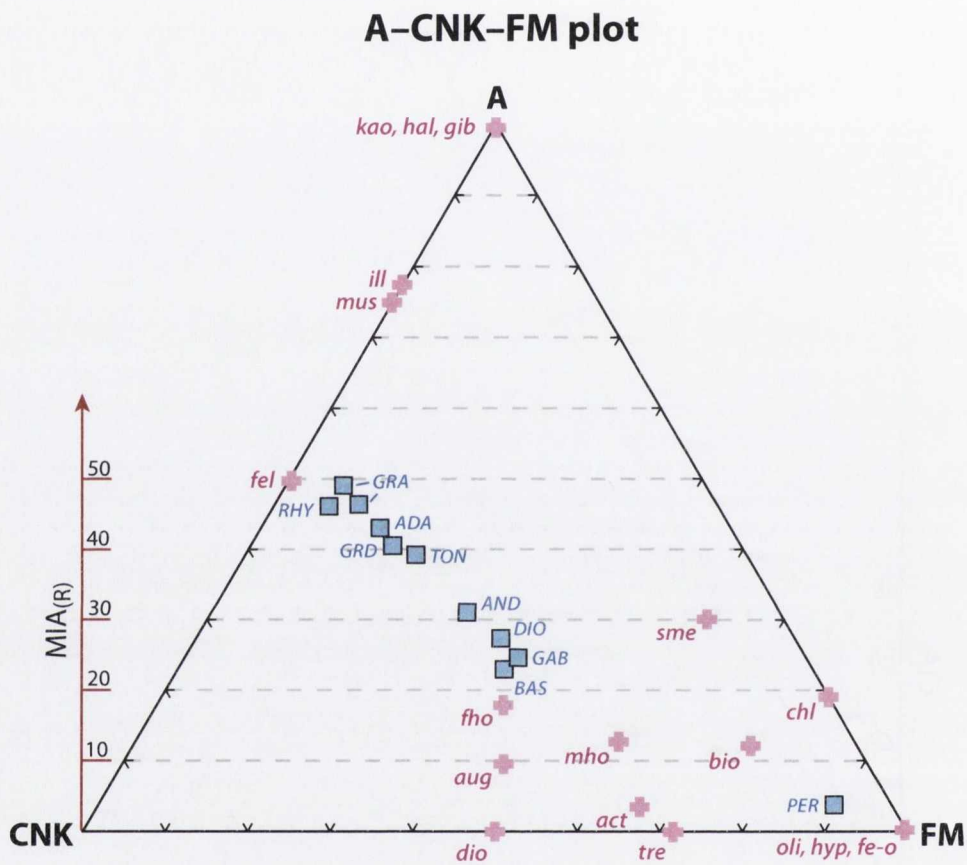


Figure S3: Average igneous rock compositions (Nockolds, 1954; Table S1) and selected minerals (Table S2) within the A–CNK–FM plot showing the projection of the $MIA_{(R)}$ values.

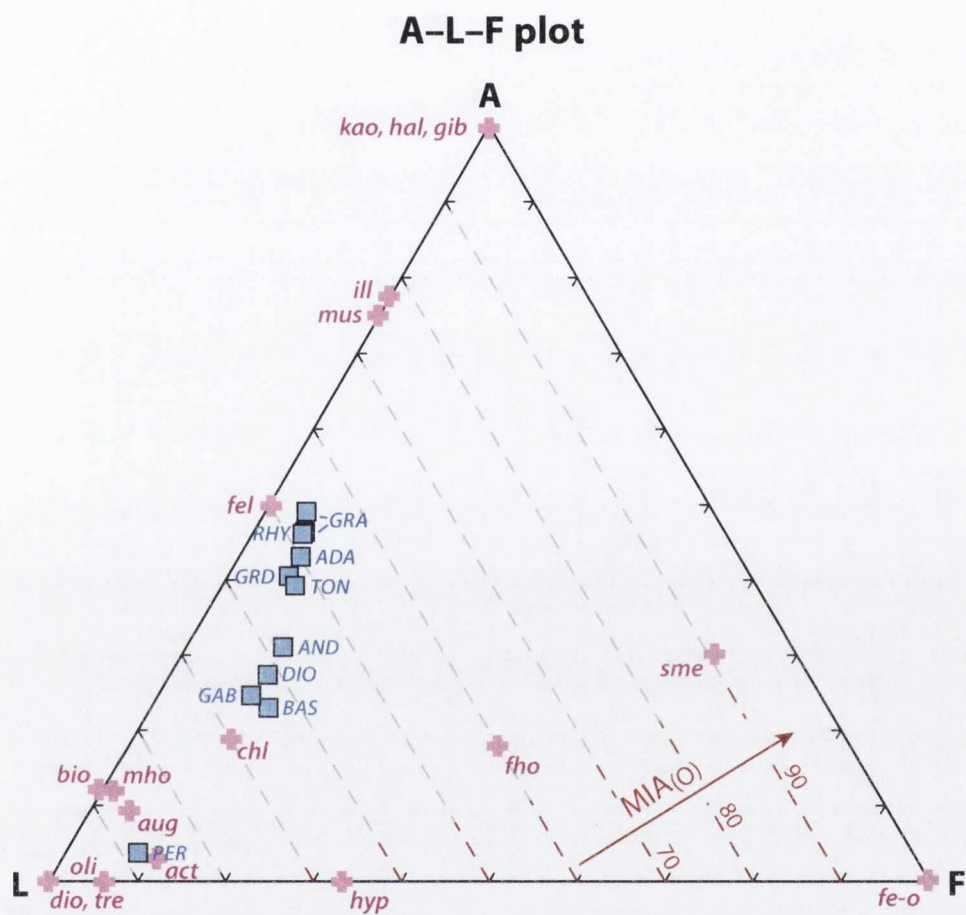


Figure S4: Average igneous rock compositions (Nockolds, 1954; Table S1) and selected minerals (Table S2) within the A–CNKM(L)–F plot showing the projection of the $MIA_{(O)}$ values.

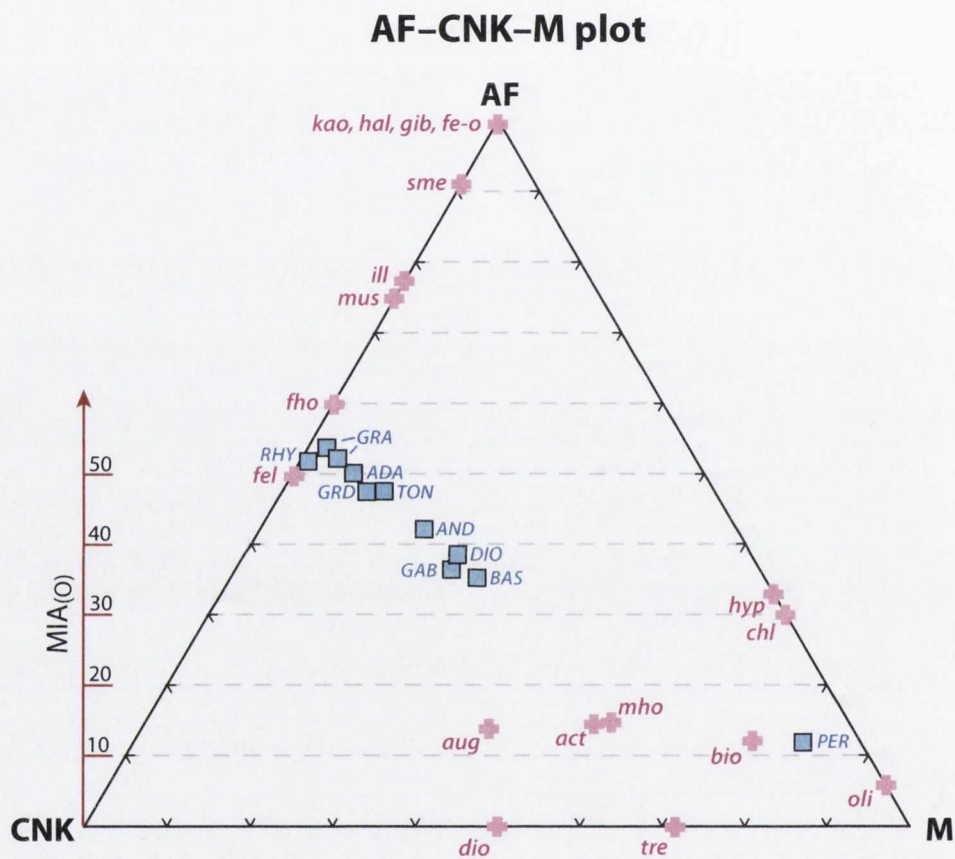


Figure S5: Average igneous rock compositions (Nockolds, 1954; Table S1) and selected minerals (Table S2) within the AF–CNK–M plot showing the projection of the $MIA_{(O)}$ values.

Reference

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Chapter 3: A combined Y/Ho, high field strength element (HFSE) and Nd isotope perspective on basalt weathering, Deccan Traps, India

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Abstract

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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 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 sub-aerial 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. $^{143}\text{Nd}/^{144}\text{Nd}$) 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 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-HNO₃ (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 HNO₃ (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% HNO₃ stock solution. Inspection revealed no undissolved material after these steps. A calibration standard [United States Geological Survey (USGS) W-2a] and quality control standards [typically USGS and Geological Survey of Japan (GSJ) rock standards] were prepared following a similar procedure (omitting the addition of HCl after first step of digestion) and were analysed along with batches of sample unknowns. The ICP-MS analyses followed the experimental design of Eggins et al. (1997) with the

modifications described in Kamber et al. (2003) and Babechuk et al. (2010), as per the following description. For analysis, an aliquot of stock solution was diluted to produce a 2% HNO₃ solution with an elemental and enriched isotope internal standard mixture containing ⁶Li, Rh, Re, Bi, and ²³⁵U in order to correct for the effects of matrix-related signal suppression and instrument drift. Immediately prior to running each batch of unknowns, two preparatory experiments were performed using the daily tuning conditions: a determination of the ²³⁵U/²³⁸U and ⁶Li/⁷Li ratios in the GSJ standard JA-3 or USGS standard AGV-2 to determine the natural contribution of the enriched isotope in the sample dilution mixture of unknowns; and, a series of pure element solutions containing Ba+Nd, Dy, and Zr to monitor the production rate of oxides with common isobaric interferences on the analytes of interest. Further details of these two steps are reported in Ulrich et al. (2010). Analyses of samples (n=15-25) were also preceded by procedural blanks, two or more separate W-2a solutions for calibration, and quality control standards. After the procedural blanks, standards and unknowns were bracketed with a drift monitor solution spaced every 5-7 samples to externally correct for instrument drift remaining after internal standard correction. Following blank subtraction and internal standard, interference, and drift monitor correction, intensities were quantified as concentrations using the laboratory's preferred values for the USGS standard W-2a, as reported in Table 1 for the HFSE and for the other analytes as reported in Kamber et al. (2003) and Babechuk et al. (2010).

Method reproducibility and accuracy was assessed using the long-term average of USGS and GSJ standards run as unknowns (e.g., see Babechuk and Kamber, 2011 for Sm/Nd ratios). Table 1 reports the reproducibility of element (Y, Ho, Nb, Ta, Zr, Hf, Mo, W, Th, U) concentrations and ratios of relevance to the present study for mafic standards routinely analysed at Laurentian University (BHVO-1, BHVO-2, BIR-1, BCR-2, JB-2). Apart from Mo, the concentrations of the HFSE reproduce at 2% RSD (1 sigma) or better in the standards, with exception of BIR-1 which returns slightly higher RSD values due to very low concentrations. The long-term reproducibility of HFSE ratios is generally even better due to the cancelling of weigh-in and dilution errors that only affect absolute concentrations. Overall, the high level of precision indicates that: i) procedural blank levels were consistently low; ii) these elements are relatively homogeneously distributed in the powders digested at Laurentian University; and iii) that laboratory and experimental parameters such as sample dilution, instrument wash-out, and drift correction are suitable for HFSE determination even at very low concentrations (e.g., see Babechuk et al., 2010 for a discussion of factors which influence W determination). A comparison of the long-term mean concentration with literature values (Table 1) suggests that the applied W-2a concentrations used for calibration are accurate; in the event that consensus regarding the concentration of any element in W-2a evolves, all calibrated data can be recalculated relative to the presently preferred values (Table 1).

Table 1: Mean concentration and standard deviation (1 σ) of HFSE concentrations and ratios in basalt rock standards analysed at Laurentian University (LU)

	W-2a Calibration Values	no of digests no of analyses	BHVO-1				BHVO-2				BIR-1				BCR-2				JB-2			
			11				14				15				9				7			
			LU	±	%	GeoReM	LU	±	%	GeoReM	LU	±	%	GeoReM	LU	±	%	GeoReM	LU	±	%	Literature ^a
Y	ppb	20113	24562	200	0.8	26000	24353	183	0.8	26000	14728	169	1.1	15600	33627	333	1.0	37000	22148	242	1.1	24900
Ho	ppb	803	1006	9	0.9	980	999	6	0.6	980	585	6	1.0	560	1326	12	0.9	1280	881	7	0.8	750
Nb	ppb	7275	18484	155	0.8	18600	18299	161	0.9	18100	536	8	1.4	550	12340	116	0.9	12600	489	11	2.2	1580
Ta	ppb	454	1156	9	0.8	1210	1145	10	0.9	1140	37	1	1.5	36	765	7	0.9	740	35	0	1.4	130
Zr	ppb	87866	172225	3126	1.8	174000	169345	3048	1.8	172000	14632	316	2.2	14000	185317	3025	1.6	184000	45956	1029	2.2	51200
Hf	ppb	2356	4386	81	1.8	4460	4333	66	1.5	4360	573	8	1.5	582	4846	68	1.4	4900	1450	33	2.3	1490
Th	ppb	2104	1198	17	1.4	1230	1180	13	1.1	1220	29	1	3.3	32	5783	64	1.1	5700	248	3	1.2	350
U	ppb	505	430	4	1.0	409	421	4	1.1	403	10	0.2	2.2	10	1699	15	0.9	1690	155	2	1.4	180
Mo	ppb	423	998	39	3.9	1000	4441	892	20	4000	40	15	39	70	258083	13948	5.4	250000	939	26	2.7	1080
W	ppb	240	193	4	2.0	210	192	4	2.2	210	6	1	9.1	7	421	6	1.3		272	7	2.7	260
Y/Ho			24.37	0.13	0.5		24.37	0.17	0.7		25.17	0.19	0.8		25.36	0.24	1.0		25.14	0.20	0.8	
Nb/Ta			15.96	0.10	0.6		15.98	0.12	0.7		14.49	0.16	1.1		16.12	0.11	0.7		14.07	0.33	2.3	
Zr/Hf			39.30	0.22	0.6		39.08	0.37	0.9		25.55	0.33	1.3		38.24	0.29	0.8		31.70	0.28	0.9	
Zr/Nb			9.318	0.17	1.9		9.262	0.15	1.6		27.28	0.59	2.2		15.02	0.23	1.5		93.92	2.48	2.6	
Hf/Ta			3.793	0.06	1.5		3.787	0.05	1.4		15.47	0.26	1.7		6.332	0.08	1.3		41.69	0.84	2.0	
Nb/Th			15.38	0.21	1.4		15.50	0.20	1.3		18.34	0.58	3.1		2.13	0.03	1.3		1.97	0.05	2.4	
Ta/W			5.976	0.10	1.6		5.959	0.11	1.9		5.078	0.56	1.1		1.817	0.02	1.1		0.128	0.00	2.7	
Ta/Mo			1.160	0.04	3.7		0.267	0.05	18		1.023	0.24	24		0.0030	0.0002	5.9		0.0371	0.0009	2.4	
Th/U			2.791	0.02	0.8		2.802	0.03	1.1		2.871	0.12	4.1		3.404	0.02	0.7		1.603	0.02	1.3	

GeoReM (Jochum et al., 2005) preferred values as of December 2014

a Compiled values reported in Imai et al (1995)

By contrast to the other HFSE, Mo exhibits a poorer precision in each of the USGS standards. Several lines of evidence point towards this being related to a more heterogeneous distribution (i.e., 'nugget effect') within individual aliquots of some standards in addition to variable levels of contamination during the production of the original USGS powders (e.g., Weis et al., 2005, 2006; Lin et al., 2000), as opposed to analytical factors such as instrument memory or a higher blank/sample ratio. Firstly, very similar HFSE concentrations (not differing by more than 2%) and ratios are measured in both BHVO-1 and BHVO-2 apart from Mo which reproduces to a much lower precision and Mo concentration differs by 127% where BHVO-2>BHVO-1 (Table 1). This was discussed in Weis et al. (2005, 2006) and was attributed to the use of hardened steel during powder production that resulted in greater contamination in the second generation standard. Comparison of our long-term mean values with those of Weis et al. (2005) suggests that the degree of Mo contamination within each standard is relatively consistent (Table 1). However, a comparison of Mo values for separate BHVO-2 aliquots reported in Kamber (2009) suggests that some, although minimal, variability remains between different BHVO-2 powder stocks. Secondly, an unexpectedly high Mo concentration is evident in BCR-2 ($258,080 \pm 13950$ ppb) that suggests a far more severe contamination during the production of this standard, as also noted by Weis et al. (2006). Heterogeneity of Mo in the W-2a calibration standard could also cause additional inaccuracy and imprecision. However, it is worth noting that a standard addition experiment by Baldwin et al. (2012) yielded a Mo concentration in W-2a of 424 ± 2 ppb, identical to the laboratory's preferred calibration value (423 ppb). Furthermore, Mo data obtained with the present technique compared very favourably with Mo concentrations determined by isotope dilution of a separate aliquot (Baldwin et al., 2013).

These observations illustrate the limitations of using second generation USGS rock standards for calibration and why long-term mean values for heterogeneously distributed metals in these standards do not accurately represent the achievable level of the method's analytical reproducibility. By contrast to these USGS standards, the GSJ standard JB-2 has a much more reproducible Mo concentration ($RSD < 3\%$) at low concentrations and suggests that these standards may not possess the same 'nugget effect', despite showing evidence for W contamination in some cases (e.g., Babechuk et al., 2010). Therefore, the reproducibility of Mo in the JB-2 standard is adopted to estimate the precision of Mo measurements in unknowns.

The HFSE data for the weathering profiles in this study are reported in Table 2 (Chhindwara) and Table 3 (Bidar), whereas the full trace element data set is reported in the Supplementary Material. Babechuk et al. (2014) previously reported and discussed a more limited suite of these trace element data (i.e., alkali, alkaline earth, rare earth elements, and Nb). It is noted that Ta, W, and

Mo data are not reported for the Bidar samples since the powders were originally prepared using a tungsten carbide swing mill.

2.2 Nd isotope analysis

Chromatography and neodymium isotope analyses were conducted at the National Centre for Isotope Geochemistry (School of Geological Sciences, University College Dublin) using a 100 mg aliquot of the sample powders and digested and converted with concentrated HNO₃ following the same procedure as described for the trace element analysis (Section 2.1; Babechuk et al., 2014). Following conversion, the residue was dissolved in 2 mL 1 N HNO₃ for use in chromatography. The chromatographic procedure followed the methods of Pin et al. (1994) and Pin and Zalduegui (1997), whereby the solution was passed over TRU Spec resin to separate the REE and then flushed directly onto LN Spec resin to purify the Nd.

Accuracy and external precision were monitored by repeated analysis of the La Jolla standard, which returned a mean ¹⁴³Nd/¹⁴⁴Nd of 0.511842 ± 8 ppm (2σ S.D., n=4) during the experiments that is identical to the long term laboratory average with an external reproducibility of 10 ppm (2σ S.D., n=25) and consistent with previous high-precision work (e.g., Thirlwall, 1991). All Nd isotope data were normalised to a ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. The ¹⁴³Nd/¹⁴⁴Nd ratio along with the in-run precision (2σ S.E.) are reported in Table 2 and Table 3. Neodymium and strontium isotope data were previously collected on the Bidar profile sample suite in an unpublished project (Mason, 1999; Mason et al., 2000). These new data are consistent with these previous analyses but offer improved internal precision.

2.3 Data presentation

Throughout the remaining text, all element ratios are calculated on a mass basis. Mean values are reported with one standard deviation (1σ SD) unless otherwise stated. Element mass balance calculations for each sample are calculated as the percent change (e.g., Kisakürek et al., 2004; Kurtz et al., 2000; Brimhall and Dietrich, 1987) of an element relative to the least-weathered parent rock (hereafter referred to as protolith), after normalisation to an immobile or least-mobile element from the following equation (1):

$$\text{Eq.1: \% change in } R = \left[\frac{(R_{\text{sample}} - R_{\text{protolith}})}{R_{\text{protolith}}} \right] \times 100$$

where R is the mass ratio of an element pair with the immobile element in the denominator (here taken as Nb or Ta based on the analysis in Section 4.1) and the protolith ratios are those from samples ChQB12 or BB1 for the Chhindwara and Bidar profiles, respectively. Chemical

Table 2: Chhindwara profile trace element ratios and Nd isotope data

Sample	Depth (cm)	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	$\epsilon\text{Nd}_{t=0}$	Nb/Ta	Zr/Hf	Th/Nb	U/Nb	Zr/Nb	Hf/Ta	W/Ta	Mo/Ta	Y/Ho
ChQB11	0				15.48	37.57	0.2162	0.0431	14.66	6.037	0.3001	0.8443	23.35
ChQB10	10				15.37	37.38	0.1809	0.0319	16.50	6.784	0.1093	0.6719	25.22
ChQB9a	90				15.38	37.43	0.1753	0.0451	16.28	6.690	0.1604	0.8004	23.65
ChQB9b	90				15.49	37.93	0.1757	0.0480	16.47	6.727	0.1315	0.7275	24.92
ChQB9c	90				15.46	37.55	0.1744	0.0444	16.36	6.733	0.1350	0.7376	26.29
ChQB9d	90				15.28	36.59	0.1756	0.0726	16.01	6.686	0.1264	0.6590	26.52
ChQB8	110				15.49	37.92	0.1761	0.0427	16.41	6.703	0.1518	0.7699	25.17
ChQB12*	140				15.64	37.68	0.1736	0.0474	16.29	6.763	0.1681	0.8444	24.71
ChQB7	210				15.29	37.18	0.1775	0.0408	16.50	6.787	0.1083	0.7756	23.89
ChQB6	310				15.41	37.44	0.1757	0.0495	16.43	6.762	0.1623	0.7554	24.26
ChQB5	330				15.48	37.77	0.1775	0.0424	16.49	6.756	0.1126	0.8335	23.95
ChQB4	350				15.33	37.49	0.1786	0.0448	16.50	6.745	0.1259	0.8650	23.91
ChQB3	370				15.56	37.57	0.1796	0.0414	16.29	6.746	0.1602	0.8831	23.12
ChQB2	390				15.23	37.13	0.1849	0.0460	16.43	6.738	0.2607	0.8444	22.61
ChQB1	405				15.32	37.05	0.1794	0.0470	16.42	6.790	0.2840	0.8306	22.89
ChQA12	410	0.512625	0.000004	-0.26	15.30	37.64	0.2331	0.0388	15.49	6.298	0.9095	0.6513	22.81
ChQA11	420	0.512643	0.000004	0.10	15.19	37.43	0.2303	0.0319	15.13	6.139	0.3922	0.5121	22.22
ChQA10	430	0.512648	0.000004	0.20	15.37	37.44	0.2197	0.0299	15.31	6.286	0.2219	0.5064	21.89
ChQA9	450	0.512651	0.000004	0.25	15.37	38.47	0.2091	0.0345	14.75	5.895	0.1263	0.6137	22.95
ChQA8	470				15.48	37.56	0.2090	0.0415	15.41	6.350	0.1987	0.6827	22.75
ChQA7	490				15.28	37.72	0.2101	0.0435	15.51	6.285	0.0622	0.5662	22.24
ChQA6	510	0.512650	0.000004	0.23	15.45	37.69	0.2141	0.0374	15.36	6.298	0.0597	0.5208	22.38
ChQA5	530				15.47	37.74	0.2080	0.0346	15.32	6.282	0.0711	0.5375	22.86
ChQA4	550				15.36	37.56	0.2049	0.0341	15.60	6.380	0.0265	0.5002	22.07
ChQA3	590	0.512658	0.000004	0.39	15.64	37.88	0.2060	0.0402	15.27	6.307	0.0646	0.7470	22.62
ChQA2	610				15.57	38.20	0.2071	0.0428	15.54	6.333	0.0240	0.5842	22.19
ChQA1	630				15.38	37.92	0.2088	0.0428	15.66	6.350	0.0212	0.5336	22.63

* Protolith basalt

Table 3: Bidar profile trace element ratios and Nd isotope data

Sample	Depth (m)	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	$\epsilon\text{Nd}_{t=0}$	Zr/Nb	Th/Nb	U/Nb	Nd/Nb	Y/Ho
BB9	2	0.512462	0.000003	-3.43	19.67	0.4573	0.1102	0.410	17.13
BB8	5	0.512429	0.000004	-4.08	13.11	0.5295	0.1125	0.532	18.72
BB7	6	0.512455	0.000004	-3.56	12.76	0.2515	0.0807	0.794	17.28
BB6	11	0.512532	0.000003	-2.07	13.79	0.1550	0.7760	5.779	14.71
BB5	13	0.512515	0.000004	-2.39	12.95	0.1455	0.0879	0.737	16.64
BB4	15	0.512552	0.000009	-1.67	12.97	0.1067	0.0563	0.389	19.42
BB3	26	0.512703	0.000004	1.27	13.01	0.0978	0.0517	3.934	30.15
BB2	35	0.512863	0.000003	4.38	12.96	0.0975	0.0244	1.741	25.58
BB1*	47	0.512859	0.000004	4.31	12.85	0.0957	0.0250	1.674	24.42

*Protolith basalt

weathering indices are calculated on a molar (chemical index of alteration) or mass (index of lateritisation) basis using the major element data reported in Babechuk et al. (2014) and Kisakürek et al. (2004) that are available in the Supplementary Materials. Epsilon Nd isotope values are reported relative to the present day CHUR (chondritic uniform reservoir) $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512638 (Jacobsen and Wasserburg, 1980), calculated from the following equation $\epsilon_{\text{Nd}} = [(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1] \times 10000$.

3. Overview of Weathering Profiles

In situ weathering profiles should display an uninterrupted continuum of ‘alteration horizons’ progressing from unaltered basal bedrock, through to saprolite (e.g., Chhindwara profile) and, in the case of lateritic profiles, upward through a ‘mottled zone’ of oxyhydroxide accumulations, to highly indurated iron-rich duricrust capping (e.g., Bidar profile). The horizons are separated by interface zones made evident in outcrop from observable changes in colour, mineralogy and texture.

More precisely, the weathering front at the base of the profile is the junction between the unaltered bedrock (protolith) and overlying chemically weathered materials; this transition can occur over a narrow vertical interval (i.e. < 1m). Above the weathering front, a horizon containing a mixture of weathered material and unweathered ‘corestones’ occurs. This passes upward into a saprolitic zone in which structures and crystal pseudomorphs from the parent protolith may still be recognised. With further alteration, a microaggregated texture develops, known as the ‘mottled zone’, consisting of kaolinite particles along with crystals of Fe oxyhydroxides. With further maturation of the profile these develop into nodules; this texture promotes good vertical drainage and further accelerates the alteration process. Under alternating dry and wet conditions, this zone becomes characterised by a strong accumulation of iron oxides. Upward, the nodular accumulations coalesce and interlock culminating in an indurated ‘vermiform’ or ‘tubular’ laterite comprising a massive, interlocking fretwork of Fe- (and Al-) oxides and hydroxides at the top of the profile.

3.1 Chhindwara profile

This Quaternary weathering profile spans two identifiable basalt flows in the Deccan Traps, exposed in a quarry east of Chhindwara (22° 04.213' N, 79° 01.393' E). Its structure and chemical composition are described in detail by Babechuk et al. (2014). The upper flow (ChQB) is fully exposed and capped with a thin (~20 cm) topsoil, whereas only the upper 215 cm of the lower flow

(ChQA) is exposed. Fifteen samples were taken from the upper flow (ChQB1-ChQB12), including four samples that transect a corestone at a depth of 90 cm (ChQB9a-ChQB9d), and twelve samples from the lower flow (ChQA1-ChQA12) as summarised in Figure 2. Overall, this essentially saprolitic profile has progressed to an intermediate weathering intensity, with chemical index of alteration (CIA) values of 36-80 and oxidative mafic index of alteration values [$MIA_{(O)}$] values of 38-71 (Babechuk et al., 2014). The sample ChQB12 from a depth of 140 cm into the upper flow, and extracted using a coring drill, is adopted as the profile protolith based on position/relationship with the profile, its mineralogy (primary basaltic minerals), lowest chemical weathering index values (e.g., CIA: 36), and highest Fe(II)/Fe(III) ratio (Babechuk et al., 2014).

3.2. Bidar profile

Laterite is widespread in the Bidar region of the Deccan and, due to the resistant lateritic upper levels of the profile, forms a series of elevated mesa-like topographic features. The Bidar site is worthy of investigation since it has an important historical precedent: it was near here that Newbold (1846) first suggested that laterite developed as *in situ* (i.e. autochthonous) chemical residuum through the segregation and subsequent rearrangement of the minerals and elements originally comprising the parent rock (i.e., protolith). The investigated lateritic weathering profile is well exposed at the edge of a hillside near Bidar (17°54.87'N, 77°32.39'E), and extends down to a depth of ~ 50 m preserving a complete progression from unaltered basalt to a highly indurated laterite at the surface; this transitions occurs within two or three flows of the chemically uniform Ambenali Formation (Widdowson et al., 2000).

The Bidar profile is part of the high-level duricrust (Widdowson, 1997) that is interpreted to be the upper remnant of the lava pile that was subjected to a long period of intense weathering that post-dated volcanism (ca. 65 Ma), but dwindled following uplift associated with the Himalayan orogeny (ca. 50 Ma). After this point, changes in climate and hydrology resulted in the water table dropping, valley incision, and the duricrust being 'fossilised'. This presents a protracted interval of exposure (ca. 65 Ma to present) during which dust influenced the area during or after lateritisation (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2008), although the timing of dust addition and its source, as well as its fate in the profile are still poorly understood.

A total of 9 samples (BB1-BB9) were collected as part of detailed field logging of the Bidar profile; each sample was chosen to represent horizons at which there was an observable change in mineralogy or texture. This lateritic profile has progressed to an extreme end-member of weathering intensity, with chemical index of alteration (CIA) values of 37-100 and oxidative mafic index of alteration values [$MIA_{(O)}$] values of 36-99 (Babechuk et al., 2014). The sample BB1 from

a depth of 50 m where the basalt shows no signs of alteration is adopted as the profile protolith; it contains similar chemical features as described above for ChQB12, including a primary basaltic mineralogy (pyroxene and plagioclase) and the lowest chemical weathering index values (e.g., CIA: ~37). Additional information on the Bidar profile samples is reported in the Supplementary Materials.

4. Results and Discussion

Results and discussion are grouped into three separate themes. Firstly, the relative mobility of the HFSE during weathering of the Deccan Traps basalt is investigated (Section 4.1), followed by the use of the least-mobile HFSE as potential chemostratigraphic ‘fingerprints’ for determining pre-weathering basalt stratigraphy and mass balance, and a separate discussion of comparatively more mobile HFSE (U, Mo, W). Secondly, the Th-U-Nb-REE and Nd isotope systematics are used to evaluate the dust accumulation and downward migration during weathering, and as a possible proxy for evaluating surface exposure duration; for instance, periods of repose between the arrival of successive lava flows, and longer-term exposure resulting in lateritisation (Section 4.2). Thirdly, the mobility of Y and the fractionation of Y/Ho are considered with respect to their importance in the chemical cycling of these elements within the hydrosphere and the potentiality of using Y/Ho as a proxy for oxidative weathering (Section 4.3).

4.1 High field strength elements

4.1.1 Zr, Hf, Nb, Ta, Th

The Chhindwara weathering profile is developed across two individual lava flows; the upper one (~4 m thick) is fully exposed whilst only a 2.15 m section of the lower flow is exposed. This succession was described by Babechuk et al. (2014), where it was shown that an offset in ‘immobile’ element concentrations (Al and Ti) and an abrupt change in the Al/Ti ratio marked the transition between the flows, highlighting a small difference in the original lava chemistries. The high-precision trace element data of this study permit a more detailed evaluation of the protolith HFSE characteristics and their behaviour during the early stages of basalt weathering.

In general, the concentration of the HFSE (Zr, Hf, Nb, Ta, Th) increases with increasing weathering intensity (i.e., greater loss of mobile major elements such as Ca, Na, and Mg) within each of the flows. Superimposed on this, however, is an offset towards higher concentrations in the lower flow (ChQA) relative to the upper flow (ChQB), comparable to that observed for Ti (Babechuk et al., 2014). While these HFSE concentration offsets appear to also detect the variation

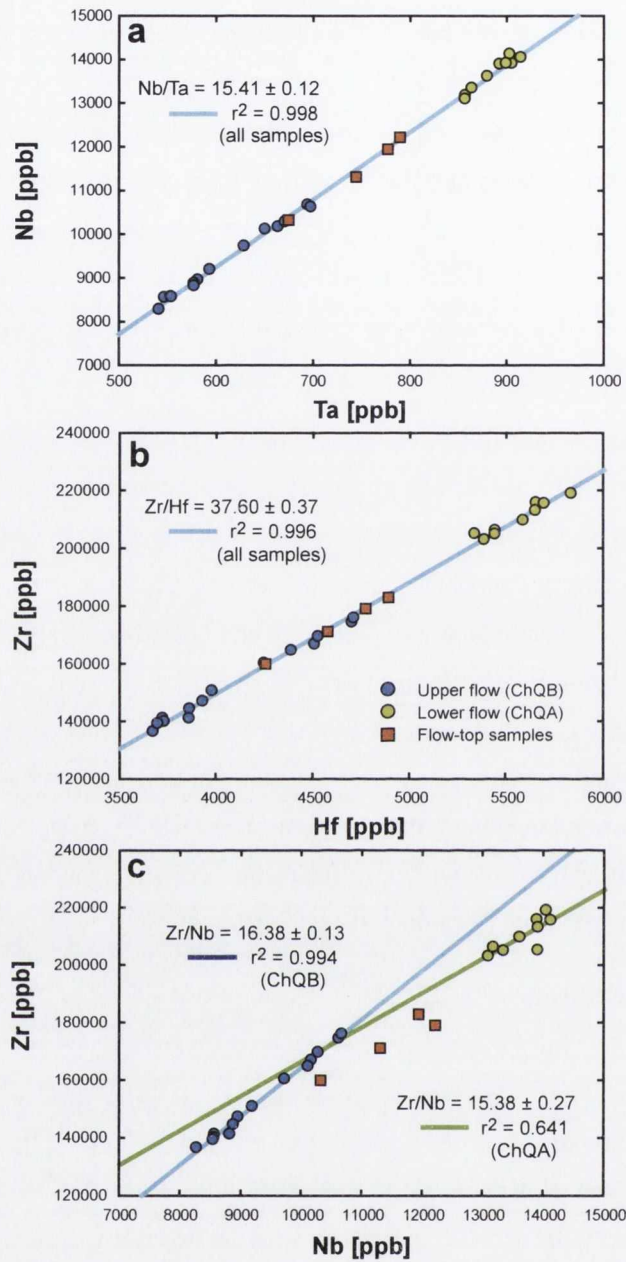


Figure 1: X-Y scatter plots of Ta-Nb (a), Hf-Zr (b), and Nb-Zr (c) for samples of the Chhindwara profile, divided into the upper flow [ChQB: dark (blue) shaded circles], lower flow [ChQA: light (green) shaded circles], and those at the current and paleo flow tops [shaded (orange) squares]. Constant Nb/Ta (15.41 ± 0.12) and Zr/Hf (37.60 ± 0.37) ratios across both flows indicates that the two isovalent element pairs are equally immobile and do not separately fingerprint each flow. By contrast, HFSE ratios of Zr-Hf-Nb-Ta-Th that combine elements with non-equal valence and/or more contrasting ionic radii (e.g., Zr/Nb) are unique in each flow and show excursions in the flow tops (c). However, each flow contains an internally constant HFSE ratio (e.g., Zr/Nb of 16.38 ± 0.13 and 15.38 ± 0.27 in the upper and lower flow, respectively) that still indicates limited mobility of this element group.

in the two flow chemistries, we focus on ratios of these elements since they are more revealing in this regard by eliminating effects of weathering-related density or dilution/enrichment changes on the concentrations and have the additional benefit of reflecting relative mobility.

The isovalent geochemical twins (Zr-Hf and Nb-Ta) exhibit constant ratios ($Zr/Hf=37.60\pm0.37$; $Nb/Ta=15.41\pm0.12$) in all samples of the Chhindwara profile (Figure 1a,b). Relative to the inferred protolith (ChQB12), the Nb/Ta and Zr/Hf ratios do not deviate by more than 3% in all samples despite the general increase in element concentration that occurs with increasing chemical weathering intensity. This indicates that these elements exhibit near-equal extent of immobility in the profile (Kurtz et al., 2000), and, further, that these geochemical twin ratios are incapable of discriminating between the two lava flows. The latter feature is most likely because the isovalent elements are hosted in the same minerals making them less sensitive to primary magmatic differentiation processes. By contrast, when ratios of the HFSE elements with non-equal valence and different ionic radius (e.g., Hf/Ta, Zr/Nb, and Th/Nb) are inspected, a discrete ratio offset is evident between the two flows (Figure 1c) similar to Al/Ti (Babechuk et al., 2014) that also illustrates, but with greater resolution, the parental HFSE chemistry. Apart from this primary compositional offset, excursions from the constant ratio that characterises each flow are present in the three uppermost samples of the lower flow (ChQA10-ChQA12), and the uppermost sample of the top flow (ChQB11). This is most evident in the Th/Nb and Zr/Nb ratios. Our hypothesis that these samples have been modified by incorporation of dust will be discussed in Section 4.2. Excluding the potentially dust affected samples, the Hf/Ta and Th/Nb ratios display the least intra-flow variability. The Th/Nb ratio distinguishes the lower (ChQA, $n=9$) from the upper (ChQB, $n=14$) flows with mean values of 0.209 ± 0.003 and 0.177 ± 0.003 , respectively (corresponding to a ~20% offset in ratio). The Hf/Ta ratio ratios of 6.74 ± 0.03 and 6.28 ± 0.06 (corresponding to a ~7% offset in ratio) also separate the two flows. Finally, the Zr/Nb ratio is also characteristic for each flow (Figure 1c), but there is more variability within the lower flow (ChQA) compared to the upper flow (ChQB). This could indicate increased mobility of Zr (and Hf) over Nb at greater weathering intensity (Widdowson and Cox, 1996).

In the more profoundly altered Bidar profile, the concentrations of Zr, Hf, and Nb are highly correlated and exhibit near-constant ratios, with the exception of the uppermost sample (BB9). For instance, Zr and Nb correlate particularly well, yielding an r^2 value of 0.999 and an average Zr/Nb of 13.05 ± 0.32 (excluding BB9). Similarly, Zr/Hf and Hf/Nb in samples BB1 to BB8 are near-constant at 37.81 ± 0.58 and 0.345 ± 0.009 , respectively, with a significant deviation present only in BB9 (Zr/Hf: 42.40; Hf/Nb: 0.464). The uppermost sample BB9 may have been subjected to mineral sorting, heavy mineral addition, or greater mobility of Nb over Zr and Hf in the most

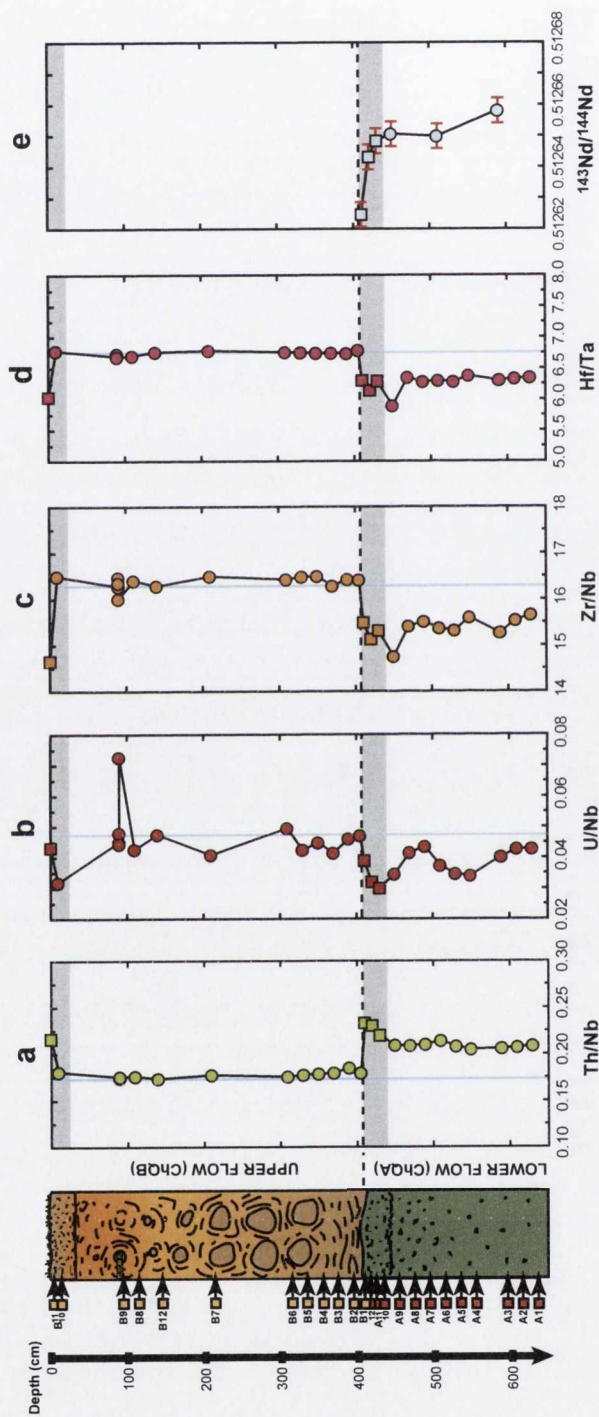


Figure 2: Chhindwara profile HFSE Th/Nb (a), U/Nb (b), Zr/Nb (c), Hf/Ta (d) and Nd isotope ($^{143}\text{Nd}/^{144}\text{Nd}$) ratios vs. depth (cm) below the modern surface. Error bars on the $^{143}\text{Nd}/^{144}\text{Nd}$ are the 2σ internal errors. The profile sketch (from Babechuk et al., 2014) illustrates the colour and texture variation between the two flows (ChQA and ChQB) and the sampling depth information. The contact between the two flows is shown on each plot as a horizontal dashed line. The HFSE ratios of the protolith basalt (ChQB12: 140 cm) are shown as a vertical lines in the plots. These selected HFSE ratios fingerprint each flow and show very limited intra-flow element mobility apart from U/Nb (due to U mobility). Deviations in most of the HFSE ratios are evident in the modern soil surface and paleo-flow surface (square symbols) denoted by the horizontal shaded horizons, which in the latter case is accompanied by a Nd isotope ratio deviation.

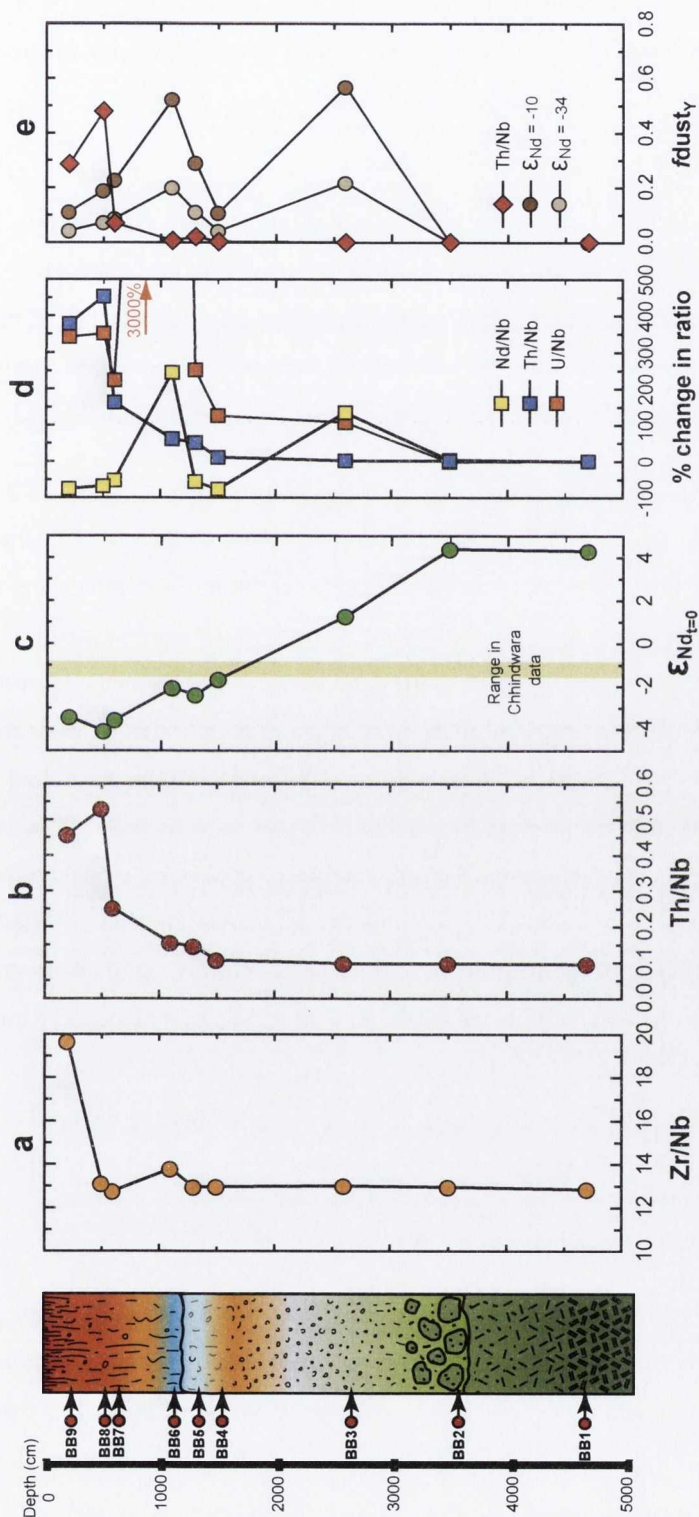


Figure 3: Bidar profile HFSE Zr/Nb (a), Th/Nb (b) and Nd (expressed as ϵ_{Nd}) isotope (c) ratios along with calculated percent change in Nd/Nb, Th/Nb, and U/Nb ratios (d) and mass fraction of dust (e) calculated from Th and Nd chemistry. The percent change in each ratio for each sample was calculated relative to the respective ratio in the protolith (BB1), assuming that Nb was immobile during weathering, as described in the text. The mass fraction of dust ($fdust_Y$) in each sample was calculated from the elements (Y: Th or Nd) based on a dust composition (Table 4) with the following characteristics: Th/Nb ratio (0.856), Th concentration of 10.64 ppm, Nd concentration of 27.21 ppm, and an ϵ_{Nd} of either -10 (Chauvel et al., 2014) or -34 (Mohan et al., 2013) for the reasons described in the text (Section 4.2.2).

intensely weathered horizon of the laterite. Regardless of sample BB9, it is evident that Zr, Nb, and Hf are highly immobile, both relative to each other and during different stages of weathering, including the intense stages of lateritisation. By contrast to these elements, however, Th displays a very different behaviour that indicates selective enrichment; this is interpreted to be due to aeolian dust accumulation within the profile, as discussed in Section 4.2.

Although a clear offset in the Al/Ti ratio related to the flow transition in the Chhindwara profile was described in Babechuk et al. (2014), this ratio exhibits more intra-flow variability by comparison with the trace HFSE (Zr-Hf-Nb-Ta-Th) ratios. The concentrations of the latter elements correlates more significantly with Ti than Al in the profile, and suggests that Al may be more susceptible to physical translocation of clay minerals or preferential leaching by comparison. In other words, it appears that Ti and the trace HFSE are less mobile and more suitable for assessing variation in the protolith chemistry.

The near equal Zr-Hf-Nb-Ta immobility in the basalt profiles in this study contrast with findings of Kurtz et al. (2000) who found more intense Zr leaching and reprecipitation at depth during the tropical weathering of Hawaiian basalt exposed to high levels of rainfall. Regardless of this difference, we agree with Kurtz et al. (2000) in promoting the use of Nb or Ta as the least-mobile elements for mass balance calculations. The high-precision data and sampling at a reasonable density to achieve statistical significance in this study effectively fingerprint the individual lava flows. This exposes the limitation of using mass balance calculations in profiles developed across flows of variable parental chemistry. For example, in the absence of geological evidence for a separate flow, the offset could be interpreted as preferential leaching and deposition of the HFSE in different soil horizons of a uniform protolith composition. In the case of the Chhindwara profile, the lack of a sufficiently unweathered protolith sample in the lower flow precludes a separate mass balance analysis and necessitates assumptions regarding the parental chemical composition of the mobile elements in order to calculate full profile mass gains or losses relative to the least-weathered sample (Babechuk et al., 2014).

4.1.2 Implications for flood basalt stratigraphy

The comparative Zr-Hf-Nb behaviour of the Bidar and Chhindwara profiles has important implications for the basalt lava eruption history. Although the thick (~50 m) Bidar profile is likely to have developed across several lava flows (i.e., 2–3 units), the HFSE ratios imply that there was little inter-flow chemical variability compared to the Chhindwara profile. This indicates that minimal magmatic fractionation or crustal contamination occurred between eruptions, consistent with the compositional uniformity exhibited by the thick (c. 500 m), uncontaminated MORB-like

Ambenali Formation, which is widespread across the Main Deccan Province (MDP; Jay and Widdowson, 2008). By contrast, the Chhindwara area was peripheral to the MDP, possibly more distal from the eruptive source, and accordingly received flows only from the largest, most voluminous outpourings; this episodic arrival of lavas would allow for a greater degree of magmatic evolution and contamination between successive eruptions. This interpretation is further supported by the more juvenile $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the protolith of the Bidar profile ($\epsilon_{\text{Nd}}=4.3$) compared to the apparently non-dust influenced Chhindwara flow centre ($\epsilon_{\text{Nd}}=0.2$ to 0.4).

These results are consistent with those of Widdowson and Cox (1996), who demonstrated that Zr/Nb ratios could be used to map basalt stratigraphy over long distances, even when the substrate was lateritised. By extension, the ability to fingerprint variations in the stratigraphy of mafic lava flows using other HFSE is of benefit in localities where flow contacts are not necessarily identifiable, such as in ancient, metamorphosed paleosols or drill-hole samples (e.g., Millet et al., 2014). It is important to stress that in such circumstances chemical stratigraphies can only be produced from those elements from the primary magmatic inventory that are demonstrably immobile and not added to the profile from an external source during or after weathering.

4.1.3 U

By contrast with the HFSE already discussed (Zr-Hf-Nb-Ta), U commonly exhibits enhanced mobility in oxygenated environments through the formation of the uranyl ion [UO_2^{2+}] following the oxidation of U(IV) to U(VI). Within the Chhindwara profile, U mobility greater than that of the other HFSE is evident through the scatter and U loss expressed by the U/Nb ratio that is superimposed on the compositional variation between the upper and lower flow (Figure 2b); relative to the U/Nb in the parent basalt (ChQB12: 0.0474), U loss dominates relative to Nb (lower U/Nb) within the individual flows apart from the enrichment evident within the centre of the corestone at a depth of 90 cm (ChQ9d). In addition to redistribution or loss of U originally hosted in the basalt, some U may have been introduced to the profile along with Th at the lava-flow tops and subsequently mobilised within the profile, but this is impossible to quantify at present. The U/Nb topology of the Bidar profile differs substantially from that of Chhindwara due to the far more complex and protracted evolution of the former that includes dust accumulation and fluctuating water table deposition, as discussed in Section 4.2.

4.1.4 Mo and W

Continental weathering is the most important means of delivering bioessential trace elements to the oceans. Secular changes in the flux of these elements from land have been linked with key events in early Earth history, such as the onset of sulphide weathering (e.g., Scott et al., 2008; Large et al.,

2014). Continental fluxes are also affected by the dominant type of rock exposed to weathering at the Earth's surface. For example, a decrease in the Ni supply to oceans occurred after the near-complete disappearance of newly erupted very high-Mg (Ni-rich) komatiites in the Neoproterozoic. In addition to affecting the oceanic Ni/Fe ratio, Konhauser et al. (2009) postulated that this acted to 'starve' the methanogens, who depend on Ni for respiration, and may have helped trigger an ecological niche transition that facilitated the Great Oxidation Event (GOE). However, little is known about the behaviour of Ni during weathering throughout Earth history. Examples such as this underscore the necessity to better constrain the weathering behaviour of key bioessential elements in order to quantify their flux from the land surface.

Like U, W and Mo form soluble oxyanions, namely tungstate [WO_4^{2-}] and molybdate [MoO_4^{2-}], respectively, in natural waters. In contrast to U, however, these elements serve a biological function as metal cofactors in enzymes (e.g., Kletzin and Adams, 1996; Hille, 2002; Anbar, 2004; Andreessen and Makdessi, 2008; Wang, 2013). It is therefore possible that changes in their oceanic supplies and/or sinks may have exerted a limiting control on the evolution of oceanic biota and their respiration mechanisms. This motivated a more detailed analysis of W and Mo behaviour in the Chhindwara profile. It is worth noting, that although W behaviour in soils has been studied due to its potential for bioaccumulation and toxicity, especially in areas of anthropogenic and natural contamination (e.g., Bednar et al., 2009; Kennedy et al., 2012), little has been reported on its behaviour in saprolite (C horizon) profiles.

The W/Ta ratio vs. depth in the Chhindwara profile is illustrated in Figure 4a. The protolith W/Ta ratio (ChQB12: 0.168) is similar to that of modern MORB-type basalts (König et al., 2011; Babechuk et al., 2010). Throughout the upper flow, the W/Ta ratio ranges from 0.109 to 0.300, corresponding to up to 36% depletion and 79% enrichment relative to the protolith sample. Enrichment of W is restricted to three samples: the uppermost topsoil sample (ChQB11: 79%) and the two samples lowest in the flow (ChQB1/B2: 55-69%). In all remaining samples, which represent the main stratigraphic thickness of the flow, loss of W relative to Ta (decrease in W/Ta from the protolith) dominates. Within the lower flow, a much wider range of W/Ta ratios (0.021-0.909) is present. Although an offset in W/Ta at the flow boundary is expected, the magnitude is more difficult to assess as a result of the greater mobility exhibited by W relative to the other HFSE (Zr-Nb-Hf-Th). Nevertheless, the independent W/Ta topology of the lower flow reveals factors influencing the chemistry of W in the profile. Firstly, W enrichment is clearly evident in the samples at the paleo flow-top that also show Th enrichment. If Th enrichment derived from the addition of an allochthonous component with trace element enriched characteristics closer to that of continental crust (Section 3.2), a parallel argument can be made for W enrichment in these

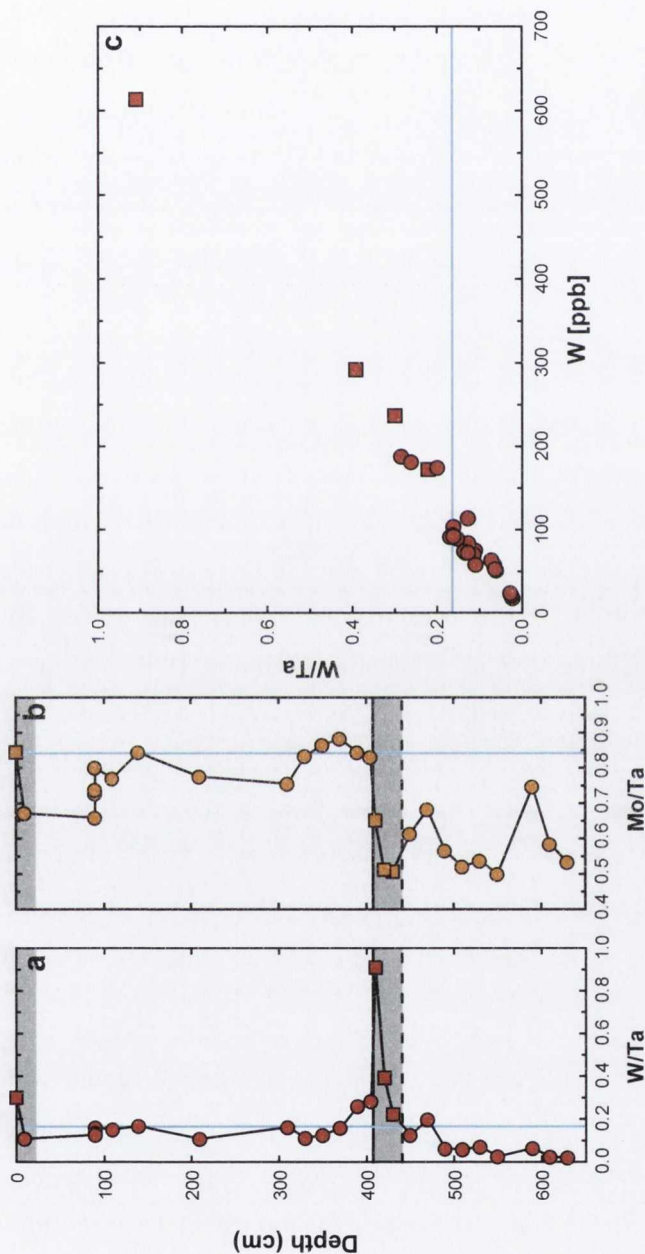


Figure 4: Chhindwara profile W/Ta (a) and Mo/Ta (b) ratios and a plot of W vs W/Ta ratio (c). The contact between the two flows is shown as a horizontal dashed line and the shaded areas at the tops of both flows are the areas with excursions in immobile HFSE ratios [square symbols; Figure 2]. Solid (blue) line indicates the ratio of the protolith basalt (ChQB12). Greater intra-flow variability in Mo/Ta and W/Ta indicates greater mobility of Mo and W relative to T a (c) by contrast to the other HFSE (Zr-Hf-Th). This includes substantial W loss from the lower flow and areas of W enrichment relative to Ta.

horizons. Since the upper continental crust contains significantly higher W concentrations (e.g., ~1 ppm; Kamber et al., 2005) than the basalt (ChQB12: 92 ppb), the increase in W/Ta is not surprising. Secondly, a distinct trend of downwardly decreasing W/Ta ratios is evident, starting from samples ChQA8-ChQA9 (0.199-0.126; those below the dust-influenced flow-top) towards the lowest exposed samples of the flow (0.064 to 0.021 in ChQA1-ChQA3). If the original W/Ta ratio of the unweathered basalt in the lower flow was the same as in the upper flow (ChQB12: 0.168), the W/Ta ratios near the base of the flow would correspond to a W loss of ~60-90%. This suggests conditions that significantly enhanced the W mobility in the lower flow compared to the upper flow. In general, the downward decreasing concentration of Mg and abundance of zeolite minerals (due to increasing primary vesicularity towards the top of the lava flow) in the lower flow matches the topology of the W/Ta stratigraphy, suggesting these may be related to or directly influence the behaviour of W (e.g., loss of W from the breakdown of mafic minerals).

It is clear from a plot of W vs. W/Ta (Figure 4c), as well as the previously discussed Nb-Ta systematics, that the W/Ta ratio is controlled almost entirely by W mobility in the profile. The exact processes controlling the loss and retention of W, however, cannot be assessed from the elemental data alone. Nevertheless, it is likely that W was mobilised through the formation of tungstate or polytungstate species. Certain phyllosilicates, or Mn-Fe oxyhydroxides have been demonstrated to exert a primary control on the concentration of W in natural waters through pH-dependent adsorption or co-precipitation (e.g., Kunzendorf and Glasby, 1992; Johannesson et al., 2000; Gustafsson, 2003; Seiler et al., 2005; Bednar et al., 2009), which could also account for areas of W enrichment other than in the flow-tops. For example, the W-enriched samples ChQB1-ChQB2 are at the more highly weathered base of the upper flow that shows a sharp increase in Fe(III)/Fe(II) relative to the more massive flow centre (Babechuk et al., 2014). Overall, the W geochemistry of the Chhindwara profile indicates, through the extensive loss of W in the saprolite, that W mobility may not be restricted to soil horizons and that certain stages of weathering and/or mineral phases may promote its preferential release.

The Mo/Ta ratio for the Chhindwara profile is shown in Figure 4b. The Mo/Ta ratio within the upper flow is relatively constant (0.790 ± 0.07), but similar to W, indicates loss of Mo relative to Ta with percent ratio change from the protolith of -22 to 5. Lower Mo/Ta ratios are present in the underlying flow, ranging from 0.747 to 0.500. The change in ratio within the lower flow is internally less variable and appears to indicate a lower degree of Mo mobility relative to W, suggesting that it is either hosted in more weathering-resistant minerals (e.g., Fe-Ti oxides; Arnórsson and Óskarsson, 2007) rather than sulphides/sulphide inclusions in the basalt (Voegelin et al., 2012) which are highly susceptible to oxidative weathering. Furthermore, although

molybdate is highly soluble, it is similar to tungstate in that it is scavenged by Mn-Fe oxyhydroxides (Anbar and Rouxel, 2007; Arnórsson and Óskarsson, 2007; Kashiwabara et al., 2013), which could limit its flux from the profile. The Mo-W-Ta systematics of the Chhindwara profile could suggest that Mo is scavenged more readily than W in this case. The results of King et al. (2014) indicate that organic matter (OM) is also an important factor in binding Mo in soils, although complexing of Mo with OM outside of the topsoil and deeper within the saprolite is unlikely to outweigh the effects of primary mineral budget and influence of oxyhydroxides. A final factor that is also important with regards to Mo in the weathering profile is the potential for addition from allochthonous material (i.e., dust). By contrast to W, however, the samples at the flow-tops do not display Mo enrichments, suggesting that either any Mo received at the flow-tops was redistributed in preference to W or that dust-supplied Mo was not an important factor in the overall Mo budget of the profile, but it is difficult based on the elemental data to fully address these possibilities.

It is clear that more detailed investigations of Mo geochemistry, both elemental and isotopic, of weathering profiles developed on different lithologies and across geological time are needed. The critical zone processes that control the retention or release of Mo are of particular interest to understanding the stable isotope systematics of Mo in the hydrosphere. For instance, at present, it is known that river waters are variably enriched in the heavier isotopes of Mo relative to igneous rocks and at least some of this fractionation is caused by preferential retention of lighter Mo isotopes in soils, in tandem with catchment geology variation and riverine Mo removal (Archer and Vance, 2008; Pearce et al., 2010; Neubert et al., 2011; Voegelin et al., 2012).

The results of the present study are limited in scope by only providing bulk elemental Mo and W concentrations. Taken at face value, however, it appears that a greater mobility and flux of W over Mo occurs during weathering of the Deccan Traps basalt. This finding may relate to the absence of easily weathered sulphides, but awaits a detailed micro-mineralogical investigation. It is worth noting that Arnórsson and Óskarsson (2007) showed that while Fe-Ti oxides likely host the majority of W and Mo in Icelandic basalt, the main supply of these elements to fresh waters is linked to the dissolution of plagioclase, pyroxene, and volcanic glass. Regardless, the findings of this study emphasise a major mass balance problem with respect to the Mo/W ratios in the hydrosphere. Because W and Mo have similar concentrations in the average upper continental crust (~1 ppm; e.g., Rudnick and Gao, 2003; König et al., 2011) and display conservative marine behaviour, it is predicted that they would have similar oceanic inventories. However, the observed concentration of Mo in seawater (~100 nmol kg⁻¹) is significantly higher than that of W (~50 pmol kg⁻¹) with an average molar Mo/W of ~2000 (Sohrin et al., 1999; Firdaus et al., 2008). The mass

imbalance can be solved if W is preferentially removed over Mo from the ocean or by invoking a greater retention of W on land. Previous studies have supported the former explanation by demonstrating the greater adsorption potential of W over Mo on some Mn-Fe oxyhydroxides and clay minerals (e.g., Sohrin et al., 1987; Kashiwabara et al., 2013; Gustafsson, 2003). However, Firdaus et al. (2008) noted that Mo/W ratios tend to increase at all stages in the crust-to-ocean pathway of the elements. Therefore, on a global scale, weathering on land must preferentially release Mo over W and that W must behave less conservatively than Mo at certain and currently unconstrained stages of aqueous transport prior to reaching the oceans. The former could, in part, be explained by the flux of both elements from land being dominated by release from substrates with a high Mo/W, such as basalt, even if the loss of W exceeds that of Mo as in the case of the Chhindwara weathering profile.

In deep geological time, the marine Mo inventory was drastically different from today's and it has been reasoned that Mo flux from land only became significant after the rise of atmospheric oxygen at the GOE, due primarily to continental sulphide weathering, such that the supply was able to exceed its withdrawal into marine sediment (Anbar et al., 2007; Scott et al., 2008; Large et al., 2014). By contrast to Mo, however, very little is known about the oceanic W supply and oceanic removal in deep time, although some modern constraints may be relevant. For instance, W flux from mid-ocean ridge hydrothermal activity seems to far exceed that of Mo (Kishida et al., 2004). If W supply, whether from hydrothermal activity or increased subaerial exposure of mafic-ultramafic rocks, had coincided with a greater W solubility, the Precambrian oceans may have had a much lower Mo/W ratio than at present. This could be supported by the observation that W-containing enzymes are a more ancient biological innovation (being present only in prokaryotes) than the comparatively more prolific Mo-containing enzymes (e.g., Andreesen and Makdessi, 2008). Thus, in order to fully address these issues, future studies of oceanic Mo inventories should also consider W, but only after a more complete picture of the aqueous geochemical cycles of Mo and W in the modern environment has emerged.

4.2 Nd isotopes and Th as fingerprints of aeolian dust in weathering profiles

Immobile element and isotope ratios of weathering profiles have been used to calculate the mass of dust in weathering profiles under the assumption that the composition of the profile represents a mixture of the end-member composition of dust and the protolith (e.g., Chadwick et al., 1999; Kurtz et al., 2001). However, Ma et al. (2010) proposed incongruent release of radiogenic over non-radiogenic isotopes (^{143}Nd > ^{144}Nd and ^{176}Hf > ^{177}Hf) during intense basalt weathering which would invalidate the previous two-component mixing assumption. This proposal was based on deviations in the respective isotopic ratios and mass balance considerations that used Th as the

immobile index element. Closer inspection of the data, however, reveals that samples nearest the soil surface exhibit excursions in Th/Nb and Th/Zr ratios that inversely correlate with the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. Thus, the proposal of preferential release of radiogenic Nd and Hf rests with the validity of Th immobility and mass conservation.

In our view, the change in Th/Nb and Th/Zr ratios is more likely caused by the addition of an extraneous component with higher Th and a lower $^{176}\text{Hf}/^{177}\text{Hf}$ ratio (both general characteristics of the average upper continental crust) and redistribution of this component within the profile. Therefore, the data presented by Ma et al. (2010) can be explained without incongruent fractionation of Hf isotopes. This likely extends to the Nd isotope values as well, although the greater mobility of Nd complicates direct correlations. This example emphasises the importance of carefully evaluating the HFSE characteristics of weathering profiles and combining trace element and isotope observations. In the present study, comparative element immobility for Th and Nd and a lack of $^{143}\text{Nd}/^{144}\text{Nd}$ fractionation during incongruent weathering is assumed, such that correlated Th/Nb and Nd isotope excursions from basaltic protolith values are indicative of aeolian dust contamination in the basalt profiles.

4.2.1 Chhindwara profile

Apart from the HFSE ratio variation between the adjacent flows (Section 3.1.1), there are two subtle, but horizon-specific deviations in the Th/Nb ratio in the Chhindwara profile that were alluded to in previous discussion. The first is at the modern soil surface (ChQB11), where the Th/Nb ratio is higher at 0.216 when compared to the mean ratio of the remaining flow (0.178 ± 0.003 ; Figure 2). The second is present in the three uppermost samples of the lower flow (ChQA10-ChQA12), where the Th/Nb ratio in ranges from 0.220-0.233 compared to the mean of 0.209 ± 0.003 in the remaining 9 samples below. Due to the low solubility of both Th and Nb, these deviations are most plausibly explained by Th enrichment from the addition of an extraneous (allochthonous) material with a higher Th/Nb ratio. The higher Th/Nb ratios are accompanied in most samples by deviations towards lower Zr/Nb, higher W/Ta, and extreme alkali element enrichment (Babechuk et al., 2014). It was previously proposed in Babechuk et al. (2014) that the origin of the flow-top alkali element enrichment was the addition of aeolian dust. To test this hypothesis, the samples at the top of the lower flow were analysed for their Nd isotope composition. The data reveal an excursion towards slightly less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ values, especially in sample ChQA12 nearest the paleo flow-top, relative to samples deeper in the flow (Figure 2). The isotopic deviation is subtle, but is outside of the error of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio measurement. Although alkali element enrichment can also be achieved through fluid-rock interaction, the HFSE and Nd isotope data presented here appear to eliminate this possibility, and

instead provide strong support for an aeolian origin. By extension, this may argue against a metasomatic origin for alkali element enrichments in other Deccan Traps bole beds (e.g., Ghosh et al., 2006) and suggests that high-precision Nd isotope and HFSE data may also explain the ambiguous origin of alkali element enrichment in other weathering profiles (e.g., Sheldon, 2003). Although the exact nature of the added dust is unknown, all of the chemical features are consistent with a composition similar to average upper continental crust (Table 4).

The constancy of the ratios of the least-mobile HFSE (Zr-Hf-Nb-Ta-Th) below the paleo flow-top of the lower flow (ChQA) and in the overlying upper flow (ChQB) indicates that contamination by dust at the paleo flow-top preceded the emplacement of the upper flow. Addition of dust (e.g., ash and other atmospheric particles) could have been achieved in two possible ways: it may have been introduced at the time of flow emplacement and mixed with the lava at the surface; or, it may have settled into the flow top after cooling and then percolated in the profile as far down as the base of the porous flow top breccia and associated vesiculation. Given that these flows are of the inflation pahoehoe type, rather than those characterised by surface disruption, and were emplaced remote from exposed basement lithologies, a post-eruption period of aeolian dust accumulation seems the more plausible explanation. Crucially, although the observed shift in the Nd isotope ratio is quite subtle, it nevertheless highlights the sensitivity of the basalt to overprinting and opens the possibility that such signatures may be a useful paleoclimatic fingerprint between basaltic eruptions. Further study may reveal that isotopic and trace element fingerprinting of Deccan bole beds can contribute to estimating exposure time, degree of aeolian contamination, and the history of potentially evolving dust sources.

4.2.2 *Bidar profile*

The depth variation of isotope ratios previously demonstrated the overprinting of the Bidar profile chemistry by dust (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2008), which is expanded on here using Th-U-Nb and Nd isotope systematics.

The Th/Nb ratio of the incipiently- to intermediately-altered saprolite (BB2-BB3: 0.0975-0.0978) is similar to that of the protolith (BB1: 0.0957), but increases significantly upwards from BB4 to BB9 reaching values as high as 0.530 (BB8). This upward change parallels the increasingly open and porous structure of the upper parts of the lateritic weathering profile. Assuming near-equivalent immobility of the two elements during chemical weathering (similar to the Chhindwara profile), increases in the Th/Nb ratio indicate selective Th enrichment. The magnitude of Th enrichment can be expressed more quantitatively using a percent change in Th/Nb ratio relative to the protolith; if Nb is assumed to have been immobile and the change in Th/Nb is attributed purely

Table 4: Summary of elemental (ppm) and Nd isotope compositions of the Deccan Traps basalt and possible dust sources

	Protolith basalt		Potential dust compositions			
	ChQB12	BB1	Global loess ^a	Asian dust ^b	AUCC ^c	±
Nd	18.27	15.51	27.21	26	32.91	8.42
Zr	139.3	119.0	267.2	155	198.5	65.8
Hf	3.70	3.16	6.61	4.4	5.32	1.65
Nb	8.55	9.26	12.82	15	15.33	6.01
Th	1.48	0.89	10.64	8	11.13	4.53
U	0.41	0.23	2.55		2.83	1.50
Th/Nb	0.174	0.096	0.856	0.52	0.753	0.226
Th/Zr	0.011	0.007	0.046	0.052	0.057	0.022
Th/Hf	0.401	0.281	1.849	1.8	2.103	0.732
U/Nb	0.047	0.025	0.206		0.195	0.096
U/Th	0.273	0.261	0.243		0.254	0.066
$\epsilon_{Nd} (t=0)$		4.31	-10.3	-10	-3.79	3.75

a: Mean from loess compilation of Chauvel et al. (2014), including data from Gallet et al. (1996)

b: Asian dust composition as reported in Kurtz et al. (2000, 2001)

c: Average upper continental crust (AUCC) for comparison taken from 'MuQ' alluvial sediment compilation of Kamber et al. (2005)

to Th addition, the most contaminated samples have experienced a 400% increase in Th relative to the protolith (Figure 3b). This is consistent with the addition of a significantly more trace element enriched source. Whereas it is likely that some Nb was also contributed from dust, the relatively low Nb content of upper continental crust and the constant Zr/Nb ratio in the Bidar laterite indicate that, in this system, it has been negligible by comparison to Th (Kurtz et al., 2001). Similar to Th/Nb, the U/Nb ratio increases progressively upwards to a value of 0.113-0.110 in BB8-BB9, with a distinct excursion in sample BB6 with U/Nb ratio of 0.776. Trends towards higher U/Nb ratios are not predicted based on the greater mobility of U relative to Nb, indicating that the U chemistry is highly influenced by dust and more complex internal cycling and deposition. In addition to the Th-U-Nb trends, significant variation with depth is expressed in the Nd isotope ratios, where the ϵ_{Nd} is identical in the protolith and incipient saprolite (BB1-BB2: 4.31-4.38), but decreases upwards towards significantly less radiogenic values from BB3 to BB9, following a more linear upward trend (Figure 3c). These isotope and trace element fingerprints of dust are similar to those observed in the Chhindwara flow tops and other basalt profiles (Kurtz et al., 2000, 2001), although indicate a substantially greater magnitude of contamination; this is likely a function of the protracted exposure of the laterite profile.

Quantitative assessment of the amount of dust added to a weathering profile requires reasonable knowledge of the dust composition. Outside of examples of young soil chronosequences with constrainable exposure histories (e.g., Chadwick et al., 1999; Kurtz et al., 2001), linking the fingerprint of dust in older weathering profiles to a specific source and unravelling the timing of dust addition are inherently more complicated. Nevertheless, based on the current location of the Bidar profile and the paleogeographic context of the Indian plate, two source areas of dust delivered to the Deccan Traps are deemed plausible: the exposed Archean-Proterozoic terrain outcropping to the south and east of the Deccan Volcanic Province; or, areas known to be prominent dust sources at present day (i.e., Sahara/Arabia or from the central Asia region; Grousset and Biscaye, 2005), as visualised in Figure 5.

Previous studies have determined the mass fraction of a dust-derived element in a sample (Chadwick et al., 1999; Kurtz et al., 2001) from isotope or trace element ratios, as shown for Nd and Th using equations 2 or 3, respectively, under the assumption that the ratios in both equations change from that of the basalt in the weathering profile only or primarily as a function of the added dust:

$$\text{Eq. 2: } f_{dust}^{Nd} = \left(\frac{\epsilon_{Nd}^{sample} - \epsilon_{Nd}^{basalt}}{\epsilon_{Nd}^{dust} - \epsilon_{Nd}^{basalt}} \right)$$

$$\text{Eq. 3: } f_{dust}^{Th} = \left(\frac{\left(\frac{Th}{X}\right)_{sample} - \left(\frac{Th}{X}\right)_{basalt}}{\left(\frac{Th}{X}\right)_{dust} - \left(\frac{Th}{X}\right)_{basalt}} \right)$$

where X is an immobile trace element (e.g., Nb, Ta, Zr, Hf) that is less influenced by dust input than Th.

Based on the known or assumed trace element concentration of the dust source, i.e., $[Y]_{dust}$, the concentration of the element associated with dust in the sample and the mass fraction of dust (f_{dust}^Y) can be calculated from the f_{dust}^{Th} value and the ‘bulk’ concentration of the element in the sample $[Y]_{sample}$ from equation 4:

$$\text{Eq. 4: } f_{dust}^Y = \left(\frac{f_{dust}^{Th} \times [Y]_{sample}}{[Y]_{dust}} \right)$$

The mass of a dust-derived element (mg cm^{-2}) can be determined from the sample density (ρ) and extrapolated to horizons of defined thickness (h) in the profile using equation 5:

$$\text{Eq. 5: } Y_{dust}^{mass} = f_{dust}^Y \times [Y]_{sample} \times \rho \times h$$

The mass of each element in a horizon can then be divided by the concentration of the element in the dust source $[Y]_{dust}$ and summed for each horizon to determine the total mass of dust accreted (g dust cm^{-2}) in the profile as described in Kurtz et al. (2001).

In the Bidar profile, horizons are divided by assuming that the measurements of the first sample (BB1) represent the interval between its sample depth and that of the overlying sample ($h=1200$ cm) and so on to the uppermost horizon represented by BB9 and extending to the surface ($h=200$ cm). To apply the mixing model equations to the Bidar laterite, which is contaminated by dust from an unconstrained source, assumptions have to be made regarding the dust composition. First it is assumed that the dust had a similar *elemental* composition to the average upper continental crust as represented by a global loess compilation (Chauvel et al., 2014; Gallet et al., 1996), with a Th and Nd concentration of 10.64 and 27.21 ppm, respectively, and Th/Nb, Th/Zr, Th/Hf ratios of 0.856, 0.046, and 1.850, respectively (Table 4). These values all contrast substantially with those of the parent basalt (BB1) and are similar to the Asian dust values estimated for the allochthonous component in Hawaiian basalt (Kurtz et al., 2000, 2001; Table 4). This initial assumption is reasonable because most Th/X ratios in upper continental crust proxies agree quite well (e.g., Kamber et al., 2005) and are not dependent on the age of the crust. It is also noted that upper crustal composites have the high Th concentration in the allochthonous end-member required to alter the Th/X ratios of the profile. Based on Th/Nb, Th/Zr, Th/Hf ratios, the calculated mass fraction of dust-derived Th increases upwards in the Bidar profile (see Figure 3e for mass fraction

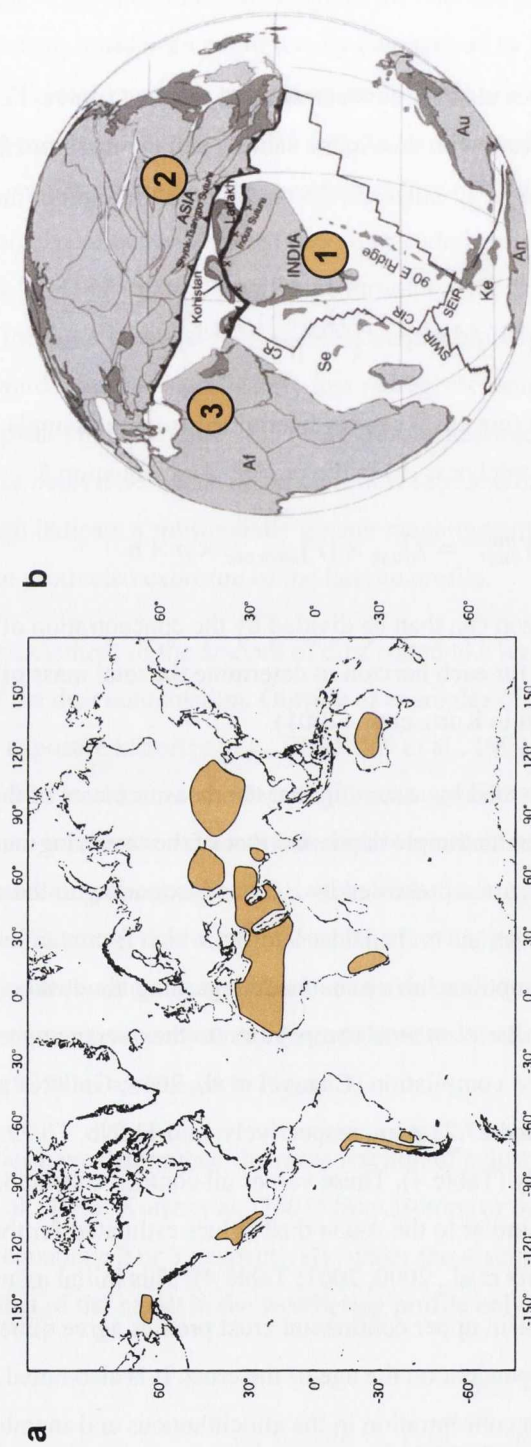


Figure 5: (a) Map of modern dust sources (modified from Grousset and Biscaye, 2005, after Sarnthein, 1978) and (b) an outline of possible dust sources to the Deccan Traps during lateritisation (modified from Chatterjee et al., 2013). For the reasons discussed in the text, it is proposed that continentally-derived dust (1 or 2) with a composition similar to modern loess (e.g., Chauvel et al., 2014) is more compatible with the Bidar laterite profile chemistry than dust derived from the Archean-Proterozoic rocks exposed adjacent to the Deccan Traps (3) although the data cannot unambiguously resolve this.

based on Th/Nb values) with similar overall dust accretion masses of 580, 760, and 740 g dust cm⁻², respectively (differences generated primarily by the variation of the Th/X ratios in BB8 and BB9). By comparison with the much thinner and younger basalt soils from Hawaii (Kurtz et al., 2001), the total amount of accreted dust added to the Bidar profile is substantially larger with a mass fraction ($f_{dust_{Th}}$) reaching greater than 0.5 in the uppermost parts of the profile, and is due to the highly protracted development and exposure history of the laterite.

By contrast to similarity in elemental composition and Th/X ratios of potential dust sources, the Nd isotope characteristics can be more divergent. The global loess compilation has an approximate ϵ_{Nd} of -10 (Table 4) whereas the antiquity of the Archean-Proterozoic shield results in substantially less radiogenic Nd isotope values in trace element rich rocks (e.g., mean ϵ_{Nd} of -34±6 for Neoarchean granitoids and rhyolites of the Dharwar Craton; Mohan et al., 2013). With the same Nd concentration of 27.21 ppm, the effect of the less radiogenic (older) Nd dust source relative to that similar to that of the UCC would be a significantly lower dust-derived Nd input and mass fraction of dust in each sample (Figure 3e). The total mass of accreted dust calculated from a source with ϵ_{Nd} of -34 is 630 g dust cm⁻², whereas a dust source with ϵ_{Nd} of -10 results in a mass of 1650 g dust cm⁻². The dust calculations based on Nd, however, are much more highly influenced by uncertainties resulting from depletion of Nd in the basalt prior to dust accumulation, the prolonged and intense weathering history that redistributes Nd, and the unknown isotopic composition of the source. At present, we suggest that the closer agreement between the fraction of dust-derived Th (f_{dust}^{Th}) and dust-derived Nd (f_{dust}^{Nd}) from a source with ϵ_{Nd} of -10, especially in the uppermost horizons of the laterite, is more consistent with the dust source being from a younger or a more diversely mixed end-member. However, it is clear that the Nd isotopes are incapable of unambiguously resolving the dust end-member at present and we propose that better constraints could be made from Hf isotope systematics due to the near-equal immobility of Hf, Zr, and Nb in the profile (Section 4.1.1).

4.2.3 The fate of dust during lateritisation

More robust estimates of dust addition (based on either Th or Nd) are principally limited by the relatively coarse sampling density throughout the Bidar profile. Rather than placing too much emphasis on the assumption that thick horizons of laterite are accurately represented by the chemistry of 9 samples, we instead focus on the qualitative chemostratigraphic trends of the dust-derived elements, which are independent of the assumed isotope composition of the dust and provide insight into the fate of dust-derived elements after addition to the profile. If the dust-derived Nd and Th had been brought in together and not separated chemically after accretion, a

correlation between the f_{dust}^{Th} and f_{dust}^{Nd} in each sample would be expected (i.e., the dust-derived Th and Nd originally had the same distribution in the profile). Instead, the diverging topology with depth in the profile for f_{dust}^{Th} and f_{dust}^{Nd} (and the mass fraction of dust calculated from each; Figure 3e) as well as the percent change in Nd/Nb and Th/Nb (Figure 3d) suggests a contrasting chemical mobility of the two dust-derived elements.

The Th/Nb ratios and associated Th-based dust estimates increase only minimally in the saprolite horizons of the profile (BB2-BB4) from the protolith (BB1), but increase substantially towards the surface within the laterite horizons (BB5-BB9; Figure 3). This chemical distribution is proposed to reflect the changing morphology of the laterite profile and is consistent with dust trapping at the surface and winnowing downwards until the transition into less porous and permeable saprolite horizons. As such, a greater proportion of the dust is retained in the upper horizons and the reduction in pore size filters the dust as it percolates down through the profile to the point that only the finest dust fraction can penetrate into the saprolite zones. In other words, the Th chemistry is interpreted to reflect primarily physical translocation of the dust in the laterite.

The Nd/Nb ratios and Nd-based dust estimates indicate a greater solubility and more complex redistribution of the REE in the laterite (Figure 3). The majority of the profile is highly depleted in Nd relative to the protolith, apart from samples BB3 (depth of 2600 cm) and BB6 (depth of 1100 cm). The isotopic composition of all samples from BB3 to BB9 indicate that they contain dust-derived Nd. Apart from the uppermost samples BB8 and BB9 it is also evident that the f_{dust}^{Nd} and mass fraction of dust calculated from Nd is higher in all samples deeper in the profile by contrast to the same parameters calculated using Th/Nb ratios (Figure 3e). These observations implicate remobilisation of the REE in the profile through dissolution and precipitation, including dust-derived Nd. The enrichment of the REE (and many other trace elements) in sample BB6 was previously inferred to represent accumulation at a paleo-water table zone (Kisakürek et al., 2004), whereas the REE enrichment in sample BB3 is interpreted to represent precipitation of secondary phosphates at a pH/porosity boundary deep in the profile (Babechuk et al., 2014; Viers and Wasserburg, 2004; Cotten et al., 1995). With regards to the deep sample (BB3), which does not contain dust-derived Th, the isotope composition independently confirms that the REE enrichment is the result of downward migration of REE, since it necessitates that at least some of the Nd was derived from the dust higher in the profile. Accordingly, it provides further evidence that the REE are hosted in a secondary phase that precipitated from weathering fluids. It also suggests that Th stayed lattice-bound to the incorporated allochthonous mineral(s) and did not penetrate as deeply into the profile. The fingerprint of dust-derived Nd at the paleo-water table is significant since it implies that the dust was present in the profile during its development and that the table was

relatively stable, such that local dissolution and precipitation of REE occurred in proximity of the horizon, which may also place important constraints on timing of dust accumulation; if the water table was only stable at the approximate position of BB6 (depth of 600 cm) prior to uplift and ‘fossilisation’ of the profile, an important finding of this study is that dust addition must have predated, or, at the very least, overlapped in time. Thus, instead of post-‘fossilisation’ dust accumulation, it appears that dust must have been added during the northward journey of the Indian plate, and prior to any substantive uplift and attendant dissection of the laterite.

If U was brought in with Th, the Th/U and U/Nb ratios also appear to indicate that U was preferentially mobilised relative to Th and deposited elsewhere in the profile. The Th/U ratio of the two uppermost samples (4.15 and 4.71) is close to that of the average upper continental crust (Table 4), but the ratios are lower at greater depth in the profile. Similarly, higher U/Nb ratios than the parent basalt throughout the profile (Figure 3d) indicate that added U has altered the profile chemistry to a depth as low as 2600 cm (Sample BB3).

4.3 Y/Ho and mobility of yttrium

The weathering-induced mobility of the REE+Y is well documented (e.g., Cotten et al., 1995; Hill et al., 2000a,b; Patino et al., 2003), although it has only recently been shown that Y loss outweighs that of its geochemical twin Ho during chemical weathering, resulting in measurable Y/Ho fractionation (Babechuk et al., 2012; Thompson et al., 2013). The high-precision Y/Ho data in this study extend our understanding of their fractionation behaviour across a wide range of observed weathering intensity and we propose that Y/Ho fractionation may have potential as a chemical weathering proxy.

4.3.1 Y/Ho fractionation during basalt weathering

Protolith Y/Ho ratios of both the Bidar (BB1: 24.42) and the Chhindwara (ChQB12: 24.71) weathering profiles are lower than the average upper continental crust (e.g., 26.24 ± 0.36 ; Kamber et al., 2005) and carbonaceous chondrites (25.94 ± 0.08 ; Pack et al., 2007), but within the range of the values of the USGS and GSJ basalt standards (24.37-25.36; Table 1). Relative to the protolith values, however, a wide range of Y/Ho ratios occur throughout the weathering profiles (Chhindwara: 21.89 to 26.52; Bidar: 14.71 to 30.15) that indicate a significant weathering-related fractionation. The magnitude of Y/Ho fractionation appears to be linked to the degree of chemical weathering experienced by the basalt and also identifies secondary rare earth element enrichment.

During the earliest stages of basalt weathering, as represented by the Chhindwara profile, Y/Ho decreases gradually to as low as 21.89 in correlation with the loss of Ca and Na inferred from the

CIA (Figure 6a). In some cases, however, the Y/Ho increases relative to the protolith basalt, most notably in the centre of the corestone (ChQB9), which could indicate preferential inward migration of Y (also seen by U; Section 4.1.3), since the ratio changes from 23.65 (ChQB9a) in the outermost section progressively to 26.52 in the corestone centre (ChQB9d). Previous work demonstrated the mobility of Y at early stages of basalt weathering (Hill et al., 2000a), which is confirmed by these results, although it is now clearer that this Y loss is measurable relative to Ho, even at a small scale.

The most highly fractionated Y/Ho ratios are found within the Bidar profile. Apart from sample BB3 (Y/Ho: 30.15), the values decrease upwards in the profile towards very low Y/Ho ratios (14.71 to 19.42). As with the less altered Chhindwara example, the overall trend of decreasing Y/Ho ratios in the laterite profile is anti-correlated with the weathering intensity (Figure 6b) – in this case, the index of lateritisation (IOL; Babechuk et al., 2014). Thus, beyond the point of complete Ca and Na loss from the profile, Y mobility relative to Ho continues into the more extreme stages of Si loss during lateritisation. The exception to the general trend of Y loss in BB3 occurs in the same sample that is heavily REE enriched (Kisakürek et al., 2004; Babechuk et al., 2014), evident in this study based on the very high Nd/Nb ratio (Section 4.2.3). The REE pattern and Nd isotope composition of this sample both imply that the REE enrichment is due to the precipitation of elements derived from weathered basalt elsewhere in the evolving profile (Babechuk et al., 2014). This is consistent with the highly elevated Y/Ho ratio since weathering fluids would be predicted to have higher Y/Ho ratios than the basalt to mass balance the lower Y/Ho ratios in the profile.

The additional factor that needs to be considered, especially for the Bidar laterite, is the substantial dust addition to the profile during its evolution, including the REE (Section 4.2). A reasonable assumption is that the dust had, on average, a Y/Ho ratio similar to the average continental crust (~26). The extremely low Y/Ho ratios in the profile, however, must reflect one of two conditions; either the REE concentration of the dust was not high enough to influence the REE signature of the profile or that the Y was removed preferentially to Ho from both the basalt and the added dust. The Nd isotope data imply that the former factor is not dominant and, therefore, the extremely low Y/Ho in the most dust influenced parts of the profile is even more significant.

4.3.2 Y/Ho as a silicate weathering proxy

The fractionation of Y/Ho due to preferential Y loss in both basalt profiles is well beyond the ‘charge and radius’ controlled behaviour of the isovalent element pair (i.e., CHARAC; Bau, 1996), consistent with the results of Thompson et al. (2013). Extreme Y/Ho fractionation has traditionally

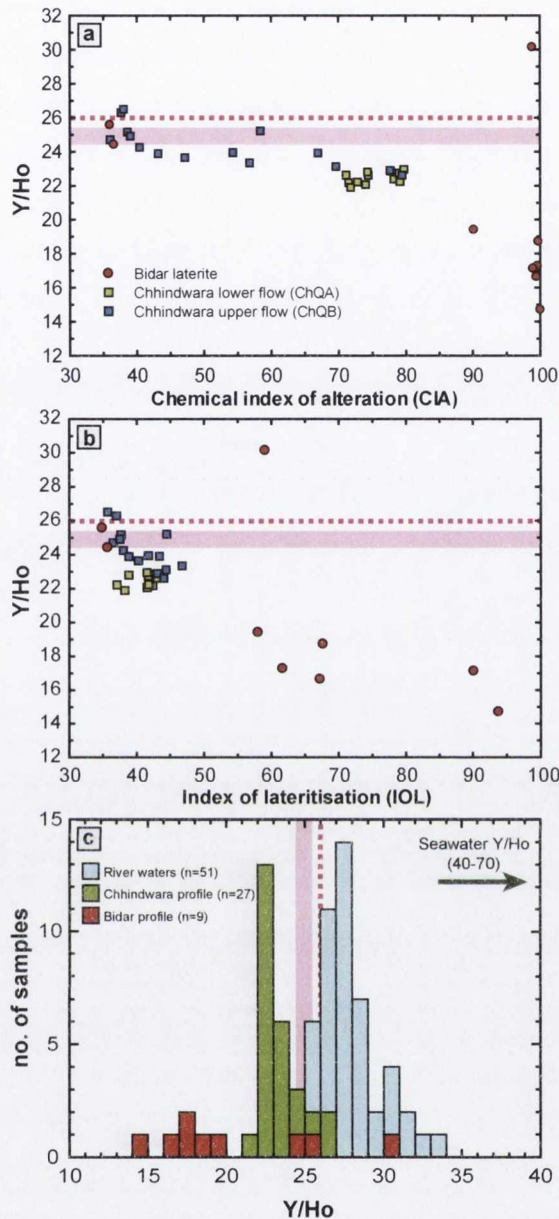


Figure 6: Changes of Y/Ho in both profiles plotted against the chemical index of alteration (a) and the index of lateritisation (b), along with a comparison of the range of Y/Ho ratios in the weathering profiles with those of dissolved river waters from the eastern Australia drainage basin (Lawrence et al., 2006a,b). The symbols in (a) and (b) are divided to show the upper flow [ChQB: dark (blue) shaded squares] and lower flow [ChQA: light (green) shaded squares] of the Chhindwara profile and the Bidar profile [dark (red) shaded circles]. For reference, the chondritic Y/Ho ratio of 25.94 from Pack et al. (2007) is shown as a broken line and the horizontal shaded area denotes the range of Y/Ho exhibit by the USGS and GSJ basalt standards and protolith basalt of this study (24.37 to 25.36). The changes of Y/Ho in the altered basalt indicate fractionation of these isovalent elements occurs during chemical weathering due to the preferential removal of Y. The data from Lawrence et al. (2006a,b) were screened to exclude samples with a salinity greater than 0.5 ‰ or conductivity greater than 150 ms/cm, and P greater than 20 ng/g to minimise the effects of salinity induced Y/Ho fractionation and phosphate fertiliser contamination. These screened data have a mean superchondritic Y/Ho ratio of 27.75 ± 2.08 and tenuously support a mass balance with respect to the lower Y/Ho ratios generated in soils.

been associated primarily with the aqueous transport of the REE (e.g., Nozaki et al., 1997; Lawrence and Kamber, 2006) or in highly evolved magmatic systems (Bau, 1996). Given the well-established mobility of Y during weathering (e.g., Hill et al., 2000a) and the results of this study that indicate Y/Ho fractionation extends across all stages of basalt weathering, we propose that Y/Ho has potential as a silicate weathering proxy. Although it is evident that changes in Y/Ho ratio track the progressive alteration of primary minerals to pedogenic clays and oxides, the mechanisms of fractionation need to be better constrained. The findings of Thompson et al. (2013) suggest that Fe-(oxyhydr)oxides are the most important phase involved in fractionation and that the maximum separation of Y from Ho occurs at intermediate pH ranges. Therefore, the lower affinity of Y for Fe oxyhydroxides and oxides in weathering profiles generates a similar result to the reactive particle shuttle in the marine realm. This is consistent with the extreme fractionation associated with degree of Fe enrichment in the Bidar laterite. By contrast, organic matter is thought to exert a suppressing effect on Y/Ho fractionation (Thompson et al., 2013). If Fe-(oxyhydr)oxides are crucial to Y/Ho fractionation, the degree of Y loss relative to Ho may also be a function of protolith lithology (e.g., Fe-rich vs. Fe-depleted igneous rocks) or specific soil types and thus also influenced by climate. Consequently, Y/Ho fractionation may be more extensive in basalt-dominated catchments and may have potential as a tracer of Fe-oxide formation (i.e., oxidative weathering intensity) in paleosols. These aspects of the weathering behaviour of Y/Ho will be further illuminated as high-precision measurements of additional weathering profiles of different ages and compositions are undertaken.

4.3.3. Influence of weathering induced Y/Ho fractionation on river water and sediment geochemistry

If the fractionation of Y/Ho during weathering is a ubiquitous process, then mass balance predictions can be made with regards to the Y/Ho geochemistry of river waters and clastic sediments, two end-products of weathering. The first prediction is that clastic sediments should contain some evidence of fractionation through a slightly lower Y/Ho ratio than their source rock. Based on results of this study, the degree of fractionation preserved in the sediment could be size fraction dependent and possibly be linked to the magnitude of weathering intensity experienced at source. The latter would therefore suggest more pronounced fractionation in sediments associated with tropical weathering conditions and stable cratonic environments. The second prediction is that the Y/Ho ratios of river waters should be higher than that of the source rocks. Here, we will address the second prediction based on the high-precision REE+Y data available to date.

A growing number of studies are recognising higher Y/Ho ratios than the average upper continental crust (as represented by shale) in river waters (e.g., Lawrence et al., 2006a,b;

Leybourne and Johannesson, 2008; Babechuk et al., 2012; Thompson et al., 2013). This observation qualitatively supports the prediction that river waters inherit high Y/Ho ratios from weathering fluids. The study of Thompson et al. (2013) previously suggested this link using the compilation of Canadian river water data from Leybourne and Johannesson (2008). However, these authors did not fully consider the complexities of aquatic REE+Y chemistry that may influence Y/Ho ratios outside of a potentially inherited weathering signature. These are summarised below and an initial attempt is made to define a better informed weathering-related Y/Ho pattern in the REE+Y data set from the studies of Lawrence et al. (2006a,b) on eastern Australian rivers.

Although there appears to be no systematic aquatic chemical process capable of fractionating Y and Ho in fresh (riverine) waters (Lawrence et al., 2006a), significant fractionation occurs in the estuarine environment. When fresh river water enters a strong salinity gradient, the higher particle reactivity of the HREE (including Ho) relative to the LREE (and Y) leads to the strong Y enrichment relative to Ho observed in seawater (Y/Ho: ~40-70; e.g., Bau et al., 1995, 1997; Nozaki et al., 1997; Alibo and Nozaki, 1999; Lawrence and Kamber, 2006). This is relevant to riverine Y/Ho chemistry in three main aspects. Firstly, only fresh waters sufficiently unaffected by the estuarine salt wedge or saline groundwaters are suitable for assessing Y/Ho inherited from the local catchment. Secondly, if the local catchment geology is rich in marine authigenic sedimentary rocks (e.g. carbonates, phosphates), river waters will be biased towards higher Y/Ho. Finally, anthropogenic contamination from the local use of marine phosphate fertilisers can modify riverine Y/Ho ratios (e.g., Marx et al., 2010; Lawrence et al., 2006b).

An initial analysis of dissolved riverine REE+Y data from eastern Australia by Lawrence et al. (2006a,b) noted Y/Ho values higher than the average upper continental crust in samples remote from salinity gradients associated with estuarine or groundwater influx. The authors considered variations in local catchment geology, soil-related processes, and local use of fertilisers as possible explanations, but reasoned that the latter was most compatible with the data. To further account for these factors, the dissolved river water data of Lawrence et al. (2006a,b) were screened in this study based on conductivity/salinity and, when available, P concentration (Figure 6). The remaining samples (n=51) are believed to be least anthropogenically disturbed and least influenced by salinity-induced Y/Ho fractionation. The mean Y/Ho of this subset of samples is still superchondritic at 27.75 ± 2.08 (Figure 6c). This appears to strengthen the case for Y/Ho fractionation occurring in soils and that the signature generated in weathering fluids may be inherited by the rivers. However, due to the complexities in fully addressing the factors influencing Y/Ho in larger rivers draining a variable catchment geology, detailed Y/Ho studies at all levels

(protolith, saprolite, soil, ground and river water) of purely igneous catchments will be necessary to unambiguously fingerprint the sources of fractionation.

5. Conclusions

A combined high-precision HFSE (Zr-Hf-Nb-Ta-Th-U-W-Mo), Y/Ho, and Nd isotope study was performed on two separate basalt weathering profiles in the Deccan Traps that contrast in their degrees of alteration, their age, and time scale of their development during the Cenozoic. The findings of this study are of direct relevance to the weathering of other basaltic terrains and, importantly, to fluvial and marine chemistries and broader global elemental fluxes. It is evident that Zr, Hf, Nb, and Ta exhibit very limited mobility during alteration of the basalt and are thus of use in reconstructing pre-weathering chemical variability in the weathered lava flows. By contrast, the oxyanion forming elements (U, Mo, W) are much more mobile. The mobility of W exceeds that of Mo substantially in certain areas of the basalt profile. The findings of this study, although limited to only bulk element concentration, draw attention to a clear need to better establish the mechanisms of Mo and W mobility both during the weathering of different substrate lithologies, and from the perspective of global flux to the hydrosphere. This is necessary to understand present fluxes but primarily to illuminate Precambrian oceanic inventories of these biochemically important elements. This will require additional study of other, more ancient weathering profiles, and detailed investigation at the mineralogical scale, as well as studies focused on constraining the source of changes of Mo/W in waters throughout the stages of aqueous transport.

The influence of dust has previously shown to be important in modifying the chemistry of the Deccan Traps (Mason et al., 2000; Kisakürek et al., 2004; Wimpenny et al., 2008) as well as other CFBPs (e.g., Liu et al., 2013) and this is expanded on in the present study with Th-U-Nb and Nd isotope systematics. Dust accumulation is shown to occur even on the short time scale between successive lava flows, particularly at sites far from the main eruptive centres. During prolonged exposure to dust and synchronicity with lateritisation process, certain aspects of physical transport (e.g., distribution of dust-derived Th) and chemical dissolution of dust (e.g., distribution of dust-derived Nd) can be reconstructed in the Bidar profile, although current data still do not permit conclusive fingerprinting of the dust source. Extreme chemical overprinting and redistribution of dust-derived Nd was previously discovered in a lateritic profile from Southern Cameroon (Viers and Wasserburg, 2004), where it is evident that local rivers also inherit some of the resulting isotopic variation from the evolving profile. These cases make it evident that following the depletion of the majority of Nd hosted in the protolith, atmospheric resupply of the REE (and other

elements) may begin to dominate the internal chemistry of the profile and progressively influence the net weathering flux. This crucial role of allochthonous element addition needs to be considered in geochemical investigations of weathering profiles. For example, although not the focus of this study, the influence of dust on Th and U (Pett-Ridge et al., 2007) becomes especially relevant when modelling weathering cycles with U-series isotopes.

The mobility of Y during chemical weathering is greater than that of the HREE and can be assessed using fractionation of Y/Ho. This study shows that Y/Ho fractionation extends across all stages of basalt weathering intensity and suggests that this parameter may be a very useful proxy for silicate weathering intensity once the mechanisms of fractionation are better established. The greater release of Y over Ho during chemical weathering may influence the dissolved chemistry of river waters (higher Y/Ho than source) and the chemistry of clastic sediments (lower Y/Ho ratios than source), but requires more high-precision data for confirmation.

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Chapter 3 supplementary information

Supplementary Table 1: Full data set for Chhindwara saprolite profile

	Lower flow (ChQA)						
	ChQA1	ChQA2	ChQA3	ChQA4	ChQA5	ChQA6	ChQA7
Notes							
Depth (cm)	630	610	590	550	530	510	490
wt. %							
SiO ₂	40.91	41.70	41.02	42.00	41.99	41.38	41.23
TiO ₂	2.97	3.03	3.10	3.03	3.10	2.92	2.91
Al ₂ O ₃	13.19	12.46	12.50	12.28	12.66	12.87	13.08
Fe ₂ O ₃ (T)	17.18	18.21	18.39	17.59	17.65	16.97	16.50
FeO	1.71	1.51	1.81	1.71	1.64	1.47	1.24
MgO	2.30	2.45	2.43	2.69	2.68	2.72	2.94
MnO	0.21	0.25	0.26	0.21	0.15	0.22	0.27
CaO	2.62	2.47	2.20	2.23	1.91	1.97	2.05
Na ₂ O	0.55	0.43	0.26	0.22	0.02	bdl	bdl
K ₂ O	0.27	0.36	0.41	0.43	0.58	0.42	0.25
P ₂ O ₅	0.25	0.26	0.24	0.24	0.21	0.19	0.23
LOI	18.41	17.00	17.90	17.85	17.90	18.95	19.12
Total	98.86	98.61	98.71	98.78	98.86	98.59	98.57
ppb							
Li	5704	6372	6893	8006	6533	5848	5279
Be	775	855	856	1013	966	901	820
Sc	41510	40170	39630	39570	42440	40960	41140
Ti	17680000	18220000	18680000	18270000	18750000	17510000	17250000
V	311200	328700	335900	328700	336700	320100	300700
Cr	94170	60460	56800	56770	84050	79390	74250
Co	43390	49810	48480	49750	38200	43490	54100
Ni	47820	44050	41060	39760	37120	38880	43360
Cu	281200	302900	306400	254800	288600	306600	311600
Zn	130900	134100	137300	130400	117900	121000	136000
Ga	23670	24160	24050	24260	22880	23260	24260
As	245	268	296	240	246	343	290
Rb	10860	12050	15800	15730	22800	16430	9251
Sr	94860	87130	71690	81900	55070	65040	58590
Y	29710	34600	31460	31190	27520	27030	32760
Zr	206400	216000	215700	219200	213200	205100	203200
Nb	13180	13900	14130	14050	13920	13350	13100
Mo	457	522	675	457	483	450	485
Ag	69	66	65	62	58	45	46
Cd	115	135	136	112	92	108	111
In	124	126	130	132	132	123	123
Sn	42	70	61	29	37	75	100
Sb	14	26	30	21	29	31	27
Cs	267	263	357	274	485	321	130
Ba	59970	59280	56570	64120	43630	67110	65600
La	13550	17020	15250	16040	14300	13480	17270
Ce	34980	38790	37270	37430	33820	38470	45310
Pr	4998	6149	5290	5747	5107	4893	6398
Nd	22620	27900	23880	26050	22890	22200	28810
Sm	6081	7479	6395	6966	6075	5961	7656
Eu	1969	2404	1958	2200	1717	1694	2082
Gd	6750	8345	7248	7737	6520	6412	8106
Tb	1092	1333	1158	1234	1043	1043	1290
Dy	6525	7847	6916	7167	6100	6083	7476
Ho	1313	1559	1391	1413	1204	1208	1473
Er	3516	4085	3666	3666	3180	3193	3884
Tm	502	574	517	513	448	459	553
Yb	3112	3503	3168	3088	2783	2870	3395
Lu	427	476	437	417	378	393	464
Hf	5443	5654	5696	5835	5651	5441	5387
Ta	857	893	903	915	899	864	857
W	18	21	58	24	64	52	53
Tl	27	32	38	40	41	48	41
Pb	1391	2211	2261	2736	2065	1970	1537
Th	2752	2878	2911	2879	2894	2858	2752
U	565	595	568	479	482	499	570

bdl = below detection limit

ChQA8	ChQA9	ChQA10	ChQA11	ChQA12	ChQB1	ChQB2	ChQB3
470	450	430	420	410	405	390	370
41.72	41.98	45.44	46.92	45.14	41.76	41.43	41.29
2.91	3.04	2.52	2.43	2.27	2.58	2.72	2.59
12.86	13.23	11.53	11.72	12.44	15.16	15.85	14.99
17.04	16.59	16.57	15.91	16.23	16.40	16.74	17.97
1.37	1.38	0.92	0.85	0.82	0.47	0.60	1.18
2.94	3.01	3.34	3.30	3.43	2.61	2.74	2.28
0.22	0.25	0.18	0.22	0.20	0.39	0.38	0.31
1.90	1.88	1.53	1.39	1.40	1.97	1.92	2.92
bdl	bdl	bdl	bdl	bdl	0.30	0.26	0.84
0.32	0.33	1.79	1.82	1.69	0.64	0.48	0.31
0.16	0.17	0.08	0.05	0.03	0.17	0.14	0.20
18.58	18.07	15.90	15.87	16.47	17.42	16.68	15.01
98.58	98.56	98.80	99.55	99.24	99.40	99.33	98.69
5899	5066	10430	10340	8789	6570	6290	5076
818	803	803	809	839	846	807	803
41710	42970	36490	36130	38420	45500	47780	44850
17830000	18320000	15430000	14290000	13620000	15460000	16390000	15450000
325200	323000	330000	329800	338700	335900	333000	302100
80590	83470	79520	77680	72010	63610	68070	63870
50930	52580	51900	44820	44070	63800	62390	59590
43710	44960	52860	49110	49020	56050	59930	57600
312600	350500	255600	257600	251100	270600	292900	262900
136100	144900	109500	103700	119600	130400	139200	127300
23460	24100	20120	20050	21390	26050	27180	25930
368	312	437	584	856	315	370	335
13770	13240	80360	75650	70450	10460	8058	5368
50270	42330	36120	34680	36640	61940	57760	102000
27670	25180	18980	18530	21410	31210	28770	35110
209900	205300	182900	171000	159900	167000	174500	164800
13620	13910	11940	11310	10320	10170	10620	10120
601	556	394	381	439	551	589	574
67	61	56	74	89	70	53	45
123	118	87	83	70	133	128	99
127	129	114	117	122	122	129	121
46	16	22	32	43	67	13	21
44	36	44	45	48	41	48	20
337	281	1963	1528	1377	111	150	236
44470	34010	76710	84040	64760	172400	91070	89130
14070	13160	11540	10260	10100	13730	11770	15300
39900	56790	33210	28960	23080	32290	35070	32620
5074	4803	3803	3305	3338	5150	4507	5556
22700	21390	16530	14440	14970	23770	20550	26090
6039	5648	4371	3844	4095	6450	5697	7083
1628	1451	1238	1173	1353	1956	1745	2367
6401	5907	4553	4161	4652	7109	6210	8054
1031	947	745	691	763	1144	1036	1274
6074	5550	4387	4133	4635	6789	6297	7569
1216	1097	867	834	939	1364	1272	1518
3260	2911	2287	2236	2543	3652	3441	3992
476	422	331	324	368	524	500	564
3024	2702	2068	2078	2356	3241	3138	3433
424	374	286	291	337	453	441	478
5587	5336	4884	4570	4248	4507	4701	4387
880	905	777	744	675	664	698	650
175	114	172	292	613	189	182	104
43	47	130	128	107	95	66	39
2115	1881	2830	2606	2429	1871	2003	1761
2846	2910	2625	2604	2406	1824	1964	1817
566	481	357	361	401	478	489	419

Chapter 3 supplementary information

Upper flow (ChQB)							
ChQB4	ChQB5	ChQB6	ChQB7	ChQB12 Protolith	ChQB8	ChQB9a	ChQB9b Corestone transect from
350	330	310	210	140	110	90	90
42.14	43.69	46.95	46.35	48.72	47.34	45.12	47.58
2.67	2.55	2.32	2.23	2.23	2.35	2.33	2.31
15.14	14.48	13.39	13.70	12.93	12.98	13.22	13.11
17.14	16.82	15.40	15.73	15.07	15.60	17.20	15.42
1.10	2.42	6.17	6.18	9.75	7.00	4.71	6.58
2.14	2.97	4.71	4.75	5.46	4.92	3.88	4.87
0.31	0.26	0.21	0.22	0.23	0.23	0.25	0.23
3.29	5.39	9.06	8.43	10.55	9.48	6.88	9.38
1.04	1.59	2.11	1.81	2.43	2.26	1.57	2.25
0.29	0.26	0.31	0.18	0.28	0.22	0.19	0.22
0.22	0.21	0.21	0.19	0.20	0.21	0.20	0.20
14.83	10.86	4.93	6.01	1.51	3.55	8.57	4.31
99.20	99.10	99.59	99.59	99.61	99.12	99.42	99.87
5351	5167	5583	6094	5713	5933	5178	5330
796	700	773	629	686	726	750	630
45680	43260	40060	40310	38490	39140	39210	38790
15790000	14890000	13740000	13010000	13480000	13950000	13760000	13270000
310300	343700	408900	396000	413900	407500	381600	396500
64840	62740	57570	62160	58730	54960	55530	57140
57300	50480	49270	50460	51970	50140	51010	51320
54270	52360	57340	59050	55670	53050	54940	54600
271200	261800	202500	210000	213400	196400	223600	221100
127700	123800	118900	113300	113400	126600	112100	114800
26040	24550	22480	22050	21580	22200	22350	21870
259	243	296	195	450	235	268	192
4333	3551	3287	1853	5226	1644	1802	1477
113400	151900	185500	166500	201500	195500	145900	191000
31910	29770	36510	29360	30780	36240	29050	33450
169600	160400	147100	136600	139300	150800	144500	141200
10280	9728	8956	8279	8554	9195	8880	8575
580	524	439	420	462	457	462	403
49	52	74	84	119	136	72	108
92	92	114	92	98	121	89	106
121	116	108	104	100	107	107	104
25	89	121	24	122	33	38	101
15	7	7	3	17	4	8	7
188	145	82	79	89	79	85	60
93010	94790	99950	86700	83570	113600	92080	95020
13710	12560	12660	10520	10800	12460	11180	11440
32290	29130	26220	24890	26790	27970	27310	26540
4901	4488	4549	3880	3876	4442	4071	4029
22960	20970	21560	18520	18270	20980	19230	19000
6283	5732	6133	5258	5137	5960	5408	5397
2116	1984	2209	1906	1809	2113	1870	1917
7185	6593	7475	6212	6103	7105	6284	6547
1130	1046	1201	1006	994	1159	1014	1072
6657	6226	7396	6090	6058	7100	6101	6573
1334	1243	1505	1229	1246	1440	1228	1342
3510	3250	4005	3283	3319	3857	3293	3599
489	456	568	466	473	547	471	509
2970	2769	3453	2842	2901	3328	2880	3115
413	389	481	398	413	468	405	441
4525	4246	3930	3674	3698	3978	3862	3724
671	628	581	541	547	594	577	554
84	71	94	59	92	90	93	73
37	25	12	14	46	17	33	21
1850	1762	1540	1313	1423	1571	1629	1425
1837	1727	1573	1470	1485	1619	1557	1507
460	413	443	338	406	392	400	411

ChQB9c	ChQB9d	ChQB10	ChQB11
centre (9d) to edge (9a)			
90	90	10	0
48.16	48.75	41.28	39.98
2.24	2.36	2.78	3.32
13.03	13.69	14.92	15.17
15.23	13.36	18.16	19.92
7.20	6.55	4.97	5.20
5.09	5.03	3.95	3.62
0.22	0.20	0.24	0.30
9.90	10.16	5.43	5.57
2.33	2.49	0.68	0.91
0.23	0.23	0.12	0.29
0.20	0.21	0.20	0.16
3.40	3.33	10.78	10.04
100.04	99.79	98.53	99.27
5526	5360	7695	11970
681	573	890	908
38690	40810	46620	45090
13210000	13920000	16470000	20330000
404600	411100	434500	585100
56160	60540	67190	77580
52530	58310	54650	66110
55620	54390	67870	82650
211500	254700	238900	250000
116300	122600	145200	139600
21450	22460	26230	26710
386	355	523	964
1447	1231	2008	13700
198000	210200	125600	112000
34690	34970	50780	30030
140100	141200	176000	179100
8566	8821	10670	12220
409	381	467	667
133	239	102	99
104	135	150	126
100	105	124	131
170	59	20	72
9	20	22	52
51	30	74	509
99650	110400	182400	165200
11130	11520	19250	12450
26810	27650	28900	32240
3936	4032	6346	4344
18620	18700	29780	19770
5290	5296	8280	5483
1846	1898	2839	1849
6383	6369	10170	6305
1036	1044	1623	1041
6389	6402	9809	6271
1319	1319	2013	1286
3560	3527	5302	3448
504	501	741	497
3070	3020	4442	3080
441	426	626	434
3731	3860	4710	4766
554	577	694	789
75	73	76	237
11	8	34	63
1456	1552	1906	3503
1494	1549	1930	2642
380	641	340	527

Supplementary Table 2: Full data set for the Bidar laterite profile

	BB-1	BB-2	BB-3	BB-4	BB-5	BB-6	BB-7	BB-8	BB-9
Depth (cm)	4700	3500	2600	1500	1300	1100	600	500	200
Notes	protolith								
wt. %									
SiO ₂	48.90	50.06	38.59	38.78	30.61	6.12	36.68	31.35	9.59
TiO ₂	2.16	2.29	5.11	4.78	5.76	1.40	2.44	2.33	2.03
Al ₂ O ₃	13.72	14.15	31.54	31.95	25.83	6.97	31.30	27.22	9.85
Fe ₂ O ₃ (T)	13.40	12.63	24.10	21.64	36.95	84.81	27.70	38.37	77.53
MgO	6.93	5.99	0.40	0.38	0.23	0.14	0.26	0.10	0.16
MnO	0.19	0.22	0.11	0.06	0.06	0.03	0.33	0.07	0.23
CaO	10.99	11.45	0.19	1.91	0.07	0.00	0.05	0.00	0.04
Na ₂ O	2.46	2.78	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K ₂ O	0.16	0.25	0.02	0.01	0.02	0.00	0.03	0.07	0.03
P ₂ O ₅	0.16	0.19	0.18	0.03	0.08	0.33	0.07	0.08	0.12
LOI	0.60	0.72	11.70	12.40	11.10	11.10	11.40	11.10	7.31
Total	99.07	100.01	100.24	99.54	99.61	99.80	98.86	99.59	99.58
ppb									
Li	4466	5159	7019	3736	4271	1202	13230	19960	7304
Be	606	632	2435	1289	1319	3814	859	1080	718
Sc	35710	37270	71190	55240	79360	164800	35400	50470	183300
Ti	12900000	13750000	27190000	24560000	30370000	7461000	16370000	12280000	10940000
V	356100	373200	687300	638000	1834000	1037000	655800	973600	2856000
Cr	156300	150600	219300	226200	266400	828700	267000	787300	710000
Co	52230	55420	66710	10030	13050	16580	37390	18160	16020
Ni	93490	134600	299100	55820	69990	252800	60010	102600	37560
Cu	179500	196200	420500	180000	477400	946100	217600	189800	603200
Zn	104600	113100	114000	80100	52570	224600	51830	69330	31830
Ga	20680	21840	40550	38100	49790	20830	31400	42930	41000
As	321	151	644	1142	3299	8413	5475	10630	10680
Rb	956	5678	1165	335	811	321	1524	3996	1332
Sr	208500	227600	13750	23690	6022	46070	15490	9748	9974
Y	25120	29930	659100	7094	11850	13620	5186	7215	3762
Zr	119000	132200	246400	241200	304000	77890	184900	221500	275900
Nb	9262	10200	18940	18600	23480	5646	14490	16900	14030
Mo	424	468	527	513	783	1353	1811	2844	3633
Ag	105	147	52	39	71	104	318	241	261
Cd	91	187	101	90	133	100	84	89	117
In	90	98	175	139	338	132	194	366	572
Sn	394	549	628	312	4	160	189	176	201
Sb	19	16	43	79	146	104	397	724	695
Cs	8	221	114	68	102	37	142	407	98
Ba	50840	92870	59310	10600	16260	24810	398600	17800	153400
La	8587	10310	31320	4642	9357	35770	26390	13080	6333
Ce	21800	24700	25510	15510	21650	119200	285000	27490	53920
Pr	3250	3729	16140	1724	4044	8776	4007	2590	1569
Nd	15510	17760	74510	7240	17300	32630	11510	8986	5757
Sm	4448	5035	28320	1717	4166	7276	1901	1885	1264
Eu	1592	1786	12010	490	1134	1832	464	490	320
Gd	5264	6039	62890	1657	3688	5340	1444	1627	1009
Tb	850	968	12620	288	620	860	274	297	181
Dy	5083	5758	91420	1791	3642	4878	1516	1856	1091
Ho	1028	1170	21860	365	712	926	300	385	220
Er	2688	3047	63010	1022	1956	2614	848	1137	627
Tm	379	425	9016	162	310	440	137	189	103
Yb	2290	2556	53590	1087	2003	3089	933	1297	707
Lu	321	360	8079	155	280	425	131	188	99
Hf	3158	3489	6655	6323	7920	2058	5004	5748	6507
Ta	1215	1935	1301	1228	1520	450	962	1121	917
W	29530	62370	1204	484	803	5025	961	3088	4219
Tl	3	24	8	16	29	7	272	43	140
Pb	891	986	2190	3895	9476	6167	40030	17380	32160
Th	887	994	1853	1984	3416	875	3645	8951	6416
U	232	249	980	1047	2064	4381	1169	1902	1546

bdl = below detection limit

Supplementary Table 3: Density, description, and mineralogy of the Bidar laterite profile

Sample	Depth [cm]	density [g/cm ³] ^a	Physical description ^b	Mineralogy ^b
BB9	200	3.2	Vermiform laterite	Hematite, goethite, kaolinite*
BB8	500	2.6	Nodular laterite	Hematite, goethite, kaolinite
BB7	600	1.7	Base of laterite	Hematite, goethite, kaolinite
BB6	1100	2.0	Base of laterite/top of saprolite	Hematite, goethite, kaolinite*
BB5	1300	1.5	Saprolitised basalt (grey/blue colour)	Hematite, kaolinite, goethite, magnetite*
BB4	1500	1.5	Reddened saprolite	Hematite, kaolinite, goethite, magnetite*
BB3	2600	1.2	Deep weathered basalt (saprolite)	Hematite, kaolinite, goethite, magnetite*
BB2	3500	2.6	Basalt with minor alterations	Anorthite, augite, illite
BB1	4700	2.6	Unaltered basalt	Anorthite, augite

a: Density determined by Archimedes' principle where hand samples (c. 10-20 cm³) were weighed, wrapped in clingfilm, then placed in a water-filled measuring beaker and the displaced volume measured.

b: Description and mineralogy from Mason (1999) as reported in Kisakürek et al. (2004)

*mineral present in trace amount

Supplementary Table 4: Calculations for dust addition to Bidar profile

Note: Calculations assume Th and Nd concentration of global loess (UCC) and test with Nd isotope composition from old (DC: Dharwar Craton) or young (loess) source

Sample	Depth [cm]	density [g/cm ³]	horizon depths [cm]	thickness [cm]	horizon mass/area [g/cm ²]	Nd	Th	Nb	Zr	Hf	U
BB9	200	3.2	0 to 200	200	640	5757	6416	14030	275900	6507	1546
BB8	500	2.6	200 to 500	300	780	8986	8951	16900	221500	5748	1902
BB7	600	1.7	500 to 600	100	170	11510	3645	14490	184900	5004	1169
BB6	1100	2.0	600 to 1100	500	1000	32630	875	5646	77890	2058	4381
BB5	1300	1.5	1100 to 1300	200	300	17300	3416	23480	304000	7920	2064
BB4	1500	1.5	1300 to 1500	200	300	7240	1984	18600	241200	6323	1047
BB3	2600	1.2	1500 to 2600	1100	1320	74510	1853	18940	246400	6655	980
BB2	3500	2.6	2600 to 3500	900	2340	74510	994	10200	132200	3489	249
BB1	4700	2.6	3500 to 4700	1200	3120	15510	887	9262	119000	3158	232

DUST						
Th/Nb	Th/Zr	Th/Hf	$\epsilon_{Nd}t=0$	Nb [ppb]	Th [ppb]	Hf [ppb]
UCC	0.86	0.046	1.85	12817	10641	6608
DC			-10.3			
			-34			

UCC: Average upper continental crust as represented by global loess (Chauvel et al., 2014; Gallet et al., 1996)
DC: Dharwar Craton (average of rhyolite and granitoid rocks from Mohan et al., 2013)

Th/Nb	Th/Zr	Th/Hf	U/Nb	Nd/Nb	Th/U	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	$\epsilon\text{Nd}_{t=0}$	%Nd/Nb	%Th/Nb	%U/Nb
0.457	0.023	0.986	0.110	0.410	4.15	0.1327	0.512462	0.000003	-3.43	-75	378	341
0.529	0.040	1.557	0.113	0.532	4.71	0.1268	0.512429	0.000004	-4.08	-68	453	350
0.251	0.020	0.728	0.081	0.794	3.12	0.0998	0.512455	0.000004	-3.56	-53	163	223
0.155	0.011	0.425	0.776	5.779	0.20	0.1347	0.512532	0.000003	-2.07	245	62	3003
0.145	0.011	0.431	0.088	0.737	1.65	0.1455	0.512515	0.000004	-2.39	-56	52	252
0.107	0.008	0.314	0.056	0.389	1.90	0.1433	0.512552	0.000009	-1.67	-77	11	125
0.098	0.008	0.278	0.052	3.934	1.89	0.2297	0.512703	0.000004	1.27	135	2	107
0.097	0.008	0.285	0.024	7.305	4.00	0.1712	0.512863	0.000003	4.38	336	2	-2
0.096	0.007	0.281	0.025	1.675	3.83	0.1733	0.512859	0.000004	4.31	0	0	0

Th based dust addition calculation (Th/Nb)				
f Th dust	dust Th [ppb]	mass f dust	dust Th [ng/cm ²]	dust input [g/cm ²]
0.476	3051	0.29	1952461	183
0.570	5105	0.48	3981792	374
0.205	747	0.07	126920	12
0.078	68	0.01	68249	6
0.065	224	0.02	67062	6
0.014	29	0.00	8586	1
0.003	5	0.00	6761	1
0.002	2	0.00	5384	1
0.000	0	0.00	0	0
				SUM
				584

Th based dust addition calculation (Th/Zr)				
f Th dust	dust Th [ppb]	mass f dust	dust Th [ng/cm ²]	dust input [g/cm ²]
0.413	2652	0.25	1697040	159
0.862	7715	0.72	6017520	565
0.321	1169	0.11	198746	19
0.099	87	0.01	86696	8
0.099	338	0.03	101479	10
0.020	40	0.00	12094	1
0.002	3	0.00	4480	0
0.002	2	0.00	4405	0
0.000	0	0.00	0	0
				763
				SUM

Th based dust addition calculation (Th/Hf)				
f Th dust	dust Th [ppb]	mass f dust	dust Th [ng/cm ²]	dust input [g/cm ²]
0.45	2886	0.27	1846746	174
0.81	7285	0.68	5682304	534
0.29	1041	0.10	176897	17
0.09	81	0.01	80729	8
0.10	328	0.03	98393	9
0.02	42	0.00	12570	1
0.00	-3	0.00	-3610	0
0.00	3	0.00	6324	1
0.00	0	0.00	0	0
				SUM
				742

Nd-based dust addition calculation (UCC)				
f Nd dust	dust Nd [ppb]	mass f dust	dust Nd [ng/cm ²]	dust input [g/cm ²]
0.530	3049	0.11	1951065	72
0.574	5162	0.19	4026679	148
0.539	6203	0.23	1054498	39
0.437	14245	0.52	14245231	524
0.459	7933	0.29	2379805	87
0.409	2962	0.11	888714	33
0.208	15491	0.57	20447751	752
-0.005	-388	-0.01	-908070	-33
0.000	0	0.00	0	0
				1654
				SUM

<i>f</i> Nd dust	Nd-based dust addition calculation (DC)				dust input [g/cm ²]
	dust Nd [ppb]	mass f dust	dust Nd [ng/cm ²]		
0.203	1167	0.04	747162		27
0.220	1977	0.07	1542019		57
0.206	2375	0.09	403821		15
0.167	5455	0.20	5455220		201
0.176	3038	0.11	911348		33
0.157	1134	0.04	340334		13
0.080	5932	0.22	7830479		288
-0.002	-149	-0.01	-347746		-13
0.000	0	0.00	0		0
				SUM	633

Chapter 4: Overview of paleosol identification and geochemistry

1. Introduction

Paleosols are buried remnants of subaerial weathering exposures that formed in contact with the ancient atmosphere. Prior to biological mediation between atmospheric and soil gas by vascular plants (pre mid-Ordovician), an open exchange between atmospheric gases and the lithosphere could occur through diffusion and advection into soils¹. Chemical weathering reactions such as carbonation and oxidation are then dependent primarily on the atmospheric CO₂/O₂ ratio and soil permeability. The products of these are reactions preserved in the chemistry and mineralogy of the soils. From the time of soil formation to preservation as a paleosol, however, they are at least partially eroded, buried, and often undergo metasomatism and metamorphism, all of which alter the soil texture, chemistry, and mineralogy. Nevertheless, certain chemical signatures are demonstrably undisturbed from their pedogenic state and significant effort has been made in these cases to reconstruct CO₂ and O₂ levels in the ancient atmosphere, at least semi-quantitatively (e.g., Pinto and Holland, 1988; Holland and Zbinden, 1988; Sheldon and Tabor, 2009; Murakami et al., 2011; Kanzaki and Murakami, 2015).

Reliable paleoatmospheric information can only be extracted from *bona fide* paleosols. In the absence of distinct soil features that are present in many Phanerozoic paleosols (e.g., trace fossils generated by burrowing animals or plant roots), distinguishing between fine-grained clastic sedimentary rocks, hydrothermal alteration zones, and true subaerial weathering profiles is not straightforward. Candidate paleosols are found at unconformities beneath non-marine sedimentary rocks or developed on subaerial volcanic rock sequences. The geological environment alone, however, is insufficient to unambiguously identify a paleosol. Contrast in rock permeability at unconformities can generate conduits for hydrothermal/metamorphic fluid passage that may result in chemical and mineralogical alteration resembling that of a paleosol. Importantly, some soil textures can survive burial and metamorphism and recognising these features (in combination with mineralogical, chemical, and textural evidence) is imperative for paleosol identification. More detailed aspects of Precambrian paleosol recognition can be found in previous contributions (Holland, 1984; Grandstaff et al., 1986; Retallack, 1992; Holland and Zbinden, 1988; Rye and

¹Note that the terms “soil” and “paleosol” do not *necessarily* have a biological connotation when applied to Precambrian weathering profiles

Holland, 1998), but here I focus on the essential list of five criteria proposed in the extensive review of pre-Devonian candidate paleosols by Rye and Holland (1998).

A list of all of the mafic paleosols that meet these criteria is provided in Table 1. The geochemistry of these paleosols is compiled for use in figures and discussion in this thesis so as to provide a more global context for the significance of the Flin Flon paleosol (Chapter 6). The geochemical data of these paleosols are also compared to those of the Chhindwara and the Bidar laterite (Chapter 2 and 3), as well as two other post-Precambrian mafic weathering profiles (Liu et al., 2013; Nesbitt and Wilson, 1992). The identity of the protolith for each profile is also given in Table 1 for instance where protolith-normalised data are reported. In order to better facilitate comparisons between data from numerous individual studies, total Fe was recalculated as $\text{Fe}_2\text{O}_{3(\text{T})}$ and major element data were renormalized on an anhydrous basis prior to any further calculation. These data will be revisited in Chapter 6.

2. Identification and main features of paleosols

Criterion 1: A paleosol is formed *in situ* on a homogeneous protolith and must be preserved in place

Identifying an ancient paleosol developed on a protolith with primary vertical heterogeneities, such as clastic sedimentary rock, and reconstructing their pedogenic chemistry are problematic. Igneous, high-grade metamorphic, and some chemical sedimentary rocks are often sufficiently homogeneous to establish a progressive link from the protolith through different zones of derived *in situ* regolith. Significant downslope transportation of soil also severs the physical and chemical links between the protolith and regolith. One common practice to help test for the autochthony of pedogenic materials is constancy in immobile element ratios. As demonstrated in Chapter 3, the high field strength element group (Al, Ti, Zr, Hf, Nb, Ta, Th) are typically the least-mobile during chemical weathering. During progressive chemical weathering of a protolith with a uniform composition, these immobile elements are insoluble and remain in restite minerals or are quantitatively re-precipitated in place as part of new stable pedogenic minerals. Accordingly, the concentrations of immobile elements increase from the protolith with increasing weathering intensity but the ratios between these elements remain relatively constant (Figure 1). Most studies of Precambrian paleosols unfortunately only report data for Ti and Al, plus Nb and Zr in some instances. Nevertheless, a study by Maynard (1992) addressed the Al-Ti-Zr geochemistry of paleosols through a comparison with several modern weathering profiles developed on homogeneous protolith. It was discovered that Ti/Al and Ti/Zr ratios did not deviate by more than

Table 1: List of all definite mafic paleosols and Phanerozoic profiles from which data are compiled for this thesis

Paleosol	Age	Protolith	Location	Protolith sample(s)	References
Nsuzo	2980-2960	basaltic andesite	South Africa	PMH24-1008 2,1009 3,1009 7,1011	Crowe et al. (2013)
Mt. Roe #1	2775-2755	basalt	Australia	90MH25, 90MH45, 103230, 100534,	Macfarlane et al. (1994)
Mt. Roe #2	2775-2755	basalt	Australia	90MH228, 90MH263, 90MH264	Macfarlane et al. (1994), Yang and Holland (2002)
Demison/Stantleigh	2475-2440	greenstone	Canada	S1-125 (Stanleigh)	Gay and Grandstaff (1980); Goddard (1987), Farrow and Mossman (1988), Mossman and Farrow (1992), Prasad and Roscoe (1996)
Quirke II	2475-2440	basalt	Canada	33	Prasad and Roscoe (1991, 1996)
Cooper Lake	2475-2440	diabase	Canada	Drill core	Sutton and Maynard (1993)
				Drill core - 1271, 1338	Utsunomiya et al. (2003)
Hekpoort	2245-2059	basaltic andesite	South Africa	20, 101, 103, 106, 107, 110, 111, 113, 114, 115, 226, 227	Rye and Holland (2000)
Hekpoort - Strata 1				Str/128 12	Beukes et al. (2002)
				99WY-51,52,53,54,55,56,57,58,59,60	Yang and Holland (2003)
Drakenstein	2235-1924	basaltic andesite	South Africa	72548, 72670, 72810, 72976, 73300	Wigginger and Beukes (1990)
Flin Flon	1900-1800	greenstone	Canada	P1- 85ZH-122,123, P2- 85ZH133	Holland et al. (1989)
				P2-3, P2-4	Pan and Stauffer (2000)
				FF021-FB1, FB2	This thesis
Sturgeon Falls	1100	basalt	USA	83HL-23,24	Zbinden et al. (1989)
Arisaig	450	basalt	Canada	DP 207, 208, 209, MBU 245, 247, 248, MBL 257, 258	Feakes et al. (1989)
Phanerozoic laterites					
Deccan Traps (Bidar)		basalt	India	BB-1	Borger and Widdowson (2001), Kisakürek et al. (2004); Wimpenny et al. (2007); This thesis
Columbia River		basalt	USA	Pomona and Sentinel Bluffs basalt average	Liu et al. (2013)
Modern basalt profiles					
Chhindwara		basalt	India	ChQB12	This thesis
Baynton		basalt	Australia	A-1, B-1	Nesbitt and Wilson (1992)

Notes:
List is modified from Rye and Holland (1998)
All paleosol ages are taken as interpreted from Rye and Holland (1998) or the original references
Selected protolith sample(s) as given in original reference or a calculated average when more than one is given

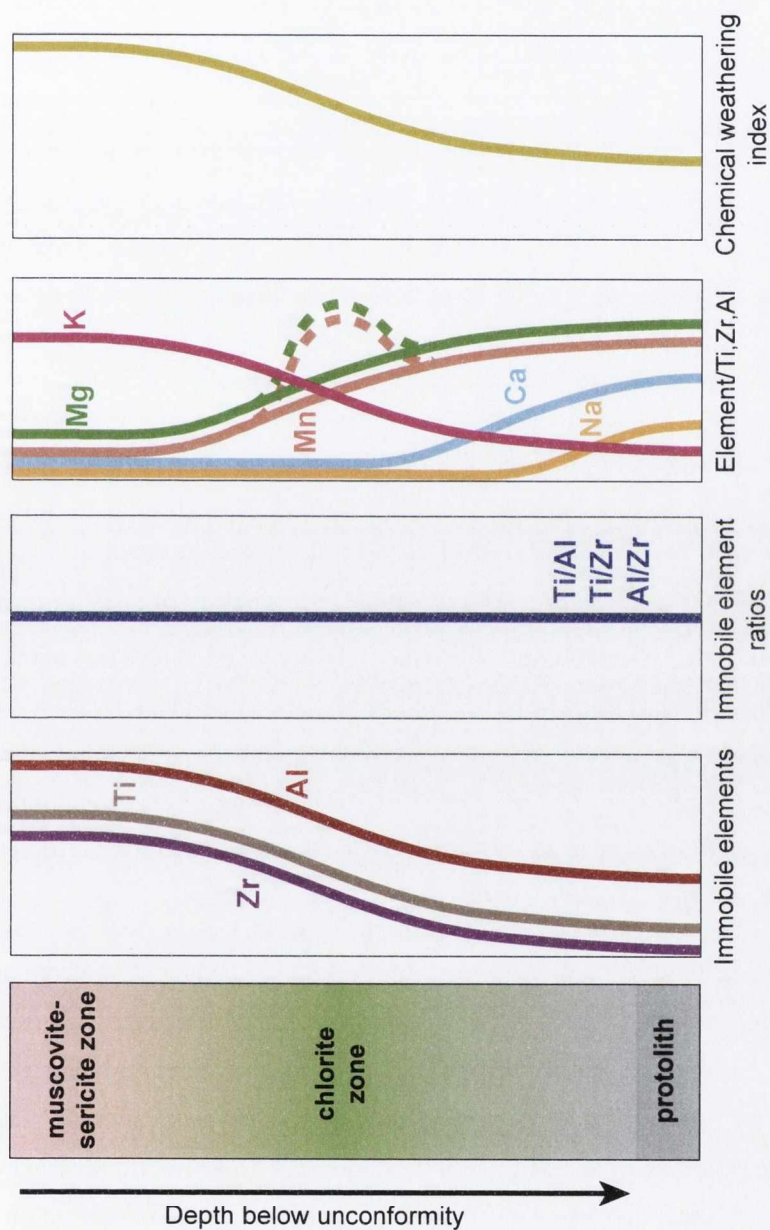


Figure 1: An overview of the common mineralogical and elemental progressions of older than ca. 0.45 Ga mafic paleosols developed on a homogeneous protolith. The protolith mineralogy generally grades upward into a chlorite zone and further into inter-stratified chlorite/illite and eventually a zone rich in micas (muscovite/sericite) nearest the paleo-surface. Immobile elements (e.g., Al, Ti, Zr) increase in concentration from the protolith to the paleo-surface with constant ratios through all zones. Relative to the immobile elements, the mobile elements decrease upwards ($\text{Na} > \text{Ca} > \text{Mn/Mg}$), resulting in an upward increase in calculated weathering indices.

50% and 40%, respectively, from the ratio of the protolith at moderate to high chemical index of alteration values.

$$\% \text{Deviation Ti/Al} = [(Ti/Al_{\text{soil}}) - (Ti/Al_{\text{protolith}})] / (Ti/Al_{\text{protolith}}) \times 100$$

These limits can be used to evaluate the autochthony of ancient paleosols. Deviation in Ti/Al or Ti/Zr any greater than the boundaries indicates that an allochthonous component should be suspected. Rye and Holland (1998) adopted these limits as part of the screening of candidate paleosols. All of the mafic paleosols compiled in this study fall within one or both of these boundaries for Ti/Zr and Ti/Al (Figure 2), with the exception of one sample from the Hekpoort Strata 1 profile (Yang and Holland, 2003; see below). In a few profiles, samples are beyond the 40% boundary for the Ti/Zr ratio, yet show consistency in the Ti/Al ratio (i.e., Cooper Lake, Drakenstein). Scatter within the limits for the Ti/Al and Ti/Zr ratios, if not related to analytical imprecision, may reflect slight heterogeneity in the protolith or indicate one or more of several factors known to influence the immobile element budget of weathering profiles.

The fine-grained, homogenous texture of most basalt generally results in a relatively uniform chemistry, but separate lava flows in a sequence may record subtle deviations in their immobile element chemistry that reflects crustal assimilation and/or fractional crystallisation occurring between eruptions. Such flow transitions are recognisable in weathering profiles when sampling density and analytical precision are sufficient as demonstrated in Chapter 3. It is plausible that such lava flow transitions also exist in Precambrian mafic paleosols, but go unnoticed due to the loss of physical evidence through the weathering event and subsequent metamorphism. However, it may be possible to decipher them from immobile element geochemistry alone. For example, it is possible that when mafic paleosols show consistent offsets in their % deviation of immobile element ratios (e.g., the Mt. Roe #1 paleosol; Figure 2), these are related to primary differences in flow chemistry from the assumed protolith.

The immobile element distribution in mafic paleosols developed on subaqueously altered protoliths may be more complex due to the element redistribution and mineralogical changes inherited from the preceding alteration event. For example, the protolith greenstone of the Flin Flon paleosol shows evidence for patchy Fe-Ti oxide distribution related to subaqueous alteration (Holland et al., 1989) and the Denison paleosol shows an unusual upward loss of Ti (Farrow and Mossman, 1988; Mossman and Farrow, 1992) that may be related to the weathering of sphene (an alteration mineral). Such subtle geochemical properties of the protolith need to be considered when normalising other data to Ti.

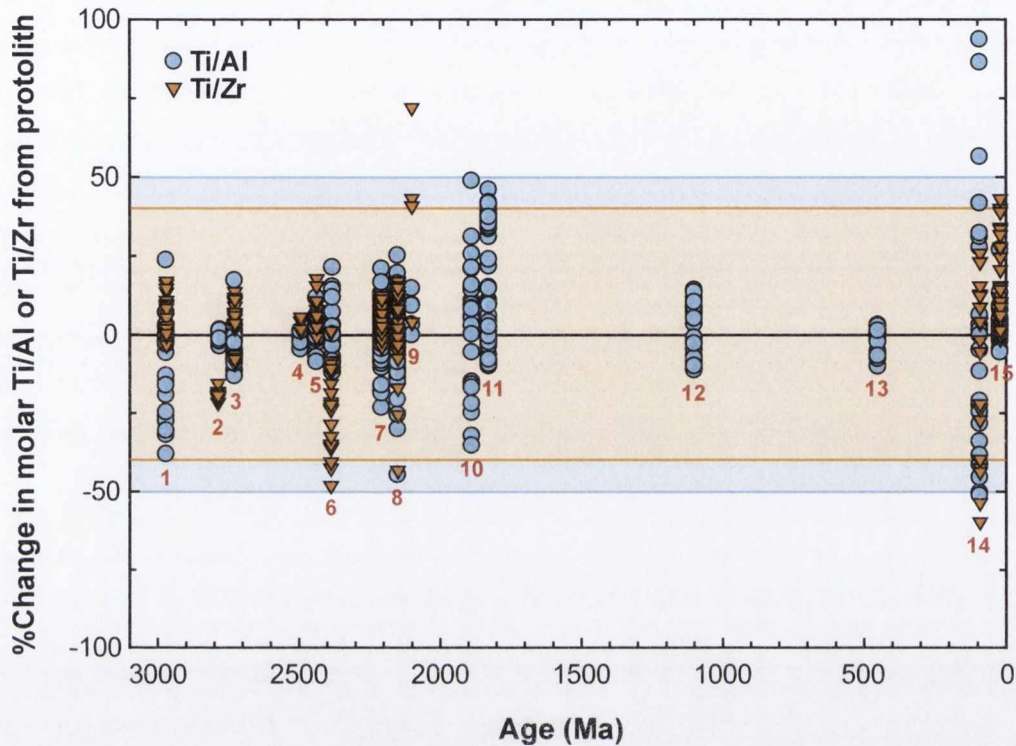


Figure 2: Percent deviation of immobile element ratios Ti/Al [shaded (blue) circles] and Ti/Zr [shaded (orange) triangles] from the protolith value in each paleosol, laterite, and modern weathering profile compiled in this thesis (see Table 1; note that this includes the new Flin Flon paleosol data from Chapter 5) plotted vs. age. For some paleosols, data from separate studies are plotted together and in other instances they are separated. The original sources of data for each time-point are identified by the numbers below each cluster in the figure and are as follows: 1) Nsuze (Crowe et al. 2013); 2) Mt. Roe #1 (Macfarlane et al., 1994); 3) Mt. Roe #2 (Macfarlane et al., 1994; Yang and Holland, 2002); 4) Stanleigh Mine (Farrow and Mossman, 1988; Mossman and Farrow, 1992); 5) Quirke II (Prasad and Roscoe, 1991, 1996); 6) Cooper Lake (Sutton and Maynard, 1993; Utsunomiya et al., 2003); 7) Hekpoort (Rye and Holland, 2000); 8) Hekpoort – Strata 1 (Beukes et al., 2002; Yang and Holland, 2003); 9) Drakenstein (Wiggering and Beukes, 1990); 10) Flin Flon (Holland et al., 1989; Pan and Stauffer, 2000); 11) Flin Flon (This thesis); 12) Sturgeon Falls (Zbinden et al., 1989); 13) Arisaig (Feakes et al., 1989); 14) Laterite profiles (Liu et al., 2013; This thesis); 15) Modern profiles (Nesbitt and Wilson, 1992; This thesis). According to Maynard (1992), modern in situ weathering profiles do not show a deviation of more than 40% or 50% for Ti/Zr and Ti/Al, respectively, from the protolith (shown with the shaded areas). Deviations beyond these ranges suggest an allochthonous component in a weathering profile or more extreme weathering intensity. Only candidate paleosols that have ratios within one or both of these ranges from the protolith should be considered a definite paleosol according to the criteria of Rye and Holland (1998).

In modern profiles, significant deviations in immobile element ratios from protolith values are linked to physical translocation of weathered material, mingling of soil with allochthonous sediment or aeolian dust, more extreme ranges in pH or weathering intensity induced by the decay of organic matter, or more intense leaching that results in severe textural and mineralogical segregations. These factors are all more prominent in the development of laterites that have the most complex and protracted exposure histories under intense leaching conditions. This is demonstrated by the more substantial variation in %Ti/Al and %Ti/Zr ratios variation from the protolith in the laterite profiles plotted in Figure 2, which are generally more extreme than those of the paleosols. The Hekpoort Strata 1 profile (Beukes et al., 2002; Yang and Holland, 2003) shows more scatter in Ti/Zr and Ti/Al in the uppermost ferricrete horizon than the remaining samples below that is attributed to the clastic texture of the horizon and contribution from allochthonous material. Since all but one of these samples still fall within the boundaries of deviation from the protolith (Maynard, 1992), they are included in further discussion of the thesis, but readers are reminded to recall their reworked nature.

Criteria 2-4: A paleosol demonstrates progressive mineralogical, textural, and chemical changes from the protolith upwards towards the paleo-surface

From the sharp contact of an unconformity, a vertical gradation in mineralogical, textural, and chemical changes between the zone of alteration and a protolith that are consistent with soil-forming processes, ideally in full exposure (e.g., not fault offset), is strong evidence for an *in situ* regolith as opposed to a sedimentary rock. There is little reason to suspect a non-uniformitarian chemical weathering progression in a Precambrian paleosol compared to Phanerozoic analogues, with the exception of the oxides formed by Fe and Mn. Prior to weathering, mafic protoliths are dominated by plagioclase, pyroxene, olivine, glass, and Fe-Ti oxides (e.g., ilmenite, magnetite) or may include chlorite, epidote, and carbonate in cases of seafloor alteration. When exposed at the surface, many of these minerals weather to pedogenic phyllosilicates (e.g., montmorillonite, kaolinite) and Fe oxides, although primary Fe-Ti oxides are more resistant to weathering. These mineralogical transformations are accompanied by the loss of their constituent soluble (mobile) elements (K, Na, Ca, Mg) relative to the immobile elements (Ti and Al). Similar trends are found in paleosols, although the original pedogenic mineralogy is altered during burial and metamorphism at which point K (as well as several of the other alkali elements) is re-introduced to nearly all documented paleosols. Evidence for the addition of the alkali elements comes from a general upward increasing concentration of K to levels far exceeding that of the protolith and beyond the level that can be accounted for purely by residual enrichment. The K addition results in illitisation of smectite-group minerals and the conversion of kaolinite to muscovite, with the final

metamorphosed mineralogical sequence in mafic paleosols being chlorite-illite overlain by muscovite/sericite. More specifically, the protolith basalt generally grades into a deep weathering zone dominated by chlorite, where the concentrations of Na and Ca often exhibit substantial depletion that is consistent with their high degree of mobility associated with replacement of the protolith minerals by clays. The chlorite zone is overlain by a muscovite zone, sometimes with gradational transition other times with a sharper contact, perhaps amplified by compaction of the paleosol during burial. The chlorite is often inter-stratified with illite and increases in K and decreases in Mg concentration upwards in tandem with the transition to the uppermost muscovite/sericite-dominated zone. However, it is common for some of the Mg mobilised from the upper muscovite/sericite horizon to be captured lower within the chlorite zone, where it was likely re-precipitated as a constituent of Fe²⁺-rich smectite. Calcium can also be re-precipitated in carbonate (often dolomite) as concretions that may represent fossil soil calcrete horizons. These mineralogical transitions are typical of many of the documented mafic Precambrian paleosols and occur within a sequence of horizons from base to top that is interpretable within the framework of pedogenesis.

Much of the texture of the protolith is lost in tandem with the above mineralogical and chemical changes, although macro-scale weathering textures such as corestones may remain. Corestones are developed during spheroidal weathering and often change in appearance according to the extent of weathering by decreasing in size and becoming progressively more rounded as the weathering intensity increases upwards, until only a “ghost” texture of the corestone remains. In the uppermost sections of paleosols, despite the greater magnitude of burial compression and foliation, other soil structures such as peds, cutans, and nodules (Retallack, 1992, 2001) are often still recognisable. These structures are important in linking the textural, mineralogical, and chemical changes to subaerial weathering vs. hydrothermal alteration.

Criterion 5: A paleosol shows evidence for soft-sediment deformation during deposition of overlying units

Stratigraphically controlled hydrothermal alteration can produce chemical signatures along unconformities that resemble those preserved in paleosols. It is therefore necessary to have substantiating evidence of subaerial exposure and pedogenesis occurring prior to deposition of the overlying unit. Several features that reflect the soft nature of soils can be used to infer this. For instance, clay-rich soils may develop vertical shrinkage cracks during drying events that can be filled in with the overlying allochthonous sediment. The soft nature of soils also makes them amenable to erosion during deposition of these units and rip-up clasts or paleosol “balls” may be entrained and preserved within the overlying sedimentary rock. Sampling of rip-up clasts for

geochemical analysis can test for the similarity in chemistry with the underlying paleosol; if comparable, this provides strong evidence for the alteration event occurring prior to deposition and thus of subaerial weathering vs. hydrothermal origin.

In summary, several criteria can help identify a true paleosol from hydrothermal alteration zones or sedimentary rocks that have physical or chemical resemblance to a paleosol and also occur below an unconformity. Geochemical analysis of paleosols is ideally performed on drill core samples with no modern atmospheric exposure, although confident paleosol identification typically requires careful analysis in outcrop to recognise the physical criteria. Immobile element ratios can help identify *in situ* regolith, although complexities in protolith composition need to be considered. When the ratios of Ti/Al or Ti/Zr deviate by more than 50% or 40%, respectively, from the inferred protolith in a candidate paleosol, it may not be an *in situ* regolith or an allochthonous component should be suspected (Maynard, 1992). Some paleosols pass all other criteria for identification apart from poorly understood complexities in their immobile element chemistry, such as the numerous studied exposures of ca. 2.45 Ga sub-Huronian mafic paleosols (Table 1). These complications frustrate attempts at deriving paleoatmospheric information, which can become unreliable. Here I followed Rye and Holland (1998) and only included data for the Cooper Lake paleosol (Sutton and Maynard, 1993; Utsunomiya et al., 2003), the Quirke II Drill Hole 268, and the Stanleigh Mine section (Farrow and Mossman, 1988; Mossman and Farrow, 1992) in the compilation for this thesis. As shown in Chapter 3, high-precision trace element analysis can perhaps test these uncertainties with new immobile element ratios in future studies. Within the list of definite paleosols (Table 1), the demonstrably immobile character of Ti and Al permits the use of either element in normalisation to assess the loss or gain of other elements (Rye and Holland, 1998). Paleosols show an upward loss of the mobile elements (relative to Ti and Al) with possible re-precipitation at depth in combination with mineralogical and textural evolution similar to those in modern weathering profiles. The presence of soil textures and evidence for soft-sediment deformation is also necessary for a fully confident positive identification. According to Rye and Holland (1998), a definite paleosol meets all five criteria in the list and the certainty of paleosol identification should be scaled to likely, possible, and unlikely based on the increasing absence of criteria. The ca. 1.85 Ga Flin Flon paleosol meets all of these criteria and is classified as a definite paleosol.

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Chapter 5: The Flin Flon paleosol revisited

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Abstract

A ca. 1.85 Ga paleosol developed on seafloor-altered mafic rocks is preserved beneath continental sandstones and conglomerates of the Missi Group near Flin Flon, Manitoba. Previous work has focused on a locality where the paleosol is developed on pillowed greenstone (chlorite + albite + epidote + calcite + quartz + Fe-Ti oxides $\pm$ mica). This area has been revisited and a new (~5 m) profile was excavated and sampled at a very high density for geochemical (major element; ~60 samples) and mineralogical (petrography, X-ray diffraction) investigation.

The high sampling density has revealed a relatively sharp immobile element offset (e.g., Al/Ti) in the profile. This could reflect weathering across two separate parent rocks or preferential addition of allochthonous material into the top of the profile. Regardless, comparison with a wide suite of volcanic rocks in the stratigraphy suggests that the original concentration of Fe and probably also Ca and Mg in the greenstone on either side of the boundary was similar, permitting quantitative treatment of major element trends.

The profile shows pronounced upward loss of Ca, Mg, Mn^{2+} , and Fe^{2+} and a corresponding increase in Al, Ti, and total Fe. Physical weathering features, such as corestones, are well preserved and show progressive alteration upwards in the profile in parallel with the chemical trends. Deep in the profile, Na and Ca are lower than the greenstone due to the weathering of albite and epidote, whereas Mg, Fe and Mn were largely retained in chlorite and secondary dolomite. Upwards in the profile, the loss of chlorite and dolomite and the increase of illite/mixed-layer clays and white mica (probably 2:1 layer or mixed-layer clays originally) and hematite are accompanied by a transition from green to maroon colour. Above a well-defined depth in the profile, carbonate is virtually absent, and the paleosol is highly depleted in Ca. This transition in the paleosol coincides with the immobile element offset. The significance of this coincidence remains to be explored.

Reworking of regolith (e.g., rip-up clasts) occurred during deposition of the Missi sediments and burial and subsequent metamorphism resulted in the upward enrichment of K and Na and the associated conversion of pedogenic clays to illite and micas (muscovite and paragonite). Cross-cutting quartz and epidote veins and tourmaline formation near the unconformity contact implies minor post-burial fluid movement. Despite these complexities, there is consistent retention of Fe through formation of pedogenic Fe oxides, attested by the near-constant $\Sigma\text{Fe}/\text{Al}$ ratio in the profile. There is very little evidence for subsequent Fe reduction by hydrothermal or organic fluids. Instead, trends in the Fe speciation are controlled predominantly by the modal variation of Fe-Ti oxides in the greenstone and spheroidal weathering textures in the paleosol.

1. Introduction

Paleosols are one of the key geological archives that yield information about the conditions of the ancient Earth surface. Extracting proxy information from the mineralogy and geochemistry of paleosols, however, is a nontrivial task, because pedogenic signatures are commonly obscured in the ancient rock record. Complications arise from alteration events that are unrelated to pedogenesis. For example, many mafic Precambrian paleosols were developed on subaqueously erupted volcanic rocks that underwent seafloor alteration prior to uplift and subaerial weathering (e.g., Zbinden et al. 1988; Polat et al. 2012; Rye and Holland 2000). Furthermore, the pedogenic mineralogy and geochemistry of weathering profiles are typically overprinted during burial diagenesis and metamorphism (e.g., Nesbitt and Young, 1989; Rainbird et al. 1990; Fedo et al. 1995).

Despite the complexity of paleosols, their mineralogy and geochemistry have been crucial in providing the earliest semi-quantitative constraints on paleoatmospheric O_2 levels (e.g., Holland 1984; Holland and Zbinden 1988; Pinto and Holland 1988; Holland et al. 1989; Prasad and Roscoe 1996; Rye and Holland 1998 and references therein). The picture that emerged was one of a unidirectional transition from a largely anoxic (PO_2 : 5 to 8×10^{-4} atm; cf. Ohmoto 1996) to an oxygenated atmosphere (PO_2 : $\geq 3 \times 10^{-2}$ atm) between roughly 2.4 and 2.2 Ga (known as the Great Oxidation Event, GOE). In recent years, several new paleoredox proxies have been established, such as the marine transition metal budget and the fractionation of metal stable isotopes (see Farquhar et al. 2011, Pufahl and Hiatt 2012, and the references therein). The sharper picture emerging from these studies suggests that restricted, but significant, accumulations of atmospheric O_2 preceded the GOE (e.g., Anbar et al. 2007) and that perturbations may have followed (e.g., Frei et al. 2009; Bekker and Holland 2012). These reconstructions are built from the geochemistry of the marine sedimentary rock record, however, and rigorous testing of the mass balance on continental landmasses is still lacking. Detailed studies of Paleoproterozoic paleosols are necessary to better understand the weathering behaviour of the elements involved in these chemical proxies.

Of the currently documented Paleoproterozoic paleosol record, the ca. 1.85 Ga Flin Flon paleosol stands out due to its exceptional preservation of unambiguous physical and chemical weathering features (Holland et al. 1989). It meets all of the criteria outlined by Rye and Holland (1998) necessary to identify a true subaerial weathering profile. The retention of Fe due to pedogenic Fe oxide formation and the fractionation of Ce and U in the paleosol demonstrate that it formed in an oxygenated ($PO_2 \geq 0.03$ - 0.01 atm) atmosphere (Holland et al. 1989; Pan and Stauffer 2000), although there is unresolved

debate regarding whether or not post-weathering Fe reduction occurred (Ohmoto 1996; Holland and Rye 1997; Ohmoto 1997; Rye and Holland 1998).

In this study, the well-known outcrop of the Flin Flon paleosol studied by Holland et al. (1989) was revisited. At this locality, Holland et al. (1989) isolated two suitable areas to sample a profile for geochemical analysis, but were careful to avoid damaging the surface of the outcrop. For the present study, a similar degree of caution was used to ensure the preservation of the outcrop because it is considered a geological heritage site. A new profile section in the area was excavated with the aim of performing detailed geochemical (major element) and mineralogical investigation. Specifically, the focus was to establish which chemical weathering signatures have survived through burial and metamorphism and provide a refined and testable model of the paleosol evolution history.

2. Flin Flon Paleosol

2.1 Regional Geology

Flin Flon, Manitoba is within the central Flin Flon Belt (FFB), which is part of the greater Flin Flon-Glennie Complex (FFGC). The FFGC is a volcanic-sedimentary-intrusive crustal collage that forms part of the western edge of the Trans Hudson Orogen (THO) known as the Reindeer zone. The FFB represents the earliest stages of the THO and is cored by an amalgamation of individual 'tectono-stratigraphic' assemblages ranging in age from 1.92-1.88 Ga (Lucas et al. 1996; Stern et al. 1999, and references within). The independent assemblages were juxtaposed between 1.88 and 1.87 Ga (Lucas et al. 1996) during the closure of the Makinewan Ocean basin (Stauffer 1984), forming an intraoceanic microcontinent (the "Amisk collage") at the interface between three Archean cratons (the Sask, Hearne, and Superior). Following the structural division of Lafrance et al. (in press), early and intraoceanic collision is represented by D_1 and D_2 deformational features in the rocks of the Amisk collage with boundaries marked by steep shear zones (Lucas et al. 1996). Post-accretion ('successor') plutonic granitoids were emplaced between 1.87 and 1.84 Ga during continued subduction beneath the FFB, 'stitching' together the assemblages of the collage. Sedimentation was coeval with this plutonism, resulting in shallow marine and continental successor basin deposits that span a depositional age range from 1.87 to 1.84 Ga. One of these deposits is the Missi Group – sandstone and conglomerate interpreted to represent the deposition of alluvial fan to braided stream sediments in synorogenic, structurally controlled basins (Mukherjee 1974; Stauffer 1990). The Missi Group

unconformably overlies the volcanic and synvolcanic intrusive rocks of the Flin Flon arc assemblage in addition to some of the successor arc plutonic rocks. The youngest concordant zircon U-Pb date obtained from the Missi Group is 1847 ± 2 Ma (Ansdell et al. 1992; Ansdell 1993). When this is combined with the U-Pb age of the youngest cross-cutting intrusion (1842 ± 3 Ma; Heaman et al. 1992; O'Hanley and Kyser 1994), known as the Boundary Intrusion, the age of Missi sedimentation is constrained to between ca. 1847 and 1842 Ma. In the Flin Flon area, well-developed, sub-Missi regolith indicates that the accreted assemblages underwent an extended interval of subaerial exposure prior to continental sedimentation (Holland et al. 1989; Stauffer 1990). Further intraoceanic amalgamation (forming the FFGC) and continental collision occurred from 1.84 to 1.80 Ga (Ansdell and Norman 1995; Norman et al. 1995). This resulted in several identifiable tectonic overprints (D_3 - D_6) on the volcanic, successor arc plutonic, and sedimentary rocks of the central FFB (Stauffer and Mukherjee 1971; Fedorowich et al. 1995; Lucas et al. 1996; Gale et al. 1999; Lafrance et al. in press), including thrust-stacking and folding of the internal units of the assemblages. During the final stages of continental collision between the Sask, Hearne, and Superior cratons (i.e., the Trans Hudson Orogeny), the Amisk collage was ultimately sliced up and imbricated as it was thrust onto the Sask craton, bounded by large-scale crustal detachment faults (Lucas et al. 1996; Ashton et al. 2005). The majority of rocks in the central FFB reached a peak metamorphic grade of sub-greenschist to greenschist facies during the culminating stages of collision (Digel and Gordon 1995; Schneider et al. 2007).

2.2 Flin Flon arc assemblage

Of the individual tectono-stratigraphic assemblages that make up the Amisk collage, the juvenile, arc-associated rocks of the Flin Flon arc assemblage (formerly the Amisk Group), are the most intensively studied since they contain three major economic volcanogenic massive sulphide (VMS) deposits (e.g., Syme and Bailes 1993; Galley et al. 2007). Recent investigations have resulted in a well-defined internal subdivision of the Flin Flon arc assemblage into footwall and hanging wall units with geologically and geochemically distinct 'formations' and 'members' (Symes and Bailes, 1993; Ames et al. 2002; DeWolfe et al. 2009a,b). Three formations (Flin Flon, Louis, and Hidden) have been defined in the assemblage beginning with the minor rhyolitic volcanism that formed the ore-hosting units (the Flin Flon formation) during extensional arc-rifting (Syme and Bailes 1993; Syme et al. 1999). The succeeding hanging wall formations (the Hidden and Louis) appear to record the transition back to a convergent environment marked by a resurgence of basaltic volcanism following ore deposition (DeWolfe et al. 2009a,b). The Hidden and Louis formations are of specific interest to the present study since they were the most widely exposed to Paleoproterozoic subaerial weathering upon

uplift of the assemblage. The Hidden and Louis formations (DeWolfe et al. 2009a,b) are dominated by aphyric to plagioclase-pyroxene-porphyrific basaltic and basaltic andesite lava flows (pillowed and massive) and synvolcanic intrusions, along with volumetrically minor volcanoclastic units. Physical flow features such as pillows, flow-banding, and hyaloclastite are commonly recognisable in the units, but very little of the primary mineralogy remains. A typical mineral assemblage of actinolite, albite, epidote, quartz, chlorite and lesser amounts of biotite, muscovite, carbonate, and pyrite are typical of the flows in the formations. In addition, areas of both formations have been affected by seafloor hydrothermal epidote-quartz alteration that is pervasive in some areas or restricted to local patches of variable intensity.

2.3 Regolith in the Flin Flon area

Near the town of Flin Flon, subaerial weathering profiles are developed on the mafic-intermediate volcanic and synvolcanic intrusive rocks of the Hidden and Louis formations. All of the currently known exposures of sub-Missi regolith are shown on the latest geological map of the Flin Flon area (Simard et al. 2010). Many of these localities were visited as part of the reconnaissance for the present study and a few have been described previously (Holland et al. 1989; Stauffer 1990; Pan and Stauffer 2000; Babechuk and Kamber 2010). The preserved regolith is highly variable in thickness, possibly as a result of original weathering depth (a common hydrological feature in modern profiles), pre-Missi topographical variation, erosion during Missi deposition, or a combination thereof. Evidence for soft sediment deformation and mixing of the Missi sediments with the regolith exists at many areas along the unconformity (Holland et al. 1989). The paleosol localities are also affected to varying degrees by polyphase deformation and metamorphism, whereby in the high strain areas, the paleosol has a strongly developed schistosity.

Regolith developed on the Hidden formation volcanic rocks was the focus of the study by Holland et al. (1989) and is described as having a lower, chlorite-rich (apple green) zone which transitions into an upper, hematite- and mica-rich (maroon) zone. By contrast, the regolith of the Louis formation is developed predominantly on a synvolcanic dolerite intrusion (Pan and Stauffer 2000; Babechuk and Kamber 2010). This regolith contains well-defined spheroidal weathering features, but is barren of an upper maroon zone.

2.4 Missi Outlier

The regolith exposure studied by Holland et al. (1989) and sampled previously by Goetz (1980) is below an erosional remnant (outlier) of the Missi Group (Figure 1 and 2). It is located about 2 km SE of the town of Flin Flon and 1 km WNW of the former Channing air strip (UTM: 14 U 0316920 E, 6070735 N). The outlier is approximately 500 m north of Channing Drive and easily accessible via cross-country ski trails.

The arcuate outlier is a tightly folded E-striking syncline (Gale et al. 1999) generated during D_4 deformation (based on temporal linkage with other structural features in the area; Lafrance et al., in press). The simplified geological map of the Missi outlier based on the work of Gale et al. (1999) and Gibson et al. (2013) shows the distribution of the regolith below the Missi as well as the surface axial trace of the F_4 syncline. The syncline was overprinted by later north-northwest-folding events (D_5), resulting in the sinuosity of the unconformity and the F_4 axial trace.

The southwestern section of the Missi outlier, which was the site of Profile #1 in Holland et al. (1989), was not sampled for this study, but was photographed and mapped at a scale of 1:100 (Figure 2b). Further information, field photos of select features, and a photomosaic of part of the outcrop are presented in the supplementary materials section. The new profile excavated for this study is located on the eastern edge of the Missi outlier (Figure 2) near the sampling area of Goetz (1980).

3. Methods

3.1 Field sampling

A rock saw was employed to ensure continuous sampling of the weathering profile and to penetrate deep enough into the outcrop to avoid areas affected by modern weathering (Figure 3e).

Approximately 125 individual samples were extracted from the continuous channel with a chisel and hammer. The profile represents a full section up to a depth of 515 cm below the unconformity (FF021A-001 to FF021H-LWB), with only one offset that is connected by samples that overlap in depth (Figure 3b). Two samples representative of the parent greenstone (FF021-FB1 and -FB2) were taken away from the profile at an estimated depth of 1000-1200 cm below the unconformity. All reported depths are measured perpendicular to the unconformity along the outcrop surface. Further

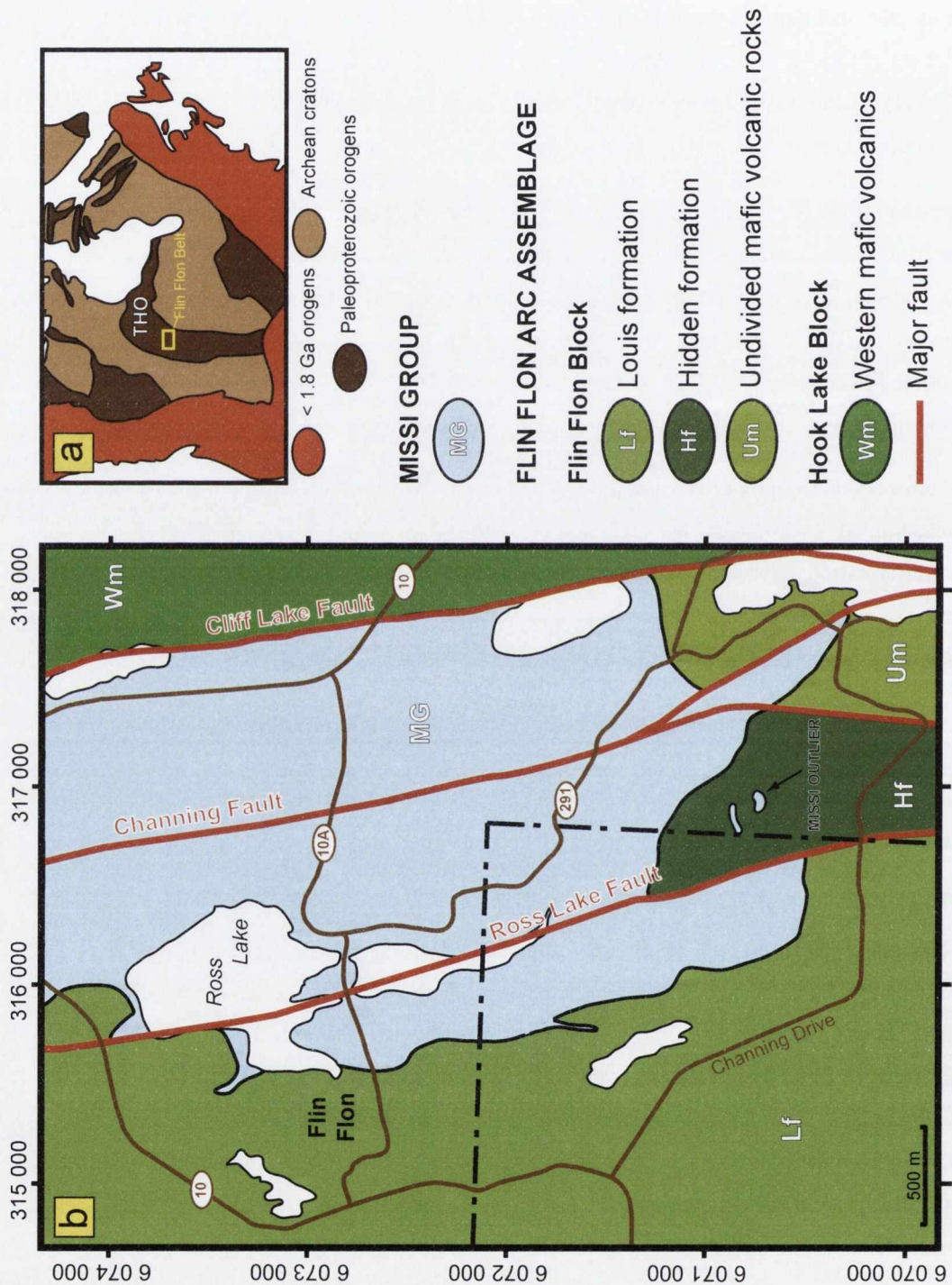


Figure 1: a) Location of the Flin Flon Belt within the Trans Hudson orogen (THO) after Hoffman (1989); b) Simplified geological map of the Flin Flon area showing the division of arc-related volcanic rocks and the Missi Group (after Babechuk and Kamber 2010). The location of the paleosol examined in this study and by Holland et al. (1989) is identified (the Missi outlier).

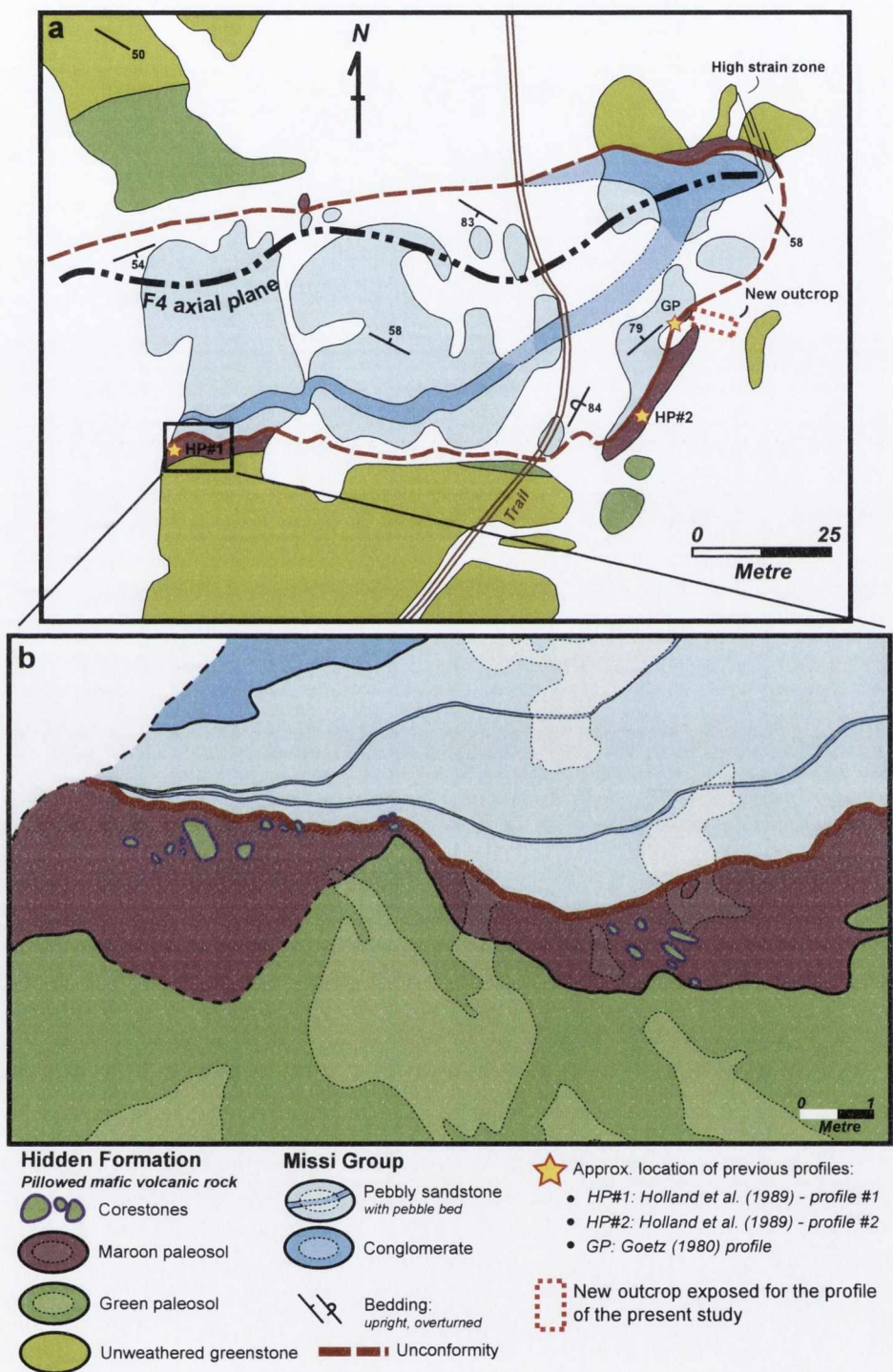


Figure 2: a) Geological map of the Missi outlier (modified from Gibson et al. 2013, after Gale et al. 1999) with the location of sampled profiles identified; b) More detailed (1:100 scale) sketch map of the southwestern edge of the outlier (near Profile #1 of Holland et al. 1989) showing the division between the green and maroon paleosol and clearly identifiable green corestones. Further information and field photographs from this area are presented in the supplementary materials section.



Figure 3: Outcrop of the Flin Flon paleosol excavated and sampled for the present study (UTM: 14U 0316989 mE, 6070745 mN): a) View of the full profile looking approximately NW showing the area of outcrop originally exposed prior to new excavation and sampling, the unconformity with the overlying Missi sandstone, and the colour of the paleosol (note the change between maroon and green paleosol); b) View of the full profile looking approximately SE from the Missi sandstone, showing the continuous channel and separate sections (A-E) created for geochemical sampling. Note the offset in the profile sections between A and B; c) Secondary dolomite in the B horizon of the paleosol; d) Green corestone in the maroon paleosol at a depth of 90 cm (Section A); e) Channel for Section A. Channel is approximately 10 cm wide.

details related to the field work and sampling strategy are found in the supplementary materials section.

3.2 Sample preparation

Prior to powder preparation, representative subsamples were cut for thin sections. Remaining material was run through a steel jaw crusher to produce chips approximately 1 cm in size. Chips free of saw marks, modern oxidation, and quartz and epidote veins were selected manually using a binocular microscope for geochemical analysis. One aliquot of chips was milled using a steel ring and puck mill to produce a powder stock suitable for major element analysis (typically >10 g), whereas a second aliquot from the same sample was milled by hand with an agate mortar and pestle to produce a metal-free stock suitable for trace element and isotopic analysis (typically 5-10 g). Only the former was analysed in the present study.

3.3 Major element analysis and loss on ignition

Major element and loss on ignition data were collected for nearly 60 samples of the profile at the Ontario Geoscience Laboratories (Sudbury, ON) via X-ray fluorescence (XRF). These measurements were performed using a PANalytical Axios Advanced PW4400 XRF spectrometer. Several samples were run in replicate and as full method duplicates to assess the precision of the analyses, which were better than 1-2% for each major element oxide. Accuracy was monitored with the analysis of several mafic USGS standards (BHVO-1 and BIR-1) as well as in-house standards. A report of the long-term averages of a selection of the lab standards can be found in Schweyer (2006). The major element oxides for the samples of this study are reported in Table 1 with the LOI measurements included in the sum.

3.4 Ferrous iron, total carbon and sulphur

The ferrous iron, total carbon, and sulphur contents of each sample were determined at the Ontario Geoscience Laboratories (Sudbury, ON). Ferrous iron was determined via potentiometric titration with a standardised potassium permanganate solution following digestion of sample powder in HF-H₂SO₄ (e.g., Pratt 1894; Goldich 1984). The redox titration point was measured with a Metrohm 670 Titroprocessor and converted to FeO wt. %. The total carbon and sulphur content of each sample was measured by infrared absorption following combustion of the sample powder in an oxygen-rich environment. The total sulphur content of each sample was consistently below the detection limit of

Table 1: Major element concentration in wt.% and molar weathering index values

Sample	FF021A-001	FF021A-002	FF021A-003	FF021A-005	FF021A-007	FF021A-009	FF021A-010	FF021A-011
Depth (cm below Missi)	0	4	11	21	30	38	47	53
SiO ₂	52.3	65.3	63.7	57.7	58.4	58.6	57.6	60.0
TiO ₂	1.55	0.78	0.81	0.90	0.90	0.89	0.88	0.95
Al ₂ O ₃	18.1	14.6	14.6	15.9	15.7	15.0	16.2	16.7
Fe ₂ O _{3(T)}	17.3	12.2	13.7	16.4	16.1	16.3	16.0	15.1
FeO	4.03	1.53	2.43	4.77	5.08	5.82	4.82	1.50
MnO	0.07	0.02	0.04	0.08	0.09	0.10	0.08	0.02
MgO	2.18	0.70	0.94	1.75	1.91	2.26	1.73	0.50
CaO	0.43	0.28	0.61	0.52	0.50	0.54	0.51	0.23
Na ₂ O	1.34	1.20	1.14	1.11	1.07	0.95	1.16	1.52
K ₂ O	1.74	2.29	2.29	2.26	2.10	1.87	2.17	2.73
P ₂ O ₅	0.28	0.19	0.44	0.36	0.36	0.37	0.36	0.15
LOI	3.19	2.35	2.55	3.30	3.30	3.38	3.31	2.72
CO ₂	0.13	0.05	0.03	0.10	0.05	0.06	0.28	0.07
Total*	98.4	99.9	100.9	100.4	100.4	100.2	100.0	100.7
CIA	81	76	77	79	79	80	79	75
CIA-K	89	88	88	89	90	90	89	87
PIA	87	86	86	88	88	89	87	84
MIA _(O)	76	89	86	78	76	72	78	93
MIA _(O) -K	79	85	84	81	80	77	81	87
CALMAG	75	78	78	75	74	73	75	80

*Total refers to the sum from XRF analysis including the loss on ignition

^aestimated depth below the unconformity

bdl = below detection limit

FF021A-014	FF021A-016/017	FF021A-018	FF021A-020	FF021A-023	FF021A-027	FF021A-030	FF021A-035	FF021A-037	FF021B-039
65	72	75	81	91	99	106	117	121	106
60.6	53.9	53.3	59.9	62.0	60.5	61.2	62.3	64.3	61.5
0.87	0.96	0.99	0.85	0.81	0.84	0.86	0.83	0.81	0.90
15.8	17.5	17.6	15.4	14.4	15.4	15.5	15.0	14.0	15.6
14.8	17.8	17.8	16.3	15.3	16.0	14.5	14.6	13.3	14.0
1.54	4.77	5.34	3.44	1.83	1.43	1.42	1.49	1.73	1.65
0.02	0.08	0.09	0.06	0.03	0.03	0.02	0.03	0.03	0.03
0.53	1.70	2.09	1.19	0.64	0.51	0.50	0.57	0.75	0.64
0.63	0.57	0.58	0.48	0.54	0.54	0.53	0.54	0.58	0.47
1.42	1.25	1.21	1.11	1.22	1.32	1.31	1.26	1.10	1.35
2.56	2.50	2.37	2.32	2.34	2.58	2.69	2.61	2.44	2.59
0.45	0.40	0.42	0.34	0.38	0.38	0.38	0.36	0.34	0.34
2.61	3.52	3.68	2.87	2.50	2.51	2.61	2.54	2.59	2.63
0.04	bdl	0.04	0.23	0.05	0.04	0.08	0.09	0.18	0.04
100.3	100.2	100.1	100.7	100.2	100.6	100.1	100.7	100.2	100.1
75	78	79	78	76	75	75	75	75	75
87	89	90	89	87	87	88	87	87	87
84	87	88	87	85	85	85	85	85	85
92	80	77	83	90	92	92	91	87	90
87	82	80	84	87	88	88	87	85	86
79	76	75	78	80	80	80	79	77	79

FF021B-043	FF021B-046	FF021B-049	FF021B-052	FF021B-054/055	FF021B-057	FF021B-058	FF021B-059	FF021B-061	FF021B-062
122	130	144	153	159	170	172	176	183	186
61.6	61.8	57.0	62.7	63.2	61.9	65.5	66.0	37.9	60.1
0.85	0.83	0.89	0.87	0.86	0.75	0.82	0.75	1.13	0.57
15.3	14.9	16.2	15.7	15.6	13.6	14.2	13.4	17.4	14.3
14.8	14.1	15.4	12.9	12.9	11.9	12.1	12.5	27.0	11.9
2.46	1.87	3.31	1.22	1.81	2.83	1.43	2.49	13.68	7.33
0.04	0.03	0.06	0.02	0.03	0.07	0.03	0.05	0.26	0.14
0.95	0.75	1.54	0.49	0.62	1.99	0.64	1.08	6.28	3.73
0.47	0.56	1.02	0.50	0.59	2.06	0.60	0.58	1.45	1.31
1.25	1.27	1.27	1.35	1.30	0.97	1.22	0.99	0.59	0.62
2.35	2.41	2.49	2.71	2.63	2.17	2.31	2.14	0.90	1.68
0.33	0.31	0.34	0.35	0.36	0.35	0.35	0.27	0.45	0.08
2.80	2.75	3.90	2.51	2.70	5.15	2.55	2.80	6.76	5.44
0.05	0.24	0.84	0.04	0.33	2.48	0.23	0.35	1.50	1.84
100.7	99.7	100.0	100.1	100.7	100.9	100.3	100.6	100.1	99.8
77	75	74	75	75	66	75	75	83	74
88	86	84	87	87	75	86	87	87	82
86	84	81	85	84	71	84	84	87	79
86	87	77	92	90	63	88	81	50	55
85	85	79	87	86	69	85	82	65	63
78	78	73	79	78	64	77	75	64	60

FF021B-063/064	FF021B-065	FF021B-067	FF021C-071	FF021C-072B	FF021C-074	FF021C-076	FF021C-077	FF021C-079	FF021C-080
192	197	214	228	241	245	252	255	261	268
57.2	58.1	60.4	54.7	55.7	52.5	52.1	51.7	49.3	50.5
0.70	0.61	0.59	0.75	0.60	0.65	0.62	0.64	0.66	0.63
15.5	16.4	15.5	16.0	15.3	16.2	15.6	16.0	15.8	16.1
14.6	12.8	12.9	14.9	13.6	13.5	13.4	13.9	14.8	13.9
7.73	7.22	6.37	7.20	7.32	8.59	8.94	8.44	8.93	8.60
0.14	0.13	0.11	0.13	0.14	0.16	0.17	0.17	0.17	0.17
3.62	3.30	2.89	3.59	4.27	4.70	5.12	4.97	5.29	5.09
0.85	0.81	0.56	1.24	1.77	2.01	2.57	2.38	2.81	2.75
0.74	0.82	0.77	0.87	0.70	0.75	0.68	0.74	0.73	0.76
1.73	2.15	2.10	1.89	1.71	1.78	1.65	1.73	1.61	1.73
0.11	0.09	0.10	0.12	0.09	0.10	0.11	0.11	0.12	0.10
5.10	5.05	4.18	5.50	6.58	7.13	8.18	7.84	8.26	8.43
1.17	1.06	0.70	1.67	2.47	2.86	3.65	3.69	3.95	3.90
100.4	100.3	100.0	99.6	100.5	99.5	100.2	100.2	99.6	100.0
78	77	78	75	72	71	68	69	67	67
86	86	88	82	79	78	74	75	72	73
84	84	87	80	76	75	71	73	70	70
60	63	66	59	53	51	47	49	47	48
68	69	72	67	62	60	57	58	57	57
65	65	67	64	59	57	54	56	54	55

FF021C-081	FF021C-082/083	FF021C-084	FF021C-085/086	FF021C-088/089	FF021C-090	FF021C-092	FF021C-095	FF021C-098M
276	288	295	300	308	313	321	328	340
47.6	51.9	50.4	51.1	57.6	63.5	57.3	60.3	42.6
0.68	0.60	0.74	0.79	0.51	0.41	0.56	0.37	0.87
16.9	16.1	16.6	15.9	12.9	10.3	13.2	10.1	20.1
15.3	12.8	15.6	16.4	12.6	9.1	12.5	10.0	20.0
9.85	8.94	11.31	11.84	6.55	6.55	9.62	7.70	13.31
0.19	0.17	0.20	0.20	0.18	0.14	0.16	0.14	0.21
5.72	5.21	5.51	5.72	5.31	4.64	5.24	5.47	5.92
2.46	2.37	1.49	1.39	2.43	3.07	2.07	3.61	0.52
0.70	0.74	0.61	0.48	0.34	0.30	0.33	0.22	0.69
1.69	1.73	1.39	1.27	1.17	1.16	1.19	0.90	1.72
0.10	0.09	0.11	0.12	0.07	0.07	0.09	0.05	0.16
8.62	8.17	6.95	6.34	7.11	7.69	7.04	8.75	6.32
4.17	3.44	2.08	1.92	3.66	4.43	2.96	5.30	0.52
100.0	100.0	99.6	99.8	100.3	100.5	99.6	99.8	99.2
70	69	77	78	68	59	71	56	85
76	75	83	84	73	64	76	60	92
74	73	81	83	71	61	74	57	91
47	48	50	49	42	38	44	33	56
57	57	60	60	54	48	55	44	66
55	54	58	58	52	46	53	43	64

FF021C-098G	FF021C-101	FF021D-102	FF021D-103	FF021D-104	FF021D-106	FF021D-108	FF021E-110	FF021E-113	FF021E-116
340	356	380	382	387	396	403	418	435	452
54.7	52.6	51.2	54.9	55.1	53.3	52.3	53.1	49.9	54.3
0.44	0.70	0.60	0.55	0.49	0.56	0.68	0.59	0.68	0.53
11.7	15.6	15.0	14.0	13.3	14.1	14.6	14.3	13.5	11.9
11.9	15.2	13.8	10.7	10.5	9.7	10.7	14.9	16.1	9.6
9.34	11.81	10.79	8.49	8.15	7.32	8.33	11.75	12.87	7.58
0.16	0.18	0.17	0.14	0.13	0.12	0.13	0.18	0.20	0.14
6.30	6.07	6.35	5.48	5.80	5.41	5.71	6.39	7.65	6.33
3.74	1.34	2.37	2.75	3.36	3.43	3.16	1.71	2.69	4.52
0.24	0.31	0.27	0.37	0.26	0.70	1.18	0.29	0.13	0.28
0.95	1.23	1.74	1.98	2.64	3.99	3.66	1.53	0.54	3.15
0.07	0.12	0.07	0.07	0.06	0.06	0.07	0.08	0.09	0.06
9.59	6.72	7.89	8.30	8.36	8.53	7.65	6.65	8.34	9.47
5.43	1.86	3.48	4.00	4.96	4.91	4.46	2.56	3.71	7.03
99.8	100.1	99.4	99.3	99.9	99.9	99.9	99.8	99.8	100.3
59	80	70	65	59	55	56	74	71	50
63	85	77	72	67	66	66	81	73	58
60	84	74	69	62	57	58	79	72	50
34	47	43	43	39	42	42	43	36	33
46	58	54	52	49	49	49	55	49	42
45	57	51	49	45	45	45	53	49	39

FF021E-120	FF021E-121	FF021F-LWB	FF021H-LWB	FF021-FB1 ^a 1000-1200	FF021-FB2 ^a 1000-1200
473	477	500	515	45.9	42.5
52.0	53.0	51.6	54.9	0.62	0.53
0.58	0.47	0.57	0.63	13.9	14.3
13.7	12.5	14.1	15.1	12.6	11.5
15.2	15.4	12.6	12.5	9.95	9.25
12.29	12.41	9.89	9.91	0.24	0.23
0.18	0.19	0.18	0.16	5.01	4.68
7.05	7.42	6.60	5.55	8.93	10.69
2.10	2.49	3.32	1.71	2.58	3.13
0.30	0.05	0.99	0.22	0.32	0.42
1.11	0.46	2.23	2.77	0.06	0.05
0.08	0.07	0.07	0.07	9.74	11.33
7.36	8.06	8.28	6.11	6.36	7.94
3.01	3.60	4.65	2.20	99.9	99.4
99.7	100.2	100.4	99.7		
72	72	59	71	40	36
77	74	65	82	41	37
75	73	61	79	40	36
39	35	38	47	33	31
52	49	48	57	40	37
50	49	45	53	40	37

0.01 wt. % and thus not reported. Total carbon is reported as CO₂ wt. % (detection limit of 0.03 wt. %) in Table 1. The accuracy and precision of these measurements are monitored using the analysis of several in-house and international reference materials that are summarised in Schweyer (2006).

4. Results

4.1 Description of the paleosol

The field description and mineralogy of the parent greenstone and paleosol profile is outlined below and summarised in Figure 4. A selection of thin section photomicrographs is reported in Figure 5. Further details regarding the mineralogy, additional thin section and back-scattered SEM images, and XRD patterns from different parts of the paleosol are reported in the supplementary materials section.

4.1.1 Parent rock

The parent rock is a plagioclase phyric, amygdaloidal, mafic greenstone, similar to other rocks in the Flin Flon arc assemblage. The greenstone is dominated by a groundmass of fine-grained chlorite, carbonate, epidote, and feldspar, with coarser patches and veinlets of chlorite and coarse-grained, sparry calcite throughout, similar to the findings of Holland et al. (1989). Feldspars are completely albitised, even in the rare relict phenocrysts, and locally found in association with sericite. Amygdales are filled with micro- to cryptocrystalline quartz and cloudy, fine to medium grained carbonate, and are occasionally rimmed and/or partly filled with chlorite. The quartz in the amygdales is commonly internally zoned, with finer-grained rims and coarser polycrystalline quartz in the centre. Opaque Fe-Ti oxides (predominantly magnetite and ilmenite) are present throughout the greenstone, although the modal abundance is variable at the hand sample and the thin section scale, as also noted by Holland et al. (1989). The parent greenstone is similar in composition to other volcanic rocks of the Hidden formation (DeWolfe et al. 2009b), with one exception: the carbonate content (calcite) is higher in the vicinity of the paleosol.

4.1.2 Paleosol profile

The paleosol profile is divided into three broadly defined mineral horizons (A, B, and C) based on its physical and mineralogical properties. In addition, a thin, dark band that separates the A and B (Figure 4) horizons is described separately.

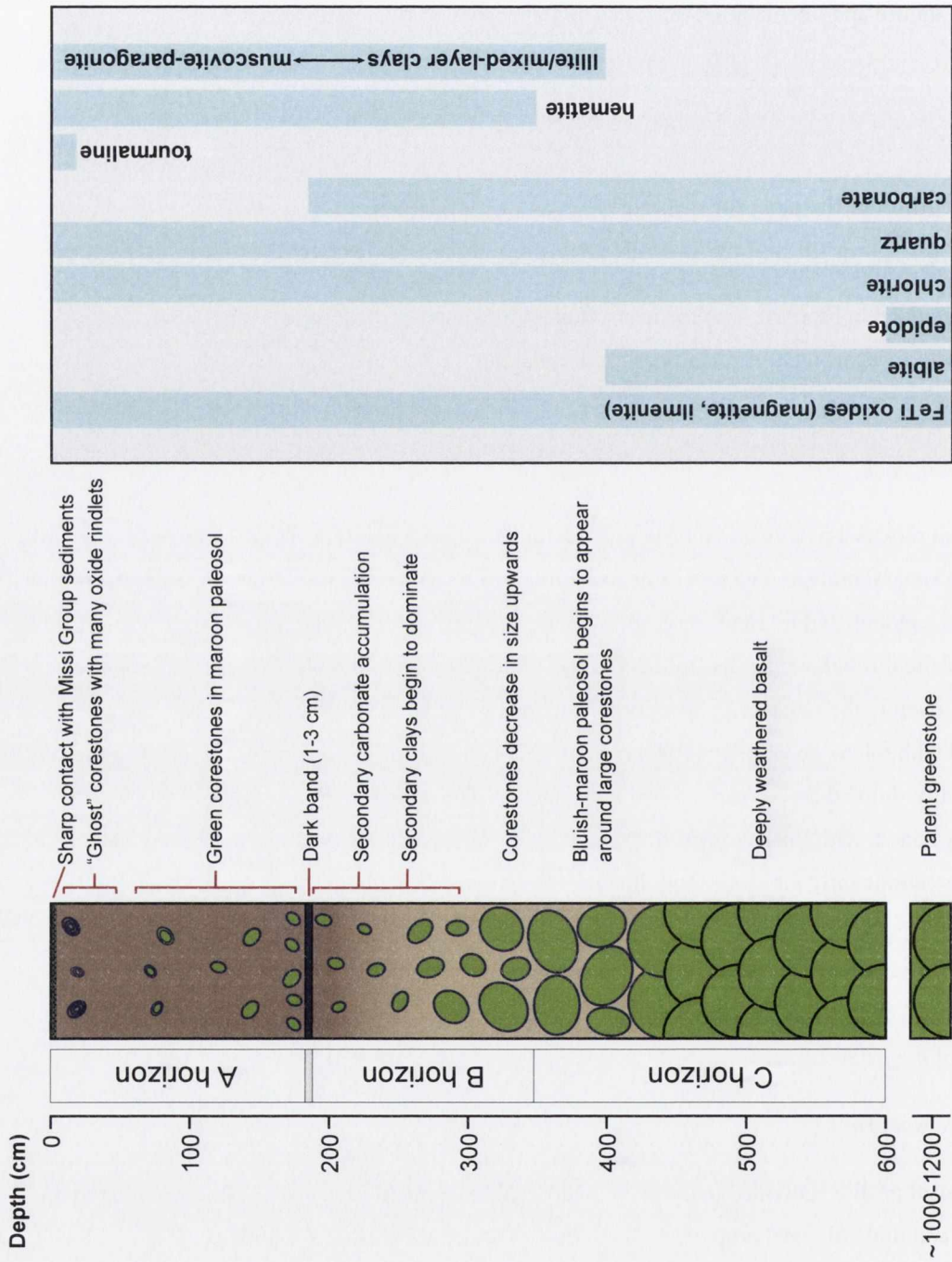


Figure 4: Geological sketch section of the profile showing the main horizons in the paleosol. Key features are listed along with a summary of the mineralogical changes based on petrography, X-ray diffraction, and scanning electron microscopy (see supplementary materials for further details). Bars indicate presence of minerals but not their modal abundances.

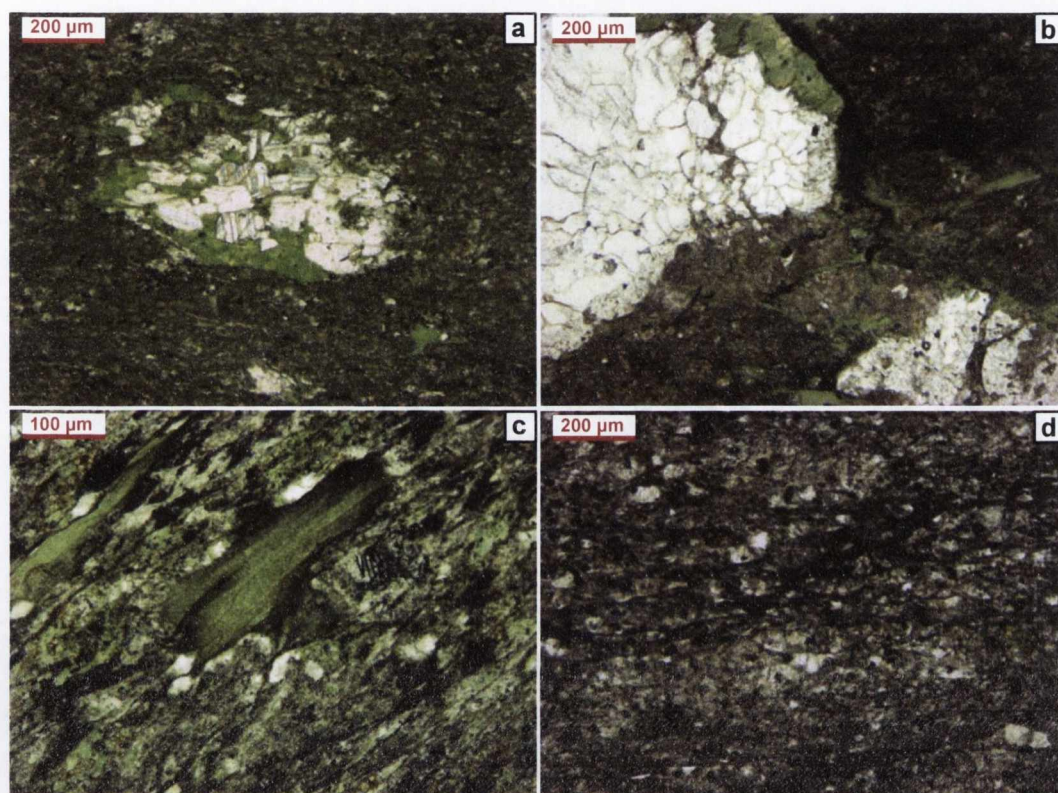


Figure 5: Thin section photomicrographs (plane polarised light) of selected parent greenstone and paleosol features: a) calcite in fine-grained parent greenstone matrix (FF021-FB1; Depth: ~1000-1200 cm); b) secondary dolomite invading polycrystalline quartz amygdale (FF021F-LWB; Depth: 500 cm); c) formation of opaque Fe oxides in chlorite grains (FF021C-074; Depth: 245 cm); d) matrix of mixed-layer clays and Fe oxides in maroon paleosol (FF021B-046; Depth: 130 cm).

C horizon (515-350 cm): In the lowest horizon of the profile, the paleosol is similar in colour, induration, and texture to the parent greenstone and the mineral variability, such as the abundance of Fe-Ti oxides and amygdals, is still prevalent. Epidote and calcite are largely absent, however, and only minor amounts of relict albite remain. Additionally, the paleosol has a higher abundance of chlorite than the parent greenstone. Significant amounts of dolomite are present throughout the entire horizon, which is fine-grained and typically associated with amygdals. The dolomite is commonly found forming around the quartz-filled amygdals or splitting and penetrating into them. Chlorite embays the dolomite at the edges of amygdals in some areas. Within some of the pillow cores, a network of thin (1 mm) anastomosing, discontinuous white veins invades the greenstone. The veins are commonly concentrated in zones (c. 3-5 cm thick) forming a concentric, ovoid pattern roughly parallel to the dominant foliation and wrap around amygdals. They are most prominent in the samples at a depth of 400-475 cm below the unconformity. Whether the veins are a deep subaerial weathering (e.g., early spheroidal weathering feature) or submarine alteration feature is unclear. Near the top of the C horizon, small patches of bluish-maroon paleosol are present, but are sparse and restricted to inter-pillow regions.

B horizon (350-183 cm): The transition into the B horizon is slightly gradational (geochemical changes have been used to place the boundary at a specific depth of 350 cm). The colour of the paleosol progressively transitions from green to bluish-maroon in colour and spheroidal weathering textures begin to dominate. The size of green corestones in the bluish-maroon paleosol decreases upwards overall. The darker colour is predominantly the result of hematite and illite/mixed-layer clays, which replace chlorite. Albite is no longer present in phenocrysts or in the matrix. Similar to the C horizon, dolomite surrounds amygdals, although it is also found in aggregates and in thin (~1 mm) veins. This is most notable at a depth interval of approximately 230-280 cm. Much of the dolomite (in aggregates and veins) on the outcrop surface is weathered (modern) to a rusty red colour (Figure 3c). The presence of Fe^{2+} and Mn^{2+} in the dolomite was confirmed with SEM. Holland et al. (1989) reported an average of 2 wt. % FeO in the dolomite. In fresh cut surfaces, Fe oxides are found within the dolomite clusters.

Dark band (183 cm): A discontinuous dark, bluish-black band is present in the profile with a laterally variable thickness of 1-3 cm. It is comprised predominantly of irregular layers of microcrystalline Fe oxides and a fine-grained groundmass that is similar in composition to chlorite. The paleosol immediately adjacent to the band contains areas with a slightly higher abundance of dolomite and apatite.

A horizon (183-0 cm): In this horizon, the colour of the paleosol is a more consistent bluish-maroon colour, the abundance of chlorite decreases significantly, and carbonate is present in only trace amounts. Overall, the paleosol is dominated by fine-grained micas, hematite, and quartz. The illite/mixed-layer clay is successively replaced by mixed-layer muscovite/paragonite (Holland et al. 1989). Remnant texture of the greenstone is lost as it is overcome by the foliation and crenulation of micas. A minor degree of colour variation is present throughout the upper metre of the profile that reflects changes in the modal abundance of the aforementioned clays. This appears to be related to spheroidal weathering. In a few distinct areas, small, green corestones are identifiable and appear to be concentrated in bands (e.g., at the very base of the A horizon and at a depth of 70-90 cm; Figure 3d). At a depth of 50-70 cm, above a corestone band, an abrupt transition to a dark maroon coloured paleosol is present. In the upper 30 cm of the profile, there are highly altered “ghost” corestones with many dark grey-black (hematite-rich) rindlets. Quartz is present throughout the fine-grained matrix and as patches of sub-rounded, polycrystalline grains (presumably remnant amygdales) throughout the horizon. In a few areas, there are isolated, sinuous quartz veins of varying thickness (<1 cm) and length (<5 cm) in the paleosol matrix that could represent the location of former pedogenic desiccation cracks.

The contact of the paleosol with the overlying Missi Group sedimentary rocks is sharp at this locality, with little physical evidence for reworking of the regolith. In the upper 10 cm of the paleosol, euhedral tourmaline is present along the unconformity contact, but drops abruptly in modal abundance below this depth. Thin (1-3 cm) quartz and epidote-chlorite veins cross-cut the paleosol, but they are sparse and do not significantly overprint the pedogenic features (Holland et al. 1989).

4.2 Major element geochemistry

The depth profiles for the major element oxides (Table 1) are plotted in Figure 6. In these plots, the parent greenstone samples from this study (FF021-FB1 and FF021-FB2) and a mean parent greenstone composition (Table A1) are placed at a depth of 550 and 575 cm, respectively. Errors on means are reported as the 1σ standard deviation. Additional major element plots are reported in the supplementary materials section.

Overall, the elemental oxide profiles from the paleosol are similar to those reported in Holland et al. (1989) and strongly parallel the mineralogical progression. The heterogeneity of the parent greenstone is expressed in the concentration variation of several elements (e.g., K, Ti, Ca, Si) in the C horizon of the profile (depth of 350-515 cm). Some of this variability may be accentuated by the small sample

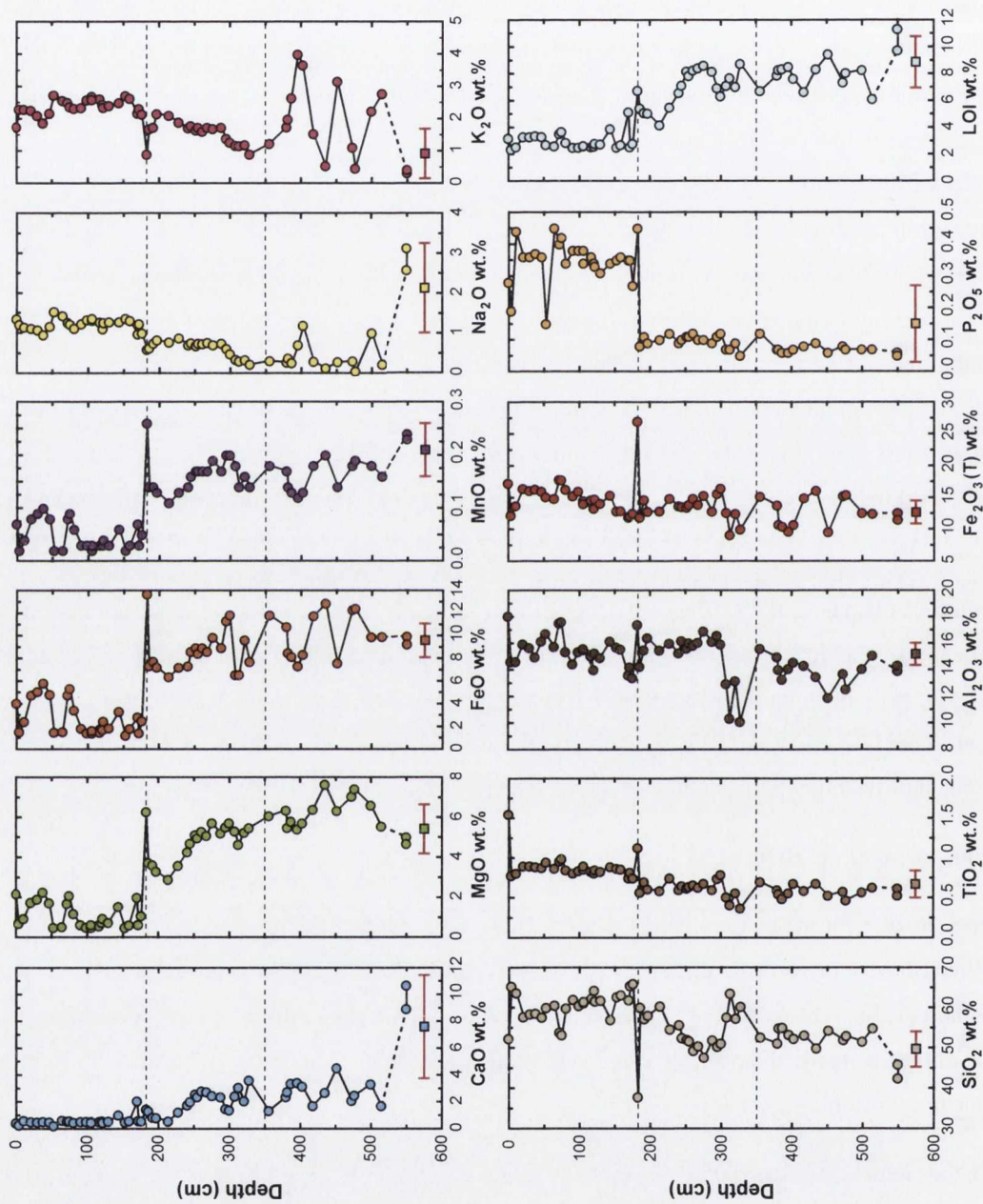


Figure 6: Major-element depth profiles. The parent greenstone samples from this study (FF021-FB1 and FF021-FB2) and a mean parent greenstone value ($\pm 1\sigma$ SD) that includes previous analyses were placed arbitrarily at a depth of 550 and 575 cm, respectively. Stippled lines represent the horizon divisions (A: 0-183 cm; B: 183-350 cm; C: 350-515 cm).

size (less than 5 cm depth in some cases) used in this study. Deep, incipient weathering horizons also tend to develop in a patchy nature. Regardless, the trends become 'smoother' after the transition into the B horizon (above a depth of 350 cm), as the maroon paleosol begins to dominate. In the A and B horizons, elemental variations (e.g., between a depth of 50-100 cm and 300-350 cm) are controlled by spheroidal weathering textures.

The concentration profiles of TiO_2 wt. %, Fe_2O_3 wt. %, and Al_2O_3 wt. % are fairly coherent throughout the profile (Figure 6), with the exception of the dark band at 183 cm (sample FF021B-61), and generally show an increase from the parent greenstone value to the unconformity. A subtle but consistent offset in the concentration of these elements is present above (A horizon) and below (B and C horizons) a depth of 183 cm, marked by the dark band. This is most prominent in the TiO_2 wt. % data and is also clearly expressed in element ratios such as $\text{Al}_2\text{O}_3/\text{TiO}_2$ (Figure 7); the upper samples have a mean $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of 17.90 ± 0.40 ($n=25$), whereas the lower samples have a higher mean ratio of 24.40 ± 2.00 ($n=34$). The two parent greenstone samples have $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of 22.45 (FF021-FB1) and 27.02 (FF021-FB2), which are close to the average of the paleosol below 183 cm. The behaviour of Si is similar to Al and Fe throughout the majority of the profile, although an increase in SiO_2 wt. % is evident in the B horizon and a minor decrease is evident from the start of the A horizon (183 cm) to the unconformity contact. This loss of Si in the A horizon is inversely correlated with the concentrations of Ti, Al, and total Fe.

A direct correlation of CaO wt. % with the total carbon (CO_2 wt. %) concentration, as illustrated in Figure 8, indicates that the distribution of Ca is predominantly controlled by carbonate in the profile. Consistent with the mineralogical observations, the parent greenstone samples (FF021-FB1 and FF021-FB2) have high CO_2 and CaO wt. % values that are close to the ideal calcite (i.e., CaO wt. %: 56, CO_2 wt. %: 44) ratio. All of the samples in the B and C horizon of the profile, however, fall on a dolomite (i.e., CaO wt. %: 30, MgO wt. %: 22, CO_2 wt. %: 48) trend line. The C horizon has a lower, but somewhat uniform Ca concentration (mean CaO wt. %: 2.7 ± 0.9) compared to the parent greenstone. The Ca concentration begins to decrease in the B horizon and very low values (CaO wt. %: <0.6) are present in the A horizon, with the exception of two samples that have CaO values of 1.0 and 2.1 wt. % (Figure 8). The CaO wt. % correlates with the P_2O_5 wt. % and falls on a trend line for apatite (CaO wt. %: ~ 51 , P_2O_5 wt. %: ~ 42) for the majority of samples in the A horizon.

The concentrations of Mg, Mn, and Fe^{2+} in the C horizon are similar to the mean parent greenstone composition (Table A1). These elements correlate well with each other in the paleosol, especially in

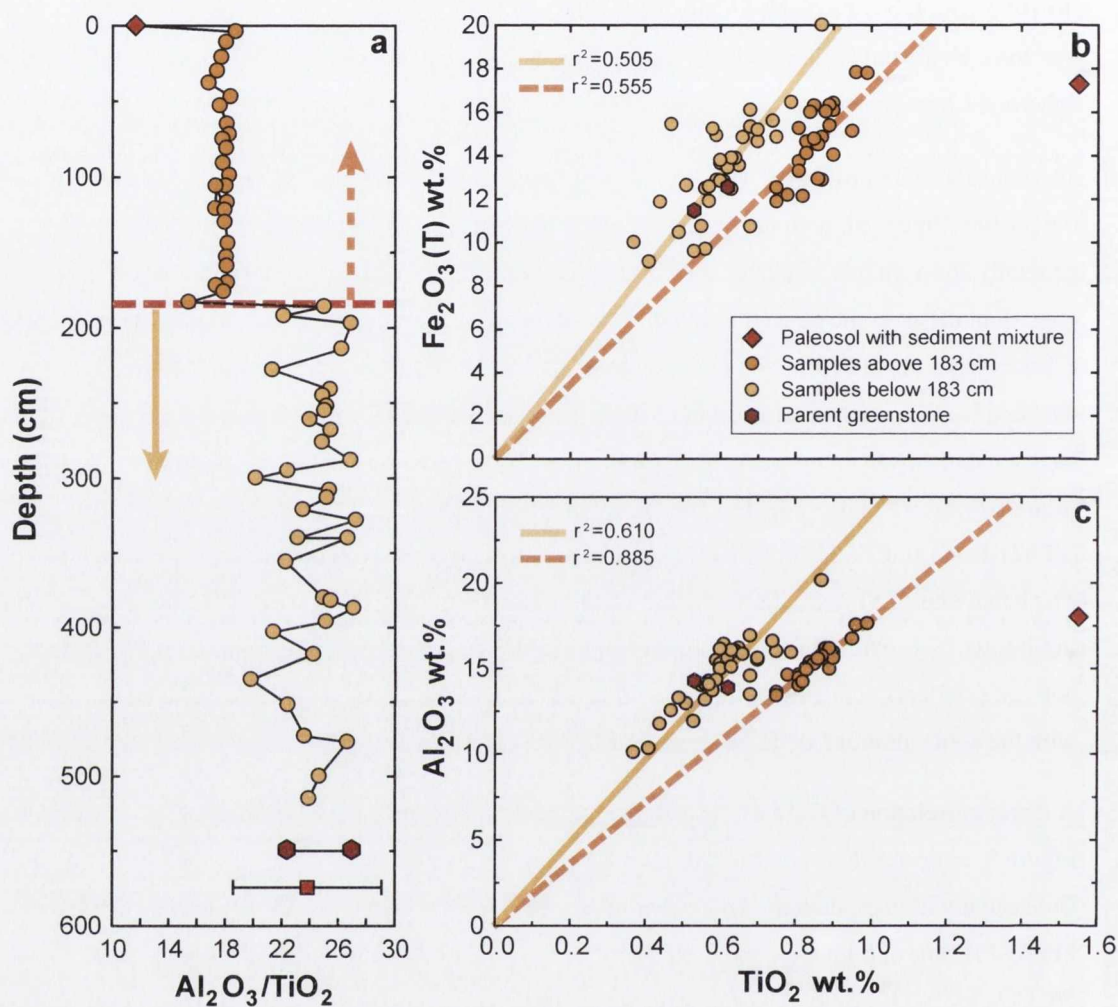


Figure 7: Immobile element geochemistry. a) $\text{Al}_2\text{O}_3/\text{TiO}_2$ mass ratio vs. depth shows a distinct offset at 183 cm (marked by the dark band in the profile) that coincides with the division between the A and B horizons. Samples above 183 cm (dark circles) have higher Ti concentrations and a distinct $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio (17.90 ± 0.40 , 1σ SD) from the samples below (light circles; $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of 24.40 ± 2.00 , 1σ SD) and the parent greenstone (hexagonal symbols). The mean ($\pm 1\sigma$ SD) parent greenstone value (Table A1) is plotted at a depth of 575 cm (square symbol). This offset is also evident in element-element scatter plots (b) and (c). The greater degree of scatter in the lower horizons is interpreted to reflect the variability in the modal abundance of Fe-Ti oxides in the greenstone. The uppermost sample in the profile (FF021A-001; dark diamond symbol) has a distinctly lower $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio (11.65) compared to the paleosol below it, suggesting it has been affected by reworking of the regolith during Missi sediment deposition.

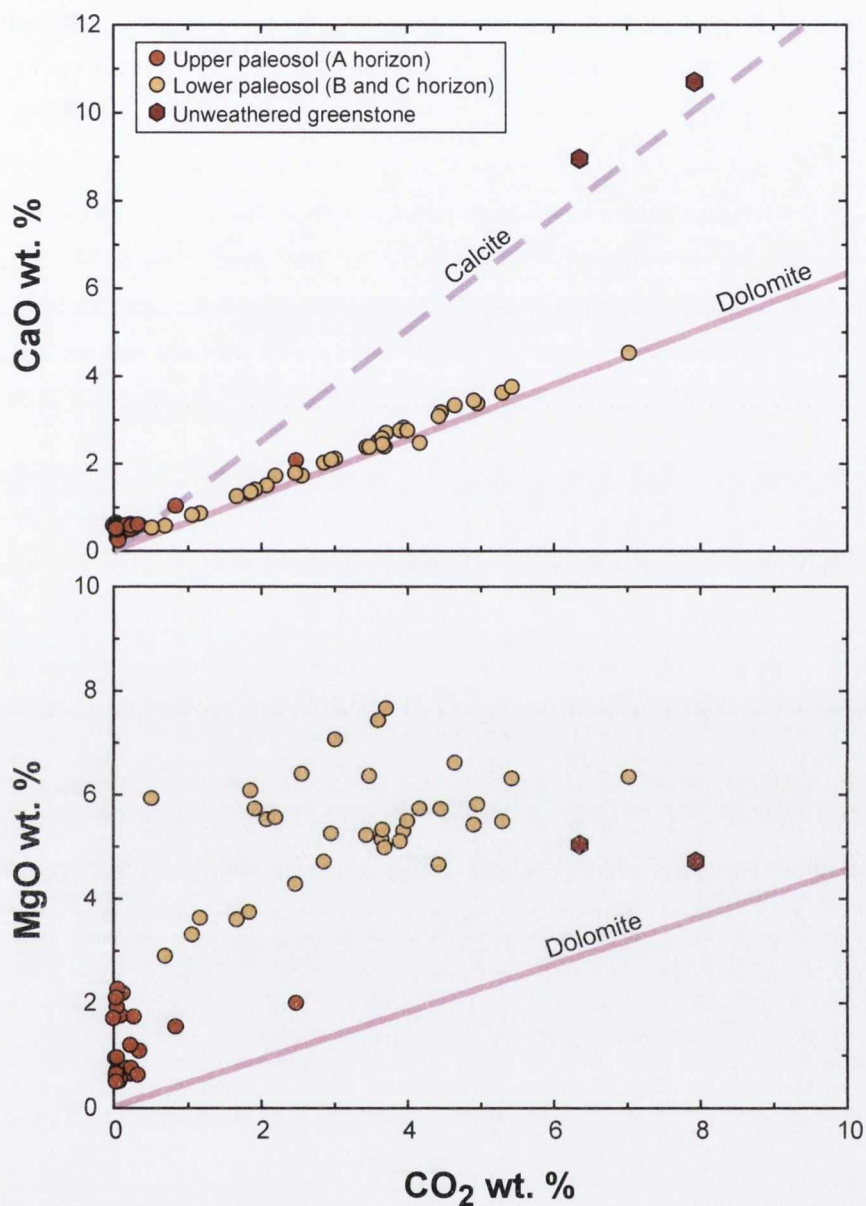


Figure 8: Correlation of (a) CaO wt. % and (b) MgO wt. % with total carbon (CO_2 wt. %). Lines that represent the ratio of the elements in calcite (CaO : 56 wt. %; CO_2 : 44 wt. %) and dolomite (CaO : 30 wt. %; MgO : 22 wt. %; CO_2 : 48 wt. %) are shown for reference. The parent greenstone samples lie close to the calcite line (a). By contrast, the samples in the B and C horizons of the paleosol fall on the dolomite line (a). In the A horizon, the samples plot above the dolomite line and indicate the presence of Ca in another mineral (apatite). The MgO is less correlated with CO_2 (b) and the samples plot above the ideal dolomite line, indicating that Mg is hosted in another mineral (chlorite) in addition to dolomite.

the A and B horizons, suggesting they are hosted in the same mineral (i.e., chlorite). In a plot of MgO vs. CO₂ wt. % (Figure 8b), the paleosol samples plot above the dolomite trend line, confirming that the Mg is divided between dolomite and chlorite. In the A horizon samples, the bulk sample FeO/(MgO+FeO) ratio is rather constant at 0.72 ± 0.03 , which is close to the ratio in chlorite (~ 0.7) analysed by Holland et al. (1989). The variations in the concentration of Mg, Mn, and Fe²⁺ in the upper paleosol correlate with the mineralogical and colour changes. In the C and B horizons, the FeO/(MgO+FeO) values are lower, more variable and the correlations between Mg, Mn, and Fe²⁺ are generally poorer, which reflects the more complicated distribution of the elements between chlorite and other phases, such as dolomite. The LOI values in the profile correlate with the divalent elements, most notably Ca²⁺ and Mg²⁺, indicating that the volatiles are hosted by carbonate and chlorite.

The concentration of Na is significantly lower in the paleosol than in the parent greenstone (Na₂O wt. %: 2.6 and 3.1), especially in the C horizon (Na₂O wt. %: 0.4 ± 0.3). The concentration of K in the C horizon is highly variable, with K₂O values ranging from 0.5 to 4.0 wt. %. By contrast with the divalent elements, the concentration of K and Na increases in the A and B horizons to the unconformity contact (Figure 6), following the increase in the abundance of illite/mica in the profile. The two elements are highly correlated with each other and inversely correlated with the trends of Mn, Fe²⁺, and Mg.

The concentration of P in the C horizon is very consistent (P₂O₅ wt. %: 0.09 ± 0.02), although a subtle increase in concentration from the base of the C horizon up to 183 cm is evident. Above 183 cm, the concentration of P₂O₅ is offset to higher values in the A horizon (P₂O₅ wt. %: 0.35 ± 0.07).

5. Discussion

5.1 Pre-weathering, submarine alteration

The rocks of the Flin Flon arc assemblage have been altered by the hydrothermal activity that also led to VMS ore formation. Consequently, the Hidden and Louis formation rocks (DeWolfe et al. 2009b) have a mineralogical assemblage that is comparable to other hydrothermally altered and metamorphosed (greenschist facies) Precambrian greenstone (e.g., Nakamura and Kato 2004; Polat et al. 2012).

The pre-weathering seafloor alteration accounts for many of the chemical variations in the parent greenstone and the C horizon of the paleosol profile. Among major elements, Ca and Si show the most variable concentrations in the parent greenstone (Table A1). This is a reflection of the amygdaloidal nature of the greenstone, in which most amygdales are unevenly distributed and filled with quartz and carbonate. Hence, the unsystematic behaviour of Ca and Si in the C horizon (below 350 cm; Figure 6) can be attributed to the uneven distribution of quartz and carbonate filled amygdales in the pillows. Furthermore, variability may also be related to the preferential alteration of glassy pillow selvages in the greenstone. Potassium is also highly variable in the C horizon, with local enrichments (Figure 6) that are probably related to patchy sericite development (after that of albite) during seafloor alteration. Finally, the distribution of the less mobile elements, Ti and Fe, in the parent greenstone and C horizon appears to be related to the variable modal abundance of Fe-Ti oxides, a feature that probably also developed during seafloor alteration (Holland et al. 1989). Above a depth of 350 cm in the profile, it seems that the superimposed effects of greenstone weathering removed much of the mineralogical and chemical variability inherited from the seafloor alteration, because compositional trends become smoother to the unconformity contact (Figure 6).

5.2 Immobile element geochemistry

Identifying at least one element that remained immobile throughout the superimposed effects of seafloor alteration, subaerial weathering, and subsequent burial and metamorphism is necessary for assessing the parent rock composition and performing mass balance calculations. Holland et al. (1989) used the correlation between Al and Fe in the Flin Flon paleosol to argue that both of these elements met this criterion, despite the variability inherited from seafloor alteration. In the new profile, Fe, Al, and Ti are also correlated, suggesting that they were immobile in the paleosol. However, there are two independent trends above and below a depth of 183 cm, generating an 'offset' that is most prominent in the Ti data (e.g., Fe/Ti or Al/Ti). This phenomenon of the immobile element profile is striking and was not noted in previous studies of the paleosol, perhaps as a result of the lower sampling density, lower data precision, or that it is only present in the area of the new profile. The dark band at a depth of 183 cm marks the boundary, although its geological significance is unclear. Conventional knowledge regarding immobile element geochemistry suggests that the most probable explanation for the offset is the presence of a pre-weathering lithological contact, generated by the different modal abundance of accessory minerals in adjacent mafic lava flows. Physical evidence for separate flows was not identified in the field, although most of the primary volcanic texture was obliterated by the combination of seafloor alteration, subaerial weathering, burial, and metamorphism experienced by the

profile. Accordingly, the dark band could represent an inter-flow hiatus feature (e.g., hyaloclastite) that was more highly altered than the flows on either side.

Another possible explanation for the immobile element offset is that the upper paleosol experienced addition of allochthonous material, whereas the lower paleosol remained unaffected (e.g., Stiles et al. 2003). The immobile element offset coincides with the transition between the A and B horizons (the appearance of secondary dolomite) and could thus be a pedogenic link. Distinguishing between the different possible explanations for the offset is difficult given the antiquity of the paleosol; the loss of many pedogenic features and density variations occurred during burial, compaction, and metamorphism. At present, the hypothesis that the offset is related to the presence of two separate flows in the paleosol is adopted.

5.2.1 Significance of separate lava flows in the profile

If the paleosol profile encompasses two separate lava flows, alteration did not proceed through a uniform parent rock. Therefore, the original concentration of the major elements in the profile may not be accurately represented by the parent greenstone below. The higher P and Si concentration and the lower $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio in the upper part of the paleosol suggest that it developed on a more fractionated parent rock. However, there is no part that is sufficiently unweathered to determine its initial mobile, major element (Ca, Mg, Na, K) composition. Thus, constraints must be made from the chemistry of the immobile elements and through comparison with other volcanic rocks from the Hidden formation (DeWolfe et al. 2009b). These data are plotted in the supplementary materials section.

Silicon: The higher Si and slightly higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the upper flow is consistent with it belonging to a more felsic flow, although the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is more consistent across the boundary and overlaps with the range of other rocks in the Hidden formation (DeWolfe et al. 2009b). Comparison of the Si behaviour to Al and Ti (e.g., element vs. ratio plots; Driese 2004) indicates that much of the variability in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is the result of preferential Si mobility.

Phosphorus: In the Hidden formation volcanic rocks (DeWolfe et al. 2009b), there are correlations between P and other elements that are consistent with magmatic fractionation. However, the elevated P concentration and the higher $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ratio in the upper part of the paleosol are significantly greater than other samples of the Hidden formation (supplementary materials). Instead of this being a fractionation feature, it is also possible that the paleosol experienced P addition. The study of Pan and

Stauffer (2000) noted two main generations of apatite in the paleosol. The first is coarse-grained and present in the unweathered greenstone and lower part of the paleosol (B and C horizons). This apatite showed variable degrees of corrosion and was probably part of the pre-weathering assemblage. The second apatite is acicular/long prismatic and free of surface corrosion. It is interpreted to have formed during regional metamorphism and is present in the unweathered greenstone, all horizons of the paleosol, and the Missi Group sedimentary rocks. Since only the acicular/long prismatic grains were observed in the upper maroon paleosol by Pan and Stauffer (2000), it appears that the earlier generation of apatite was weathered out of the A horizon during the development of the profile. Indeed, apatite dissolution is common during continental weathering and is enhanced by warmer climates (e.g., Guidry and Mackenzie 2000) and organic acids (e.g., Goyne et al. 2006). If it is assumed that the coarse-grained apatite was lost during weathering, the higher P concentration (and higher P_2O_5/Al_2O_3) in the A horizon could be related to a post-weathering enrichment event, although the mechanism and timing is unclear. In any case, P is inappropriate for use in fingerprinting the chemistry of the parent rock.

Titanium: The lower Al_2O_3/TiO_2 in the upper paleosol is the strongest evidence for a pre-weathering element variation in the profile. Despite the offset, the ratios in both parts of the paleosol overlap with the range present in other mafic volcanic rocks of the Hidden formation (DeWolfe et al. 2009b; supplementary materials). By comparison to Ti, the ratio of other fairly immobile elements to Al, such as Fe and Si, is more constant across the boundary. Some co-variation of the Al_2O_3/TiO_2 ratio with Ca, Mg, Na and K in the Hidden formation is consistent with magmatic fractionation, but the overall concentration does not change significantly with the range in Al_2O_3/TiO_2 . Therefore, it appears that magmatic fractionation is expressed in the accessory phases (e.g., Ti oxide), but has not greatly influenced the major element chemistry.

In summary, it is clear that there is a complexity in the immobile element chemistry of the profile, although its exact cause is unknown and further work is necessary to explore its significance. The higher Si and lower Al_2O_3/TiO_2 suggest that the upper part of the paleosol may have originally been a separate, more fractionated parent rock or, alternatively, that introduction of allochthonous material occurred. If the offset is related to magmatic fractionation, it seems restricted primarily to accessory phases, with the original major element chemistry of the adjacent flows being only minimally affected (most importantly with respect to Fe, Mg, and Ca). Therefore, in the following discussion, it will be assumed that the major element chemistry in the upper and lower part of the paleosol was originally similar and that the weathering trends can be connected as one full profile. When using mass balance

plots and weathering indices to calculate the loss of mobile elements, Al is used as the immobile reference element since it is least influenced by the offset.

5.2.2 Sedimentary reworking during deposition of the Missi Group

Soft sediment deformation and reworking of the paleosol is common along the unconformity contact at other locations (Holland et al. 1989; supplementary materials). In the area of the new profile, however, the unconformity contact is sharp with little evidence of physical mixture between the soft regolith and sediment during deposition. Despite this, the sample nearest to the unconformity, although similar in colour to the underlying paleosol, has a significantly lower $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio (11.65). This is interpreted as chemical evidence for reworking of the Missi sediment and regolith, with the ratio having been changed by the introduction of a greater abundance of detrital heavy minerals. If this is the case, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio indicates that the sediment influence does not penetrate deeper than approximately 10 cm (compacted depth) into the preserved regolith. Further insight could be provided by additional HFSE (e.g., Zr, Hf, Th, Nb, Ta) analysis and the attempted separation of detrital zircon from the paleosol, the latter of which were identified by Holland et al. (1989) in the samples closest to the unconformity contact.

5.3 Secondary carbonate in the profile

In the B horizon, significant amounts of dolomite are present in the matrix of the paleosol and in distinct aggregations that are associated with pre-existing amygdales (Figure 3c). Textural evidence suggests that the dolomite is secondary and, in agreement with the study of Holland et al. (1989), this is interpreted as a pedogenic feature. The most probable source of the secondary carbonate is from higher in the profile, i.e., the Ca depleted A horizon (assuming it had a similar Ca concentration to the parent greenstone originally). The dolomite contains minor amounts of Fe^{2+} and Mn^{2+} , which may have derived from weathered chlorite. Thus, it may be a pedogenic carbonate horizon similar to modern vertisols (e.g., Driese et al. 2000).

The formation of pedogenic carbonate is typically associated with hydrological boundaries and it is possible that the appearance of carbonate marks the position of a fairly stable paleo-watertable in the profile. In deep weathering profiles, groundwater weathering reactions such as hydration and hydrolysis dominate below the more permanently saturated region, whereas more acidic and oxidizing conditions are favoured above the saturated region (e.g., Ollier 1988).

The fact that the position of the immobile element offset coincides with secondary dolomite accumulation is an interesting observation that is not yet well understood. For instance, a hydrological boundary may have developed preferentially at the contact between the two volcanic rock units, promoting lateral fluid flow.

5.4 Mobile element geochemistry

In order to assess the bulk loss of mobile elements from the profile, a series of chemical weathering indices (CIA, CIA-K, MIA, CALMAG) are used, as described in the appendix. The chemical weathering trends are shown on ternary plots that incorporate the weathering indices (Figure 9) and the data are compared with other volcanic rocks from the Hidden formation (DeWolfe et al. 2009b), previously collected data from the Flin Flon paleosol (Goetz 1980; Holland et al. 1989; Pan and Stauffer 2000) and other mafic paleosols of a similar age (Wigginger and Beukes 1990; Yang and Holland 2003). Mass balance plots, constructed using the open-system tau (τ) mass transport model (Brimhall and Dietrich 1987; Anderson et al. 2002), are reported in the supplementary materials section. It should be noted that the presence of a slightly lower parent rock concentration in the upper part of the paleosol profile would result in an overestimate of the mass loss relative to the parent greenstone, but it would not significantly change the overall weathering vectors in the ternary plots or the weathering index values.

5.4.1 Carbonate correction

Traditionally, the molar chemical weathering indices, such as the CIA, are designed to include the loss of Ca from silicate minerals (i.e., feldspar) only. At the Missi outlier locality of the Flin Flon paleosol, Ca in the profile is hosted predominantly by carbonate. Without a carbonate correction, the parent greenstone samples (FF021-FB1 and -FB2) have low weathering index values, which are within the range exhibited by unweathered Hidden formation volcanic rocks and the expected values for minimally altered basalts (Nesbitt and Wilson 1992). If a carbonate correction is applied to the samples, however, the weathering trend becomes inverted such that the parent greenstone and C horizon samples have the highest weathering index values (most altered) and values decrease upwards, varying with the abundance of carbonate. This inverted trend is clearly inconsistent with the profiles bulk chemical and mineralogical progression. For all chemical weathering indices in this study, CaO values were corrected for apatite but not carbonate.

5.4.2 *Ca and Mg*

The upward depletion of Ca and Mg in the profile controls the weathering index values and trends in the ternary plots (Figure 9). Accordingly, the chemical weathering indices that include both elements are well-correlated. For example, the CALMAG index correlates well ($r^2=0.961$) with the $MIA_{(O)}$. Substantial Ca and Mg loss in the maroon paleosol is indicated by the high weathering index values, although the degree of depletion is not as severe as in the most weathered sections of the Hekpoort or Drakenstein paleosols.

In the ternary plots, the weathering trends reflect the mineralogy of the profile and are visualised with vectors projecting away from the Ca and Mg apices (Figure 9). The absence of calcite and epidote (lower Ca) in the C horizon, compared to the parent greenstone, results in a gap between the profile samples and the parent rocks in the plots. This suggests that deep chemical weathering reactions extended beyond the sampled depth of 5 m. In the Al_2O_3 -CaO-MgO (A-C-M) plot for the CALMAG index (Figure 9d), the samples in the B and C horizons define a vector away from the Ca and Mg apex where the elements are hosted by dolomite and chlorite. In the A horizon, which is nearly barren of carbonate, the weathering trend moves away from the Mg apex along the Mg-Al join, which represents further weathering of chlorite. The mafic elements (Fe and Mg) are retained to a greater degree than Ca in the profile due to the presence of chlorite. This contrasts with weathering trends of unaltered mafic rocks containing plagioclase and pyroxene, since these minerals weather at similar rates (e.g., Nesbitt and Wilson 1992) and, consequently, the loss of Ca and Mg is more congruent.

5.4.3 *K and Na*

Both K and Na are typically mobile and lost from basaltic weathering profiles (e.g., Nesbitt et al. 1980). The lower Na concentration at the base of the C horizon compared to the parent greenstone suggests that Na was lost along with Ca during deep weathering reactions (i.e., weathering of albite). Although it is possible that K was retained in pedogenic clays, the upward enrichment and good correlation of Na and K in the A and B horizons indicates that both elements were probably depleted during weathering then re-introduced to the profile. This obscures their pedogenic signature, which is typical of most Precambrian paleosols (e.g., Sutton and Maynard 1993; Macfarlane et al. 1994; Zbinden et al. 1988; Rye and Holland 2000). The most commonly accepted mechanism for alkali element enrichment is the metasomatic reaction of pedogenic clay minerals (e.g., smectite, kaolinite) with diagenetic or hydrothermal fluids during burial and metamorphism (e.g., Nesbitt and Young 1989).

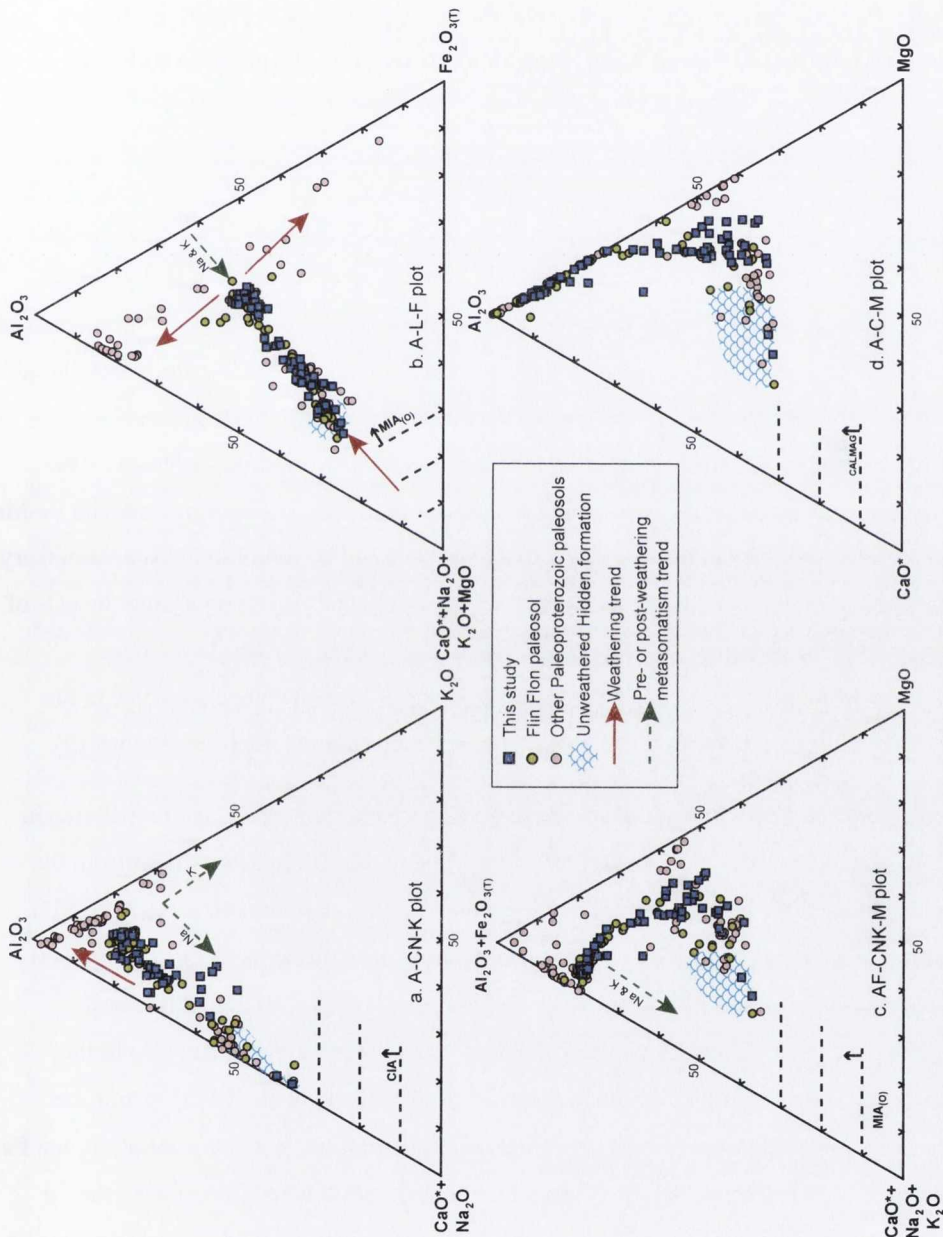


Figure 9: Ternary weathering index plots [(a) A-CN-K plot; (b) A-L-F plot; (c) AF-CNK-M plot; (d) A-C-M plot] showing loss of Ca and Mg (weathering trend) and the enrichment of Na and K (post-weathering metasomatism) in the Flin Flon paleosol. The following weathering indices can be projected into the ternary diagrams as shown in the figure: chemical index of alteration (CIA) into (a), mafic index of alteration [MIA_(O)] into (b) and (c), and CALMAG into (d). See the appendix for details of weathering index calculations. Square symbols represent samples of the present study. Circular symbols represent samples from previous studies of the Flin Flon paleosol (Holland et al. 1989; Pan and Stauffer 2000; Goetz 1980). The textured area represents the range in values for the Hidden formation greenstone (DeWolfe et al. 2009b). Light shaded circles represent other Paleoproterozoic paleosols (Wigging and Beukes 1990; Yang and Holland 2003).

The inclusion of Na and K in weathering indices has the net effect of underestimating the maximum extent of weathering and generates more complex vectors in ternary plots. The samples are pulled away from or back along their original predicted weathering vectors, as shown in Figure 9. The variable K enrichment in the C horizon (seafloor alteration) also results in a deviation from the predicted weathering vector. The addition of K can be unravelled in the A-CN-K plot (Fedó et al. 1995), whereas unravelling the addition of Na is more complicated since it is grouped with Ca.

5.5 Redox-sensitive elements

5.5.1 Fe behaviour in the Flin Flon paleosol

Although the evidence for oxidative weathering in the Flin Flon paleosol reported in Holland et al. (1989) remains unchallenged, disagreement regarding the interpretation of the Fe speciation data exists (Ohmoto 1996; Holland and Rye 1997; Ohmoto 1997; Rye and Holland 1998). The study of Ohmoto (1996) suggests there is evidence of Fe^{3+} reduction and redistribution by organic acids and/or hydrothermal fluids following oxidative weathering (i.e., it is a mixed or 'M-type' paleosol). This claim was subsequently supported by Pan and Stauffer (2000). For context, a description of the Fe-Mn-Ti-Al geochemistry of the profiles studied by Holland et al. (1989) can be found in the supplementary materials section. If this hypothesis could be substantiated, drawing conclusions regarding the pO_2 of the atmosphere at the time of pedogenesis using redox element geochemistry would be more complicated. The new profile allows for a more detailed evaluation of the Fe geochemistry. In the following discussion, molar values for Fe^{2+} , Fe^{3+} and ΣFe , normalised to Al are used (Figure 10).

Demonstrating whether or not Fe is quantitatively retained in a weathering profile is the first step in evaluating the redox chemistry. As noted earlier, retention of Fe in the paleosol is evident from the correlation of Fe with Ti and Al, and the fairly constant molar $\Sigma\text{Fe}/\text{Al}$ ratio of 0.59 ± 0.07 (1σ SD), even with the immobile element offset. The C horizon and parent greenstone have variable $\Sigma\text{Fe}/\text{Al}$ (and Fe^{2+}/Al) values, but this variability is also expressed in the Al/Ti ratio, such that it is best explained by the heterogeneous distribution of Fe-Ti oxides (e.g., ilmenite and magnetite) in the greenstone. Likewise, many of the Fe/Ti trends in the profiles of Holland et al. (1989), which are crucial to the interpretation of Ohmoto (1996), are generated by variations in Ti concentration, not Fe. Thus, seafloor alteration of the parent rock is an important consideration when interpreting the Fe speciation data. Increase in the $\Sigma\text{Fe}/\text{Al}$ of a few sections of the A horizon may be related to minor Fe addition, possibly from lateral element redistribution. In light of the overall good correlation between

Fe and Al, the paleosol will be treated as closed system with respect to these elements in the following discussion.

Despite the variability in the parent greenstone, in the profile of this study and those from Holland et al. (1989) it is clear that the Fe^{2+}/Al decreases steadily upwards with an accompanying increase in Fe^{3+}/Al . The antithetic relationship of Fe^{3+}/Al and Fe^{2+}/Al is expected if the Fe^{2+} released during weathering of the greenstone is converted to Fe^{3+} oxides prior to removal in solution, resulting in the near-complete retention of Fe. The oxidation of Fe^{2+} reached to at least the base of the B horizon (depth of 350 cm). In the B and A horizons, the trend in the Fe speciation data, including the remaining variability, closely follows the colour changes in the paleosol reflected by the phyllosilicate and Fe oxide mineralogy and the spheroidal weathering textures. The zones of lower Fe^{2+}/Al (and $\Sigma\text{Fe}/\text{Al}$) in the A horizon, are correlated with lower Mn and Mg, and enrichments in K and Na. This is best explained by pedogenic Fe oxides in spheroidal weathering rinds, which become increasingly separated from the mica-rich matrix between the rinds.

In M-type paleosols, a loss of Fe^{3+}/Al is expected at the top of a profile with enrichment in Fe^{2+}/Al at greater depths (Ohmoto 1996). In the uppermost samples of the new profile (depth of 20 to 0 cm), the Fe^{2+}/Al decreases slightly along with the $\Sigma\text{Fe}/\text{Al}$, although the Fe^{3+}/Al does not record the same depletion. There are no apparent enrichments in Fe^{2+}/Al that can be attributed to the reduction of Fe oxides higher in the profile. Hydrothermal alteration has affected the Flin Flon paleosol (e.g., tourmaline near the unconformity contact), although if it had a strong control on modifying the Fe distribution of the profile, consistent and larger-scale depletion of Fe^{3+}/Al and $\Sigma\text{Fe}/\text{Al}$ values would be expected along the unconformity contact.

In summary, variations in the Fe redox trends support the conclusions of Holland et al. (1989) and can be attributed to the distribution of Fe-Ti oxides in the altered greenstone (Holland et al. 1989; Holland and Rye 1997) and the natural complexities of pedogenesis, such as spheroidal weathering. The $\Sigma\text{Fe}/\text{Al}$ is fairly constant in the paleosol and does not differ significantly from the parental greenstone value. Therefore, the Flin Flon paleosol remains one of the oldest preserved weathering profiles showing clear evidence for near-complete Fe retention as a result of oxidative weathering (i.e., an 'O-type' paleosol of Ohmoto, 1996).

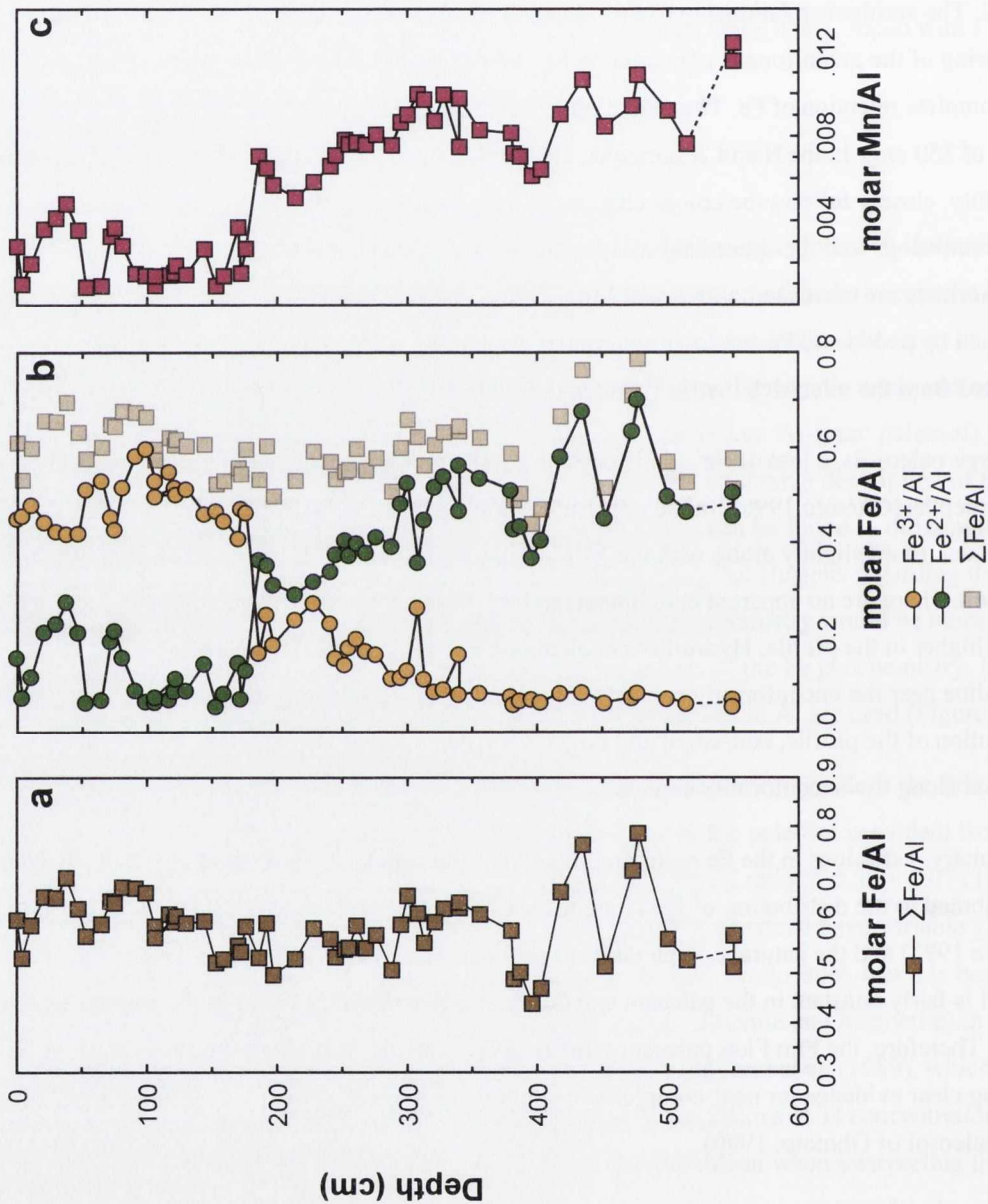


Figure 10: Molar ratios of Fe and Mn normalised to Al divided into a) total Fe ($\Sigma\text{Fe}/\text{Al}$), b) Fe^{2+}/Al and Fe^{3+}/Al , and c) Mn/Al . The $\Sigma\text{Fe}/\text{Al}$ data are also shown in b) as faded squares. The parent greenstone values from this study are plotted arbitrarily at a depth of 550 cm.

5.5.2 Fe behaviour in other Paleoproterozoic Paleosols

Temporal trends in Fe geochemistry of Paleoproterozoic paleosols are interpreted to record the transition from an anoxic to oxic atmosphere. Paleosols older than 2.3 Ga show Fe loss and those younger than 2.2 Ga show Fe retention (e.g., Rye and Holland 1999 and the references therein; Murakami et al. 2011). The ca. 2.2 Ga Hekpoort paleosol apparently formed during this transition and has a more complicated Fe speciation profile (e.g., Yang and Holland 2003; Driese 2004), with Fe-enriched and Fe-depleted zones (e.g., Figure 9b). Yang and Holland (2003) have interpreted this behaviour to reflect weathering in the presence of O₂, but at insufficient levels required to retain all Fe liberated from the weathered greenstone. The competing hypothesis, however, interprets the Hekpoort paleosol as a groundwater laterite, which would imply a highly oxic weathering environment and the possibility of a significant terrestrial biomass (e.g., Beukes et al. 2002). Both of these interpretations remain valid at present (Driese 2004). Regardless, all younger paleosols (e.g., Wiggering and Beukes 1990; Holland and Beukes 1990) exhibit a greater degree of Fe retention and appear to support the notion of an increasingly oxygenated atmosphere from 2.2 to 1.9 Ga. Recently, Polat et al. (2012) discovered a new ca. 1.9 Ga paleosol developed on Archean metabasalt. This paleosol is heterogeneously developed, thus making it difficult to study the full chemical weathering progression, but Fe oxide formation and Cr isotope values (Polat et al. 2012; Frei and Polat 2013) suggest that weathering occurred under an oxic atmosphere.

5.5.3 Mn behaviour

The concentration of Mn is highly correlated with Fe²⁺ and the Mn/Al ratio decreases upward in the profile in parallel with Fe²⁺/Al (Figure 10). This suggests that both elements were originally hosted in the same mineral (chlorite), but unlike Fe, Mn was lost from the profile prior to oxidation (Holland et al. 1989). Decoupling of Fe and Mn behaviour is also evident in other Paleoproterozoic paleosols (e.g., Yang and Holland 2003) and is most commonly attributed to Mn²⁺ oxidation being kinetically more sluggish than Fe²⁺ oxidation (e.g., Morgan 2005). Removal of Mn by reducing fluids during post-weathering alteration (e.g., metasomatism) is not a viable explanation since this would have also affected the Fe chemistry and mineralogy of the profile. Whether Mn was lost or retained is very significant since Mn oxides are important for the cycling of many of the other redox-sensitive elements during pedogenesis, such as Cr (e.g., Bartlett and James 1979; Fendorf and Zasoski 1992; Oze et al. 2007) and Ce (e.g., Koppi et al. 1996; Laveuf et al. 2008).

5.6 Overview of the Flin Flon paleosol

At the Missi outlier, the parent rock of the paleosol (depth of ~1000-1200 cm) is a subaqueous, hydrothermally altered greenstone that is similar in composition and mineralogy (chlorite + albite + epidote + calcite + quartz + Fe-Ti oxides $\pm$ mica) to the other mafic volcanic rocks in the Hidden formation of the Flin Flon arc assemblage. The greenstone was exposed to subaerial weathering at ca. 1.85 Ga and a deep weathering profile developed. In the deepest part of the profile that was sampled (C horizon: 350-515 cm), chemical and mineralogical variability from the seafloor alteration of the greenstone are prevalent. Obvious outcrop-scale physical weathering features are difficult to identify, although the amount of visible chlorite is higher than in the parent greenstone. At the thin section scale, however, it is clear that epidote and calcite are absent, albite is rare, and secondary dolomite, interpreted to be pedogenic, are present in the horizon. These features are interpreted to reflect deep weathering reactions and indicate that the depth of weathering extends beyond the 5 m profile, but seemingly not below 10-12 m (e.g., Stauffer 1990). The concentration of Fe and Mg in the C horizon is similar to the parent rock and indicates that they were only minimally affected by deep weathering reactions. The transition from the C horizon into the B horizon (183-350 cm) is placed at the first appearance of spheroidal weathering features and the progressive upward loss of dolomite and chlorite, which is accompanied by a decreasing concentration of Ca, Mg, Mn, and Fe^{2+} . The colour of the paleosol transitions to a bluish-maroon colour and mixed-layer clay/illite and hematite increase in modal abundance. The start of the A horizon (0-183 cm) is rather abrupt and is marked by the disappearance of secondary dolomite. This horizon is dominated by quartz, micas, and Fe oxides. The loss of Mg, Mn, and Fe^{2+} continues to the unconformity with variation attributed to spheroidal weathering. The majority of K and Na was almost certainly removed from the greenstone at this stage as well. The depletion of mobile elements (Ca, Mg, Mn^{2+} , Fe^{2+}) is substantial, but the behaviour of Al and Si indicates that advanced stages of weathering were not reached.

During weathering of the greenstone, chlorite probably converted to 2:1 layer (e.g., smectite or vermiculite) or mixed-layer clays (e.g., Johnson 1964; Adams and Kassim 1983; Carnicelli et al. 1997; Murakami et al. 1996; Banfield and Murakami 1998) initially, in addition to Fe oxides. The extent of alkali element loss suggested by the chemistry of the upper paleosol (prior to burial/metasomatism), could indicate that kaolinite also formed during weathering. Oxidative weathering resulted in complete retention of Fe, which is evident from secondary Fe oxide formation within chlorite and dolomite (B horizon) and in distinct spheroidal weathering rindlets. During the weathering of chlorite, there was sufficient O_2 to apparently oxidise and retain Fe^{2+} in the profile, but not Mn. This is best explained by

the rate of Mn removal exceeding the kinetic threshold of Mn^{2+} oxidation to a Mn^{3+} or Mn^{4+} phase (Pinto and Holland 1988; Yang and Holland 2003).

Following subaerial weathering, the weathering profile was buried by continental sediments of the Missi Group, which resulted in erosion and reworking of the regolith. Subsequent regional metamorphism and metasomatism influenced the preserved paleosol in a number of ways. Most notably, Na and K were re-introduced to the profile and reacted with pedogenic clays to generate the preserved assemblage of mixed-layer clay/illite (e.g., Fedo et al. 1995) and white micas (e.g., Li et al. 1994; Livi et al. 2008) during prograde metamorphism. Holland et al. (1989) proposed that the alkali elements were derived from the arkosic sandstones and conglomerates of the Missi Group. Metamorphism of deep pedogenic clays back to chlorite may have occurred (e.g., Inoue and Utada 1991; Ambers 2001), accounting for its higher abundance in the vicinity of the profile in comparison to other areas of the Hidden formation. Hydrothermal fluid movement along the unconformity contact resulted in the formation of tourmaline and possibly minor lateral re-distribution of elements.

6. Conclusions

A new profile through the Flin Flon paleosol was sampled at a much higher density than in previous studies. The mineralogical and chemical progression in the new profile is similar to other sampled localities of the paleosol (Goetz 1980; Holland et al. 1989; Pan and Stauffer 2000). The high sampling density in this study, however, has revealed the presence of an immobile element ratio offset in the profile that coincides with the appearance of secondary dolomite (the transition between the A and B horizons). This could indicate the presence of separate parent rocks in the profile or the addition of allochthonous material, although unravelling the exact cause and significance of the offset requires further work. The offset is most prominent in the minor elements and it appears that the original concentration of the major elements in the parent rock on either side of the boundary was similar. Many physical pedogenic features (corestones, Fe oxide rindlets) and the weathering signature of Ca, Mg, Mn, and Fe^{2+} loss have survived subsequent alteration events.

The high sampling density has helped to link the mineralogy of the profile with the major element chemistry variations. The mineral assemblage of the parent greenstone contrasts with unaltered mafic rocks and this has resulted in weathering trends in the paleosol that differ from modern weathering profiles. This is an important consideration when studying the geochemical evolution of paleosols. The

loss of mobile elements from the profile is tightly coupled with the loss of carbonate and chlorite. As a result, weathering indices that include Ca and the mafic elements (Mg and Fe) appear to be most effective for modelling mobile element trends in mafic paleosols.

Perhaps the most important aspect of the Flin Flon paleosol is the behaviour of the redox-sensitive elements Fe and Mn. The well-defined Fe speciation trends in the new profile confirm that it is the oldest known weathering profile that exhibits complete Fe retention via oxidative weathering. By contrast, Mn^{2+} was apparently not oxidised during pedogenesis and lost from the profile. This may have significant implications for understanding the cycling of trace metals in the paleosol.

Further insight into the paleosol development, such as the significance of the immobile element offset and secondary dolomite, better unravelling the post-weathering enrichment of elements, and more specific atmospheric and climatic information is anticipated with additional geochemical investigation (stable isotopes, paleo-redox and biomarker trace elements).

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Chapter 5 Appendix

Parent greenstone composition

The concentration of many elements in the parent greenstone is variable due to the seafloor alteration and metamorphism that occurred prior to subaerial weathering. In order to account for some of the variability in the greenstone composition, a mean composition (Table A1) was calculated from the parent rock samples of this study and those published previously from the area of the Missi outlier (Goetz 1980; Holland et al. 1989; Pan and Stauffer 2000). Each of these samples is at least 10 m below the unconformity contact. An average composition of the Hidden formation volcanic rocks, based on data for all of the sub-divided members (Reservoir, Stockwell, Carlisle Lake; DeWolfe et al. 2009) is also reported in Table A1.

Chemical weathering indices

The following chemical weathering indices were used to quantify mobile element loss from the Flin Flon paleosol: the “chemical index of alteration” (CIA: Nesbitt and Young 1982; Fedo et al. 1995); CIA minus K (CIA-K: Maynard 1992) which is equivalent numerically to the “chemical index of weathering” (CIW) (Harnois 1988); the “plagioclase index of alteration” (PIA: Fedo et al. 1995); the “mafic index of alteration” ($MIA_{(O)}$; Babechuk et al., in press); and, the CALMAG index (Nordt and Driese 2010) as listed below. The MIA was proposed recently by Babechuk et al. (in press) to consider the behaviour of Mg and Fe in addition to Al, Ca, Na, and K. Magnesium (molar MgO) is added to the mobile elements along with Ca, Na, and K, whereas Fe is allocated to the immobile elements (along with Al) or the mobile elements depending on its redox behaviour. This results in two different variations of the index. Since Fe is conserved in the Flin Flon paleosol, the oxidative weathering variation of the MIA [$MIA_{(O)}$] is used.

Each of the chemical weathering indices was calculated using the moles of the major element oxide. For all indices in this study, CaO was corrected for apatite [$CaO^* = CaO - (10/3 \times P_2O_5)$] but not carbonate for reasons explained in the text. This correction was carried through all subsequent molar weathering indices.

$$CIA = [(Al_2O_3)/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$$

$$CIA-K = [(Al_2O_3)/(Al_2O_3 + CaO^* + Na_2O)]$$

$$\text{PIA} = [(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O})]$$

$$\text{CALMAG} = [(\text{Al}_2\text{O}_3) / (\text{Al}_2\text{O}_3 + \text{MgO} + \text{CaO}^*)]$$

$$\text{MIA}_{(O)} = [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(T)}) / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(T)} + \text{MgO} + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})]$$

$$\text{MIA}_{(O)}\text{-K} = [(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(T)}) / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_{3(T)} + \text{MgO} + \text{CaO}^* + \text{Na}_2\text{O})]$$

Appendix Table 1: Average parent greenstone and Hidden formation composition

	Parent greenstone ^a		Hidden Formation ^b	
	mean	± (1σ SD)	mean	± (1σ SD)
SiO ₂	49.68	4.42	51.03	3.16
TiO ₂	0.67	0.17	0.63	0.14
Al ₂ O ₃	15.18	0.84	15.97	1.75
Fe ₂ O _{3(T)}	12.68	1.82	12.89	1.82
FeO	9.59	1.50		
MnO	0.21	0.05	0.20	0.03
MgO	5.42	1.23	4.87	0.85
CaO	7.59	3.85	8.18	1.88
Na ₂ O	2.13	1.12	3.25	0.59
K ₂ O	0.92	0.77	0.48	0.42
P ₂ O ₅	0.15	0.12	0.11	0.06
LOI	8.86	1.91	2.24	0.96
CIA	48	10	44	3
MIA _(O)	43	5	43	3
CALMAG	36	5	37	4

^aMean of 8 samples (5 for LOI): FF021-FB1, FF021-FB2 (This study); FF6, FF7 (Goetz 1980); 85 ZH-122, 85 ZH-123, 85 ZH-133 (Holland et al. 1989); P2-4 (Pan and Stauffer 2000)

^bMean of 41 samples for the Stockwell, Reservoir, and Carlisle Lake members of the Hidden formation (DeWolfe et al. 2009)

Chapter 5 Appendix references

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Chapter 5 supplementary information

1. The Missi Outlier and the new paleosol profile

1.1 Background and description

The study of Holland et al. (1989) focused on the southwestern end of the Missi outlier since it appeared least-affected by deformation and exposes several exceptionally well-preserved subaerial weathering features. This exposure is now protected, but for comparison with the new profile, the original site was photographed and mapped at a scale of 1:100. A photomosaic of the outcrop is presented in Figure S1 with the corresponding sketch map in Figure S2. Photographs of several key features of the paleosol are presented in Figure S3 with their approximate locations identified in Figure S2.

The new map of the original exposure adopted the maroon and green paleosol colour division described in previous studies. In general terms, the greenstone appears more chloritised in the vicinity of the unconformity relative to typical Hidden formation volcanic rocks. This is likely related to deep chemical weathering of the greenstone. The depth to which the greenstone was modified by subaerial weathering was often difficult to establish precisely and appears to vary along the unconformity. Moving upwards towards the unconformity, the abundance of maroon coloured paleosol increases, but is restricted to patches between large corestones initially. These corestones contain few exfoliate (rindlet) layers at their margins and appear to lack tectonic alignment or flattening. As noted by Holland et al. (1989), the corestones are often the remnant centre of pillows, indicating that the finer-grained, possibly glassy inter-pillow margins were attacked preferentially during subaerial weathering. In a few areas, a distinct transition between the maroon-dominated and green-dominated paleosol occurs (Figure S3), often within 2-3 metres of the unconformity contact. Corestones of the green paleosol are present within the upper, maroon paleosol (e.g., Figure S2; Figure S3c,e). These corestones are preserved in various stages of decay, but, in general, decrease in size towards unconformity contact with progressive rounding and increase in abundance of oxide-rich rindlets, much like modern spheroidal weathering (e.g., Patino et al. 2003; Buss et al. 2008). The most highly decayed (“ghost”) corestones are completely penetrated by many mm-sized rindlets (Figure S3d). A few of the larger corestones nearest the unconformity are rotated from their original orientation as a result of soft-sediment deformation during Missi deposition (Figure S3e). Furthermore, in certain areas physical reworking of the paleosol within the sandstone is evident, including features such as rip-up clasts (Figure S3f). The sandstone in direct contact with the underlying paleosol is arkosic, medium- to coarse-grained, fines upward overall, and contains mappable pebble beds throughout (Figure S2). The sandstone is succeeded by a conglomerate layer



Figure S1: Photomosaic of the southwestern edge of the Missi outlier (location of Profile #1 in Holland et al. 1989). A higher resolution of the photomosaic can be obtained from the first author upon request.

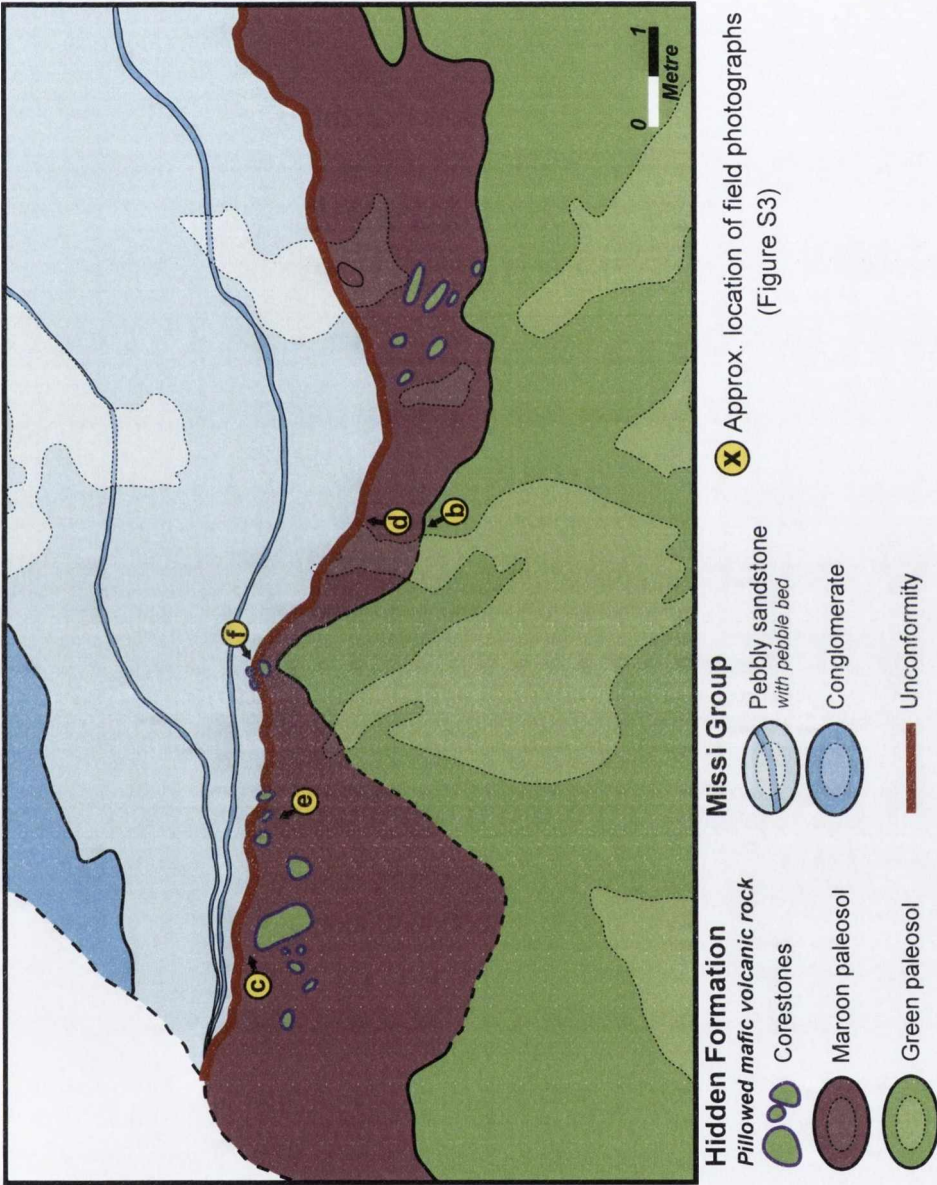


Figure S2: Sketch map of the same area as Figure S1, including scale and showing the location of additional field photographs in Figure S3.



Figure S3: a) Pillowed greenstone of the Hidden formation (parent rock of the paleosol); b) Transition from green paleosol to maroon paleosol; c) Green corestones of various sizes within the maroon paleosol; d) Highly decayed ‘ghost’ corestones within the maroon paleosol (note the thin quartz vein cross-cutting the paleosol); e) Green corestones near the unconformity, with one showing clear evidence of rotation from its original position during Missi deposition; f) Inclusion of maroon regolith within the Missi sandstone, indicative of physical reworking during erosion at the time of Missi deposition. For scale: the marker is 13.5 cm, the scale card is 8.5 cm long (with 1 cm divisions), and the distance from yellow cross to yellow cross is 100 cm.

that can be traced throughout the majority of the outlier. Within the Missi Group, clasts of weathered greenstone with maroon rims (i.e., corestones), similar to those in the upper maroon paleosol, are present several metres above the unconformity.

Although many of the subaerial weathering features are clearly identifiable, the area has not escaped the effects of the post-weathering polyphase deformation and metamorphism (Gale et al. 1999; Gibson et al. 2013; Lafrance et al. in press). In the southwestern map area of the Missi outlier (Figure S2, S3), the thickness of the maroon paleosol is highly variable, which appears to be dominantly a tectonic feature resulting from the intersection of the glacially polished outcrop with the polydeformed contact, namely refolding (D_5) of the steeply dipping contact generated by the F_4 syncline. In a few areas, the maroon paleosol appears to be in fault contact with the underlying apple green paleosol, indicating that the later deformation of the paleosol exploited areas of rheological contrast. Deformation is greater in the upper maroon paleosol, resulting in well-defined foliation and crenulated oxide rindlets and micas. In the high strain areas of the outlier, the paleosol is severely foliated and the regolith features are obscured. Small quartz veins, presumably related to later metamorphism, cross-cut the paleosol (Figure S3d) but are localised and do not obscure the overall remarkable preservation of the subaerial weathering features.

1.2 New paleosol profile

The location of the new paleosol profile is on the eastern edge of the Missi outlier. Originally, only a very small area ($\sim 0.5 \text{ m}^2$) of the maroon paleosol was exposed below the unconformity at this location. The remainder of the paleosol was covered beneath a layer of glacial till and soil in a small depression ($\sim 10 \text{ m}$) between the Missi Group to the west of the unconformity and the greenstone to the east (apparently, glacial movement and erosion had exploited the zone of soft regolith between). The soil and sediment infilling the valley was carefully excavated to avoid scouring the outcrop surface, exposing a new, full profile section through the paleosol. The outcrop was washed with water to remove mud, allow for description, and prepare it for geochemical sampling.

1.3 Sampling strategy

A channel $\sim 10 \text{ cm}$ wide was marked on the outcrop and subdivided into several 'sections' labelled from A-I, starting from the unconformity down to the visibly least-weathered greenstone. Only one offset in the continuity of the channel was necessary between sections A and B, although approximately 30 cm of overlap between each was taken to test for lateral homogeneity and link the full profile. A rock saw was used to cut the edges of the channel and a chisel and hammer were used subsequently to extract a series of 126 continuous, individual pieces of the paleosol. The dominant foliation was approximately parallel to the unconformity, causing the majority of samples to split out along parallel planes of varying size (e.g., from 10 cm down to 1 cm depth for an individual sample).

Each sample was washed, dried, labelled, and packaged at the field site. Sample names follow the scheme FF0201X-YYY, which represents the channel section (X: A-E) and the unique sample number (YYY) increasing from 001 to 125 with increasing depth in the profile. The final three profile sections F-I (YYY: “LWB”) were extracted from the centre of visibly least-weathered pillows at the base of the profile. In some cases, adjacent smaller samples were recombined during laboratory processing to ensure a more homogeneous representation. By contrast, the sample FF021C-098 is divided into two smaller sub-samples which represent the maroon paleosol (FF021C-098M) around the centre of green corestone (FF021C-098G). These samples were not shown in most depth profile figures. Sampling of the profile was terminated at a depth of just over 500 cm since the pillows in the lowest part of the profile (>450 cm depth) did not display visible evidence of weathering. The depth of each sample represents the distance below the unconformity on the outcrop surface, measured at a right angle from the unconformity contact. Thus, they are not ‘true’ depths. In addition to the profile, two samples (FF021-FB1 and FF021-FB2) were extracted from the cores of pillows in a nearby outcrop to represent the unweathered parent greenstone. The estimated depth below the unconformity for these samples is 1000-1200 cm.

*Note: the data are continuous for most elements across the overlap between the offset sections A and B in the profile (samples FF021A-037 to FF021B-043), indicating that the major element chemistry can be confidently linked as one full profile and that lateral heterogeneity was minimal at that depth range.

2. Bulk rock X-Ray diffraction patterns

A total of 19 samples covering the profile were selected for qualitative X-ray diffraction (XRD) analysis. All patterns were collected on dry, untreated powders. No attempt at detailed phyllosilicate analysis (e.g., ethylene glycol treatment or heating) was made. The XRD measurement was performed at the Central Analytical Facility (CAF) at Laurentian University (Sudbury, Ontario, Canada) with a Phillips PW 1729 X-ray diffractometer operated at 40 kV/30 mA using Fe filtered Co K α radiation. The powders were scanned from 5° to 75° (2 θ) with a step-size of 0.02° and a dwell time of 2 s at each step. Phase identification was performed using PANalytical’s X’Pert HighScore.

On the following pages, the bulk powder XRD patterns of different samples of the Flin Flon paleosol are reported as the relative intensity (I/I_0) vs. 2 θ angle (Co K α). The XRD patterns are divided into the lower paleosol (Figure S4 – FF021-FB1 to FF021B-061: depth of 183 cm and greater, i.e., B and C horizons) and the upper paleosol (Figure S5 – FF021B-061 to FF021A-001: unconformity to a depth of 183 cm, i.e., A horizon). Note that the sample FF021B-061 is the dark-grey mineral band in the profile and is reported on both figures to connect the two parts of the paleosol.

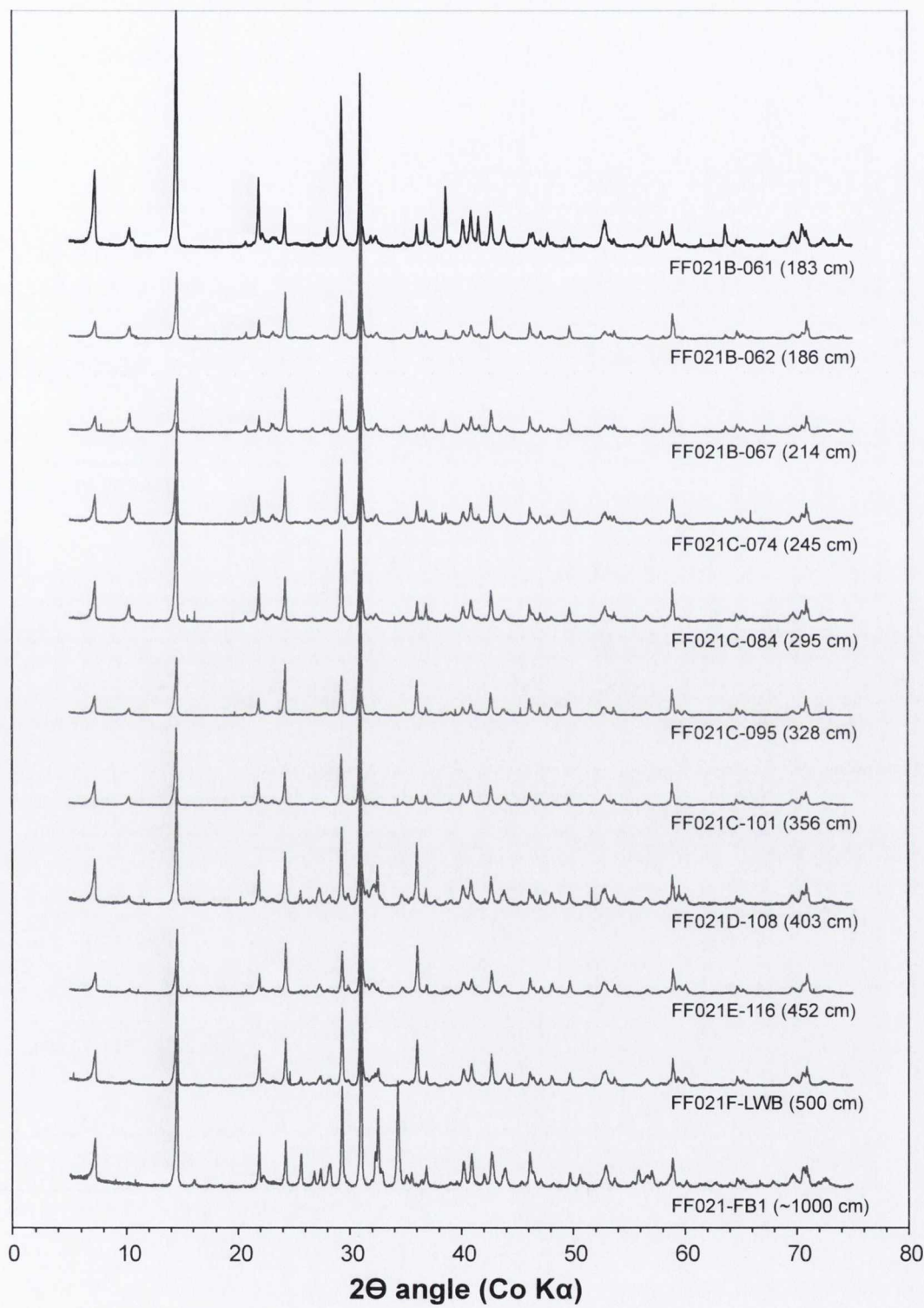


Figure S4: X-ray diffraction patterns for lower (B and C) paleosol horizons.

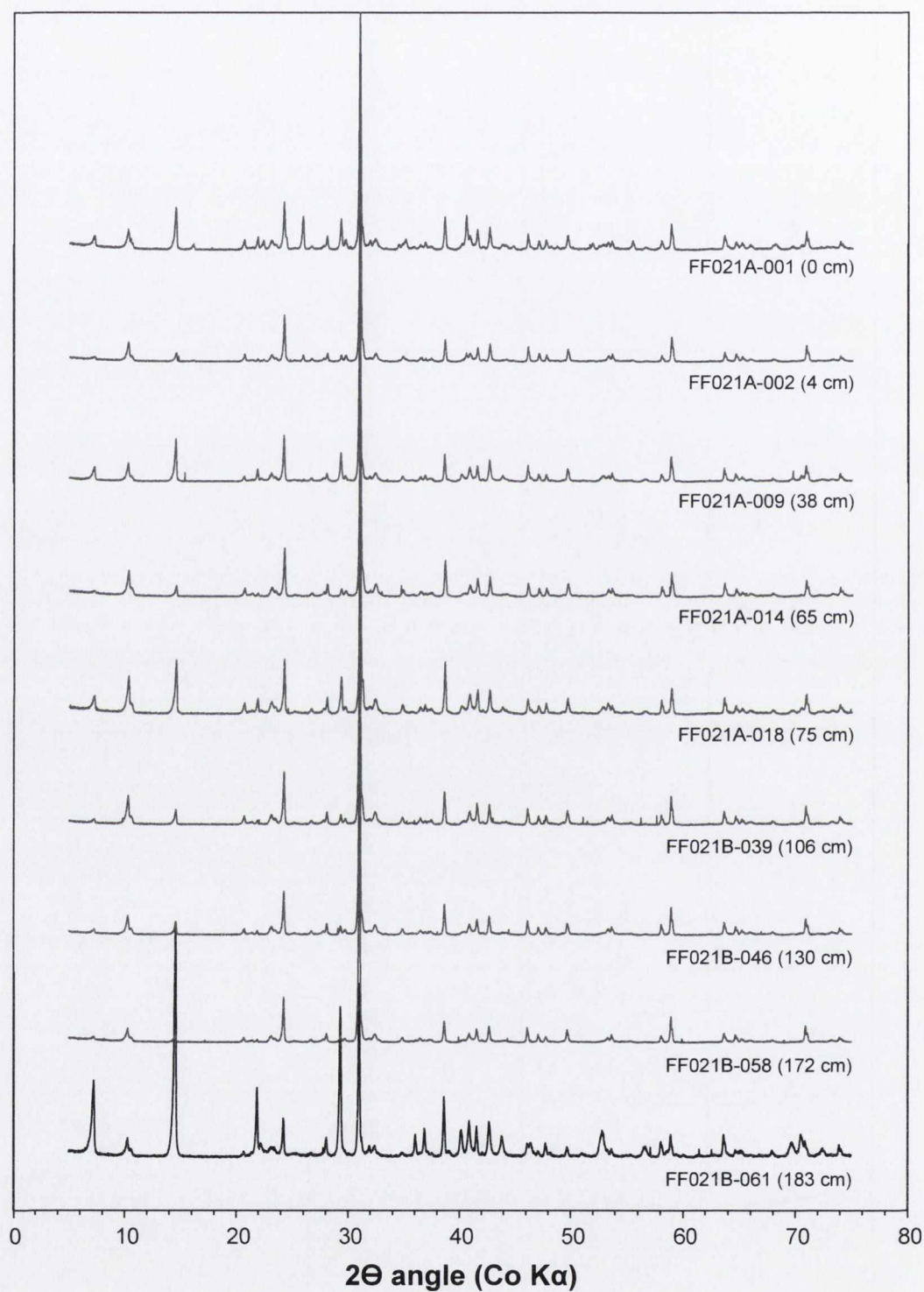


Figure S5: X-ray diffraction patterns for upper (A) paleosol horizon.

3. Microscopy

The following pages contain thin section scans, photomicrographs, and SEM images that illustrate the main mineralogical and micro-scale weathering characteristics of the paleosol profile (Figures S6-S9). Thin section photomicrographs include plane polarised light (PPL) and cross polarised light (XPL) images.

Backscattered SEM images were acquired at the Centre for Microscopy and Analysis at Trinity College Dublin using a Tescan Mira XMU field emission SEM at 20.00 kV. Qualitative energy dispersive spectroscopy was used to identify unknown minerals and approximate element ratios in minerals.

4. Additional geochemical plots and discussion

4.1 Calcium and phosphorus in the A horizon

Nearly all of the Ca in the B and C horizons is hosted in dolomite and the majority of Ca in the parent greenstone is in calcite. In the A horizon, however, there is very little carbonate present and Ca concentrations are very low. A plot of CaO wt. % vs. P₂O₅ wt. % for these samples, however, reveals that the remaining Ca is present in apatite (Figure S10). A reference line for apatite with CaO wt. % of ~55 and P₂O₅ wt. % of ~42 is shown.

4.2 Mg-Mn-Fe²⁺

The concentrations of Mg, Mn, and Fe²⁺ are correlated in the profile (Figure S11). This indicates that they were hosted predominantly in the same minerals and exhibited a similar bulk weathering behaviour. A reference line for the mean chlorite composition reported by Holland et al. (1989) is shown in Figure S11. In general, the samples in the A horizon plot closer to the composition of chlorite compared to the samples of the B and C horizons, suggesting that the elements are distributed between a different minerals in the latter (e.g., dolomite, Fe-Ti oxides).

4.3 K and Na metasomatism

In the C horizon of the profile, there is significant variation in the concentration of K and Na, which is attributed predominantly to pre-weathering seafloor alteration. In the A and B horizons, however, the two elements are highly correlated ($r^2=0.952$) and increase smoothly in concentration towards the

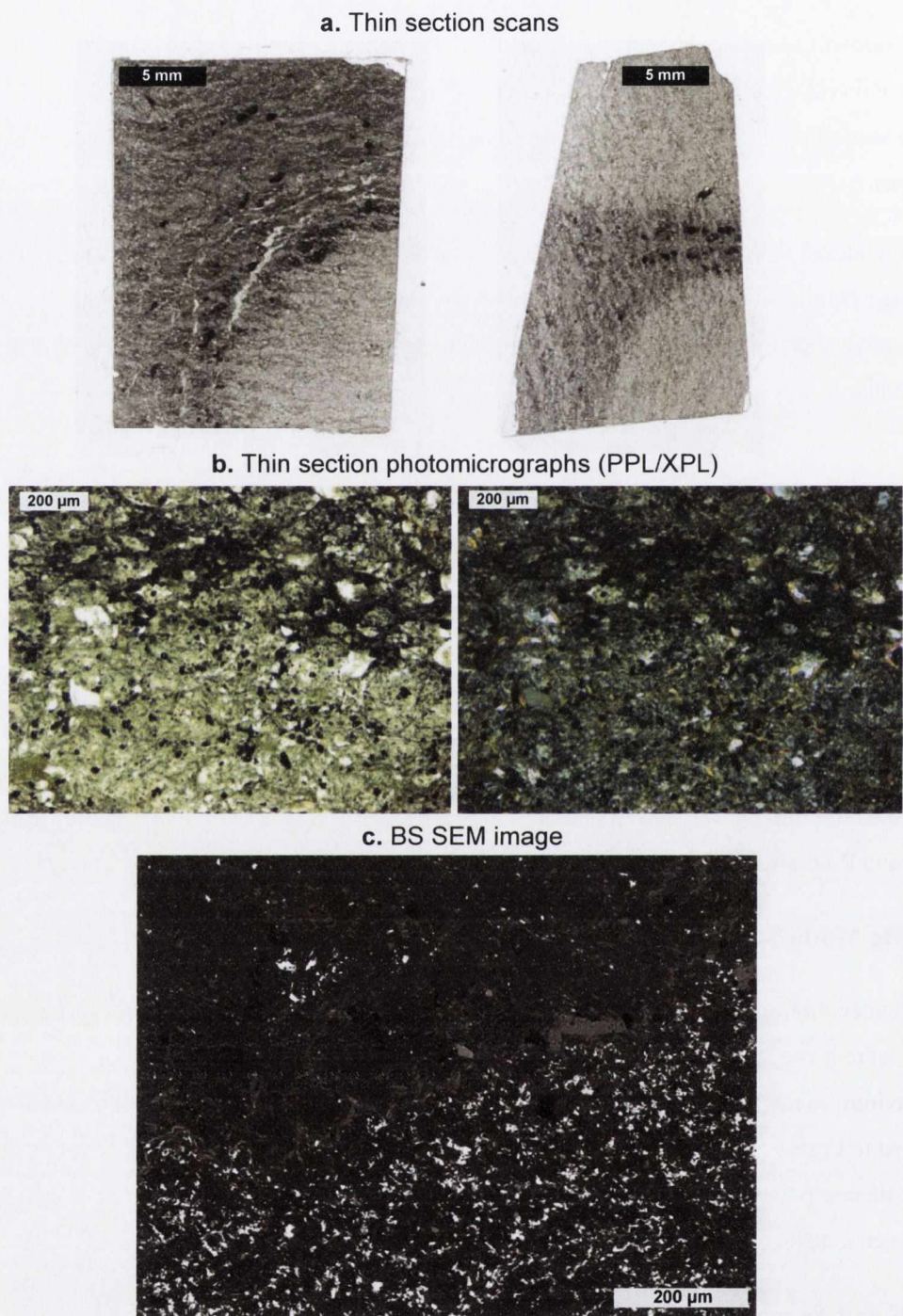
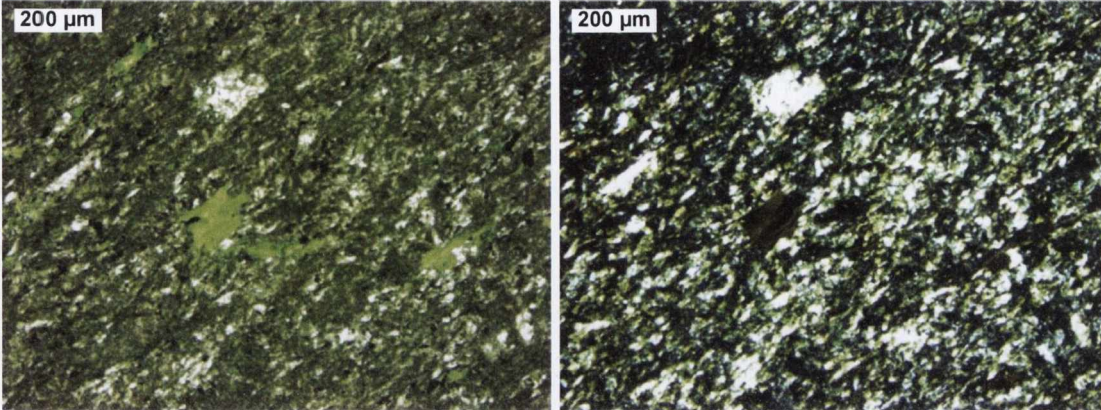
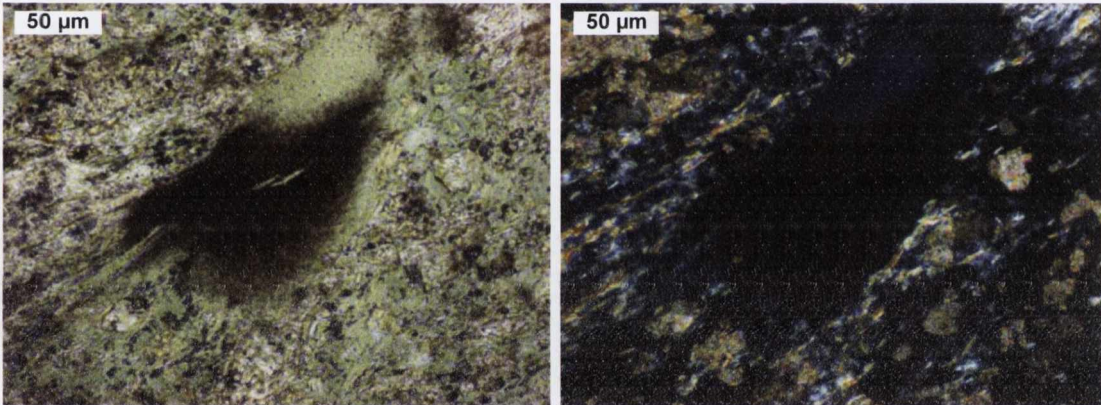


Figure S6: Micro-scale spheroidal weathering features in sample FF021A-020 (depth of 81 cm). Green corestone with darker coloured (maroon) paleosol and concentric oxide rindlets surrounding it. The paleosol surrounding the corestone can be identified with a greater abundance of Fe oxides (darker in thin section, brighter in SEM).

a. FF021-FB1 (Depth of ~1000 cm)



b. FF021C-081 (Depth of 276 cm)



c. FF021C-074 (Depth of 245 cm)

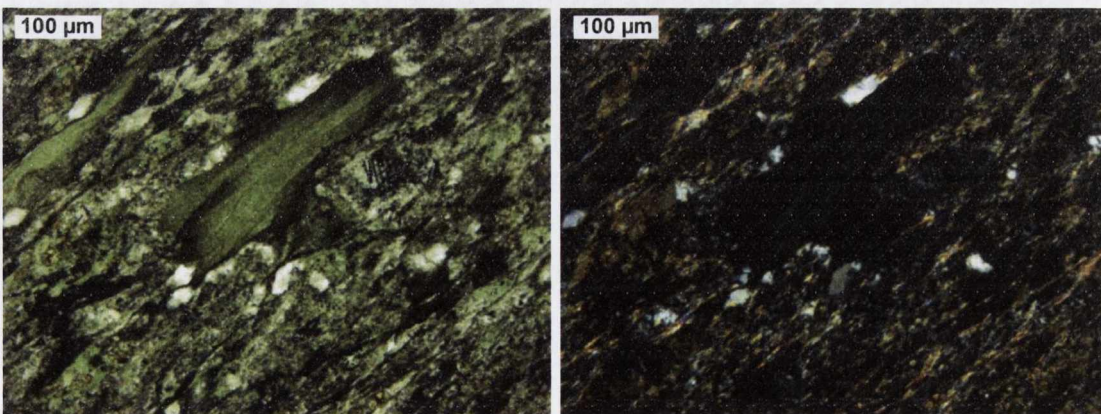


Figure S7: Photomicrographs (PPL/XPL) of the paleosol at different depths illustrating the oxidation of Fe^{2+} in chlorite to opaque Fe oxides. This is most evident in coarser chlorite grains. Note also the higher order interference colours of clays and the presence of dolomite in the samples higher in the profile (b and c).

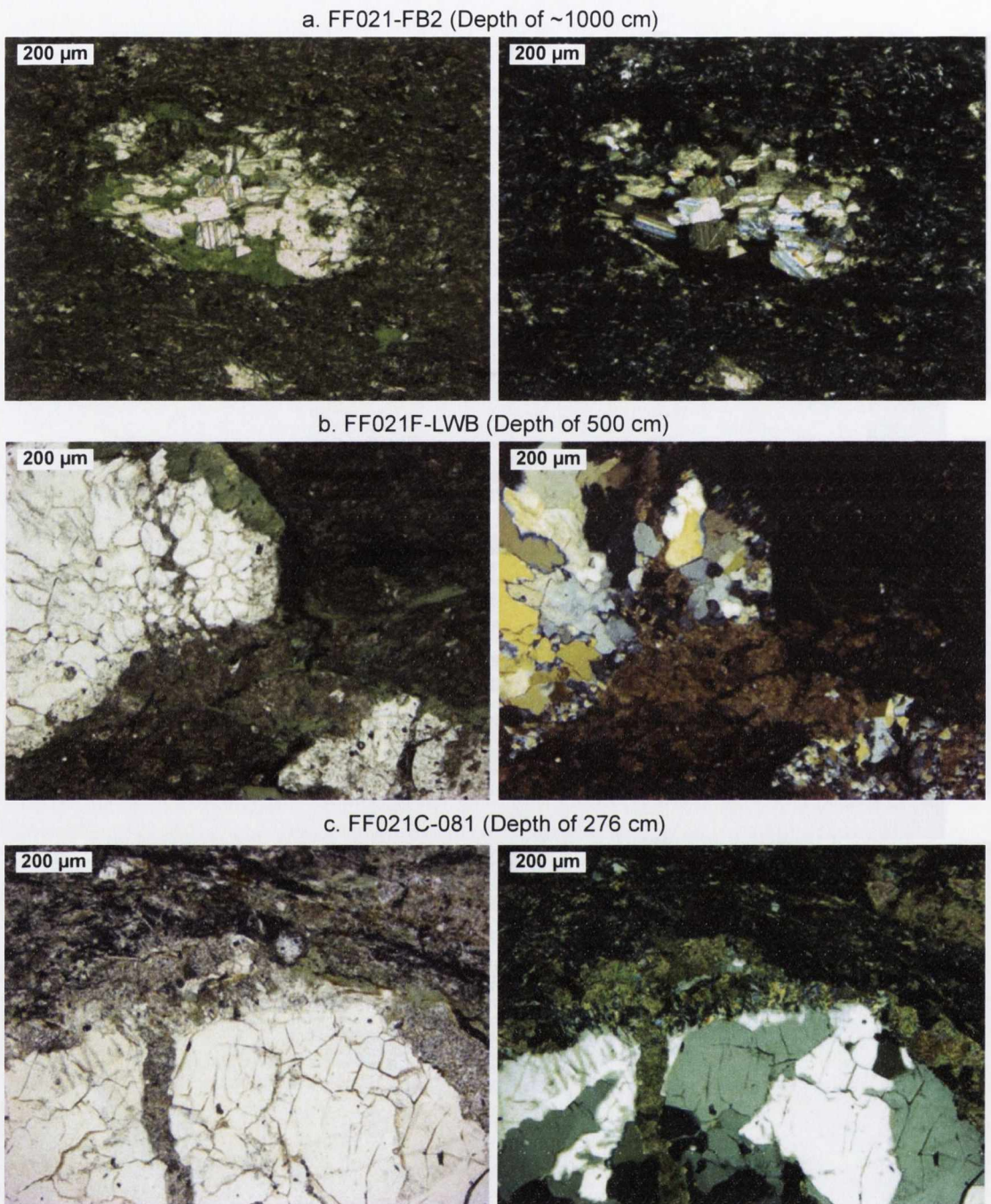


Figure S8: Photomicrographs (PPL/XPL) of the paleosol at different depths illustrating the different carbonate phases. Coarse calcite is prominent in the parent greenstone (a) but is absent in the profile. Instead, cloudy, fine-grained dolomite (b and c) is present in the C and B horizons and shows secondary accumulation features (eg., splitting and embaying amygdules). Carbonate is virtually absent in the profile above a depth of 183 cm (A horizon).

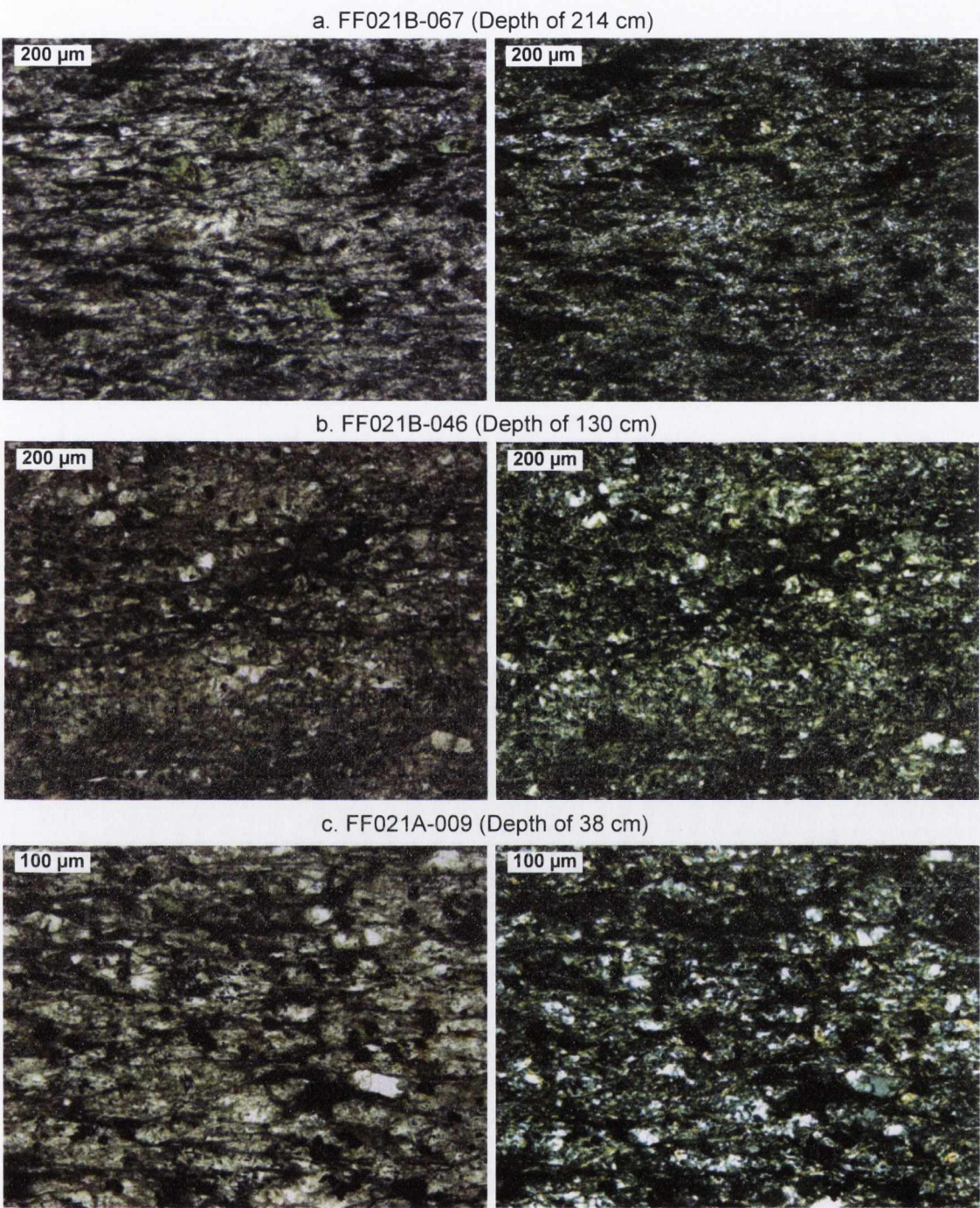


Figure S9: Photomicrographs (PPL/XPL) of the paleosol at different depths illustrating the evolution in phyllosilicate mineralogy. Moving upwards in the profile, the abundance of chlorite decreases and the abundance of finely crystalline mixed-layer clays (illite/chlorite) and mixed layer white mica (muscovite/paragonite) increases. Note also the foliation of the micas and the increasing abundance of Fe oxides higher in the profile.

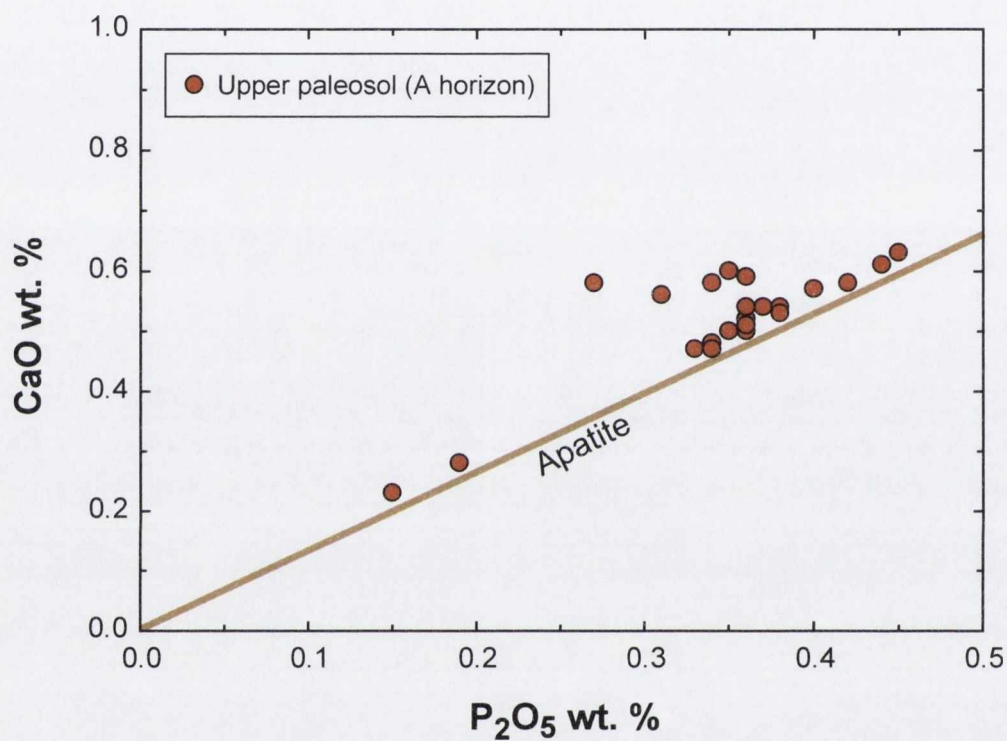


Figure S10: Correlation between CaO wt.% and P₂O₅ wt.% in the upper paleosol (A horizon) with reference line of stoichiometric apatite.

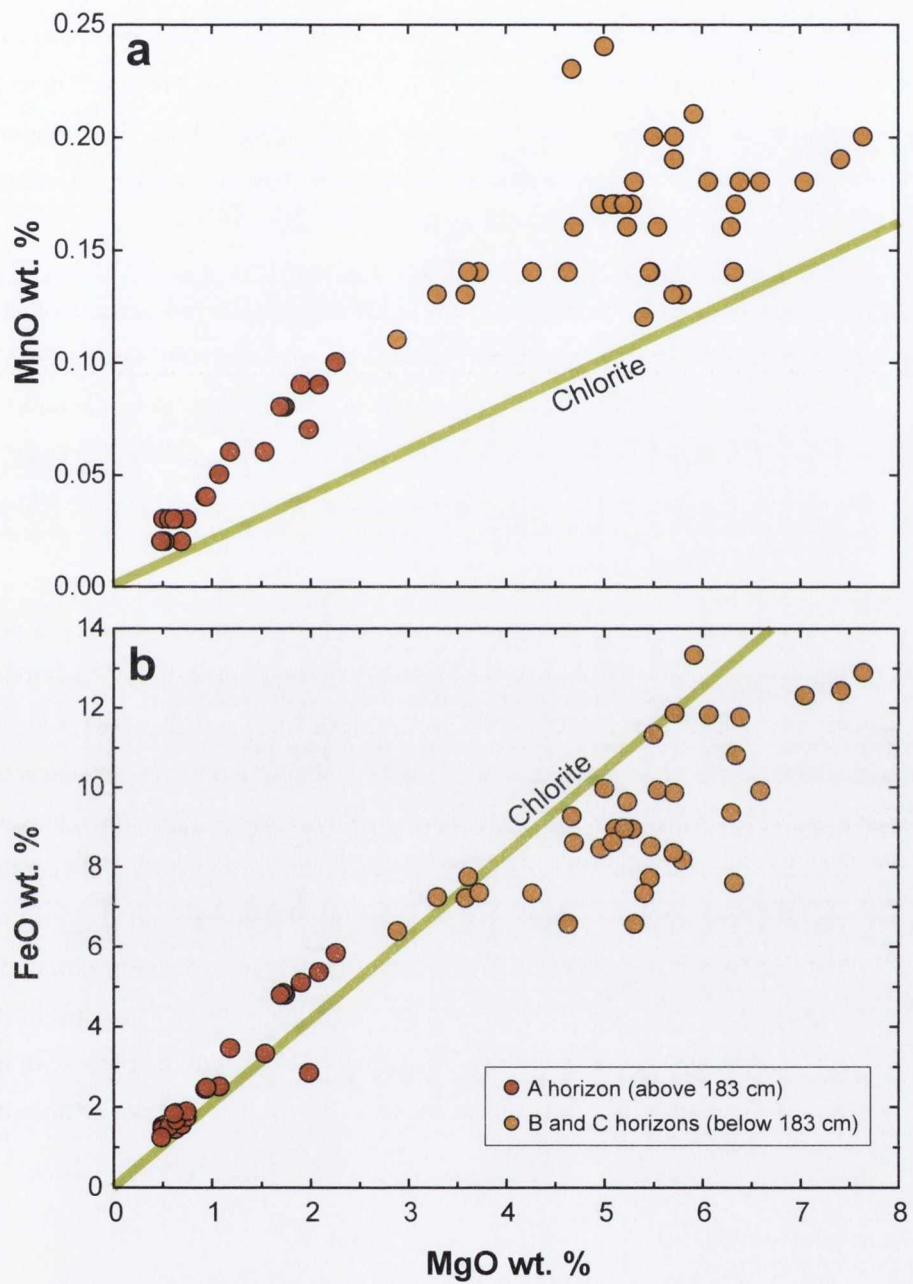


Figure S11: Correlations of MnO wt.% and FeO wt.% with MgO wt.% in all paleosol samples with reference line for chlorite composition reported in Holland et al. (1989).

unconformity (Figure S12; symbols are the same as Figure S11). This suggests that both elements were re-introduced to the profile during post-weathering alteration of the profile (e.g., metasomatism).

4.4 Comparison with other Hidden formation volcanic rocks

Our preferred interpretation is that the immobile element offset in the profile represents a more fractionated lava flow in the upper part of the profile, with a lower $\text{Al}_2\text{O}_3/\text{TiO}_2$ and higher Si, compared to the lower part of the paleosol, which belongs to a separate flow. The variation in the immobile elements is most prominently expressed in the minor elements, notably Ti, whereas ratios of Fe and Si to Al are more constant across the boundary.

In Figure S13, $\text{Fe}_2\text{O}_{3(\text{T})}$ - TiO_2 - Al_2O_3 - SiO_2 - P_2O_5 ratios in the paleosol are compared to other rocks in the Hidden formation of the Flin Flon arc assemblage (DeWolfe et al. 2009). The $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in both parts of the paleosol profile overlap with the other volcanic rocks. The high concentration of P and the high $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ratio in the upper part of the profile, however, significantly exceeds the values in unweathered Hidden formation rocks and may be related to a secondary P enrichment event.

The most important aspect of the presence of two lava flows in the profile is whether or not the original major element concentration was the same in both. In Figure S14, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios of the Hidden formation samples are plotted against the Fe_2O_3 , MgO, CaO, and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ concentrations. The broad trends in the plots suggest slightly lower Ca, Mg, Na, K, and higher Fe concentrations in rocks with a lower $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio, although there is significant scatter (possibly related to seafloor alteration). The overall concentration variation for these elements is not substantial over the range in the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of both flows in the paleosol (shown with shaded bars; upper with a ratio of 17.90 ± 0.40 and the lower with a ratio of 24.20 ± 2.00). For reference, the composition of the two parent greenstone samples (FF021-FB1/-FB2) is shown with stippled lines. Thus, it is likely that the major element concentration was similar for both prior to weathering. For the purpose of mass balance calculations it is assumed that this is the case, such that the paleosol can be treated as one full profile.

4.5 Mass balance profiles

For mass balance calculations, the open-system tau (τ) mass transport model (Brimhall and Dietrich 1987; Anderson et al. 2002) was used. In the τ model, the mass gain (positive value) or loss (negative value) of an element (j), at any point in the weathering profile (w) is calculated relative to the concentration (C) in the parent material (p) using an immobile index element (i) for normalisation:

$$\tau_{i,j} = [(C_{j,w}/C_{j,p})/(C_{i,w}/C_{i,p}) - 1]$$

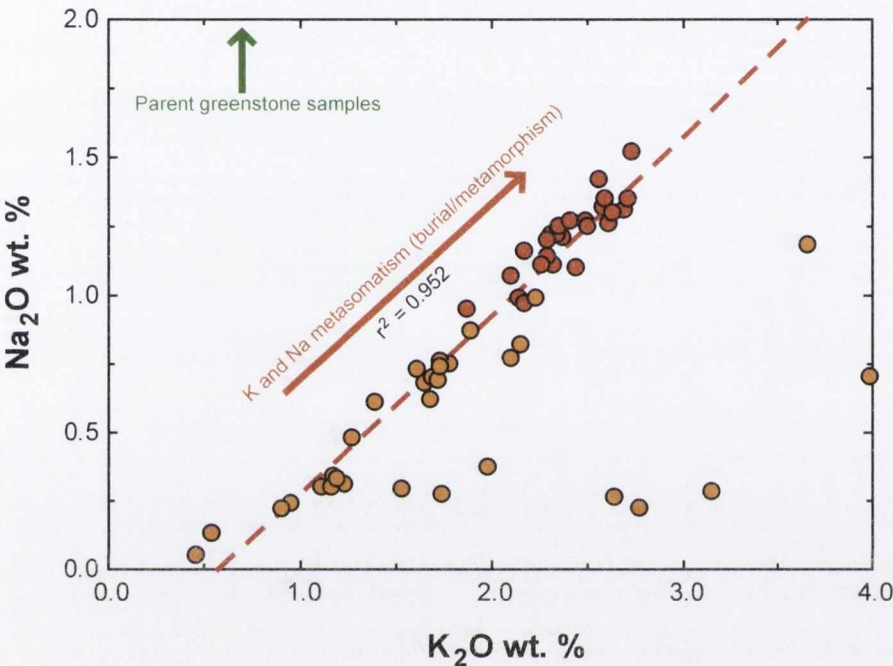


Figure S12: Correlation of Na₂O wt.% and K₂O wt.% in the paleosol. Note that the composition of the parent greenstone is outside of the plot.

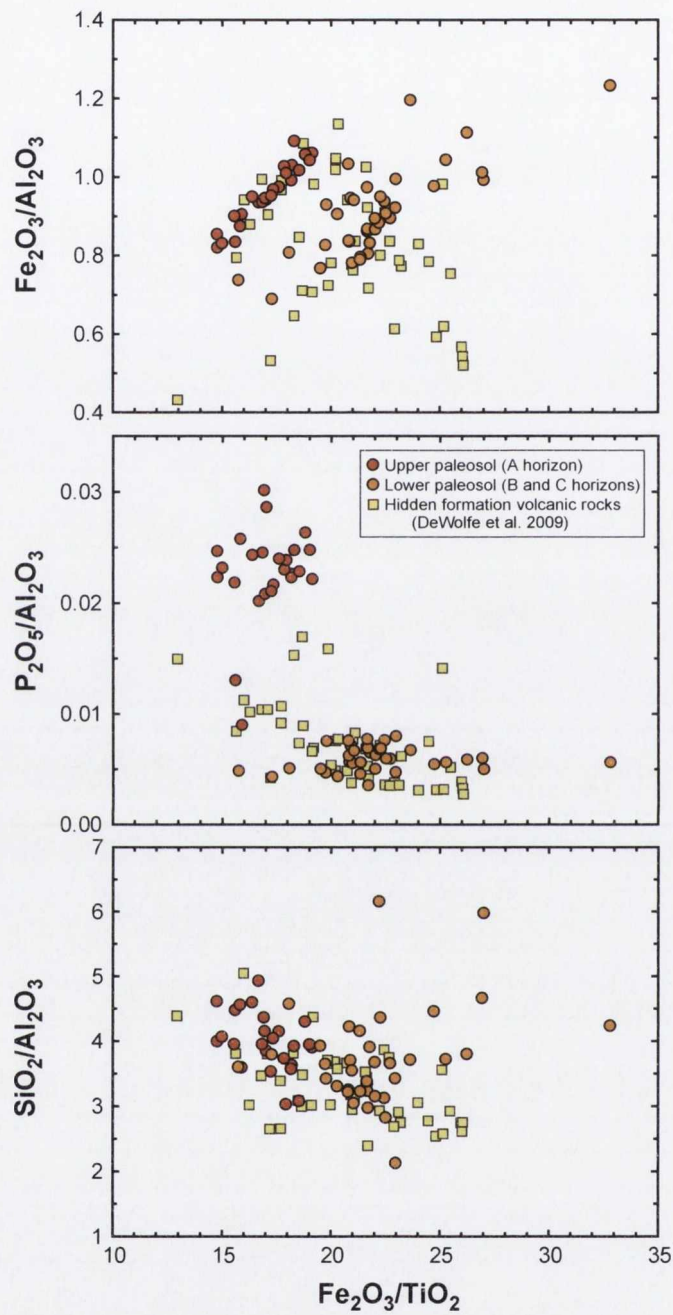


Figure S13: X-Y scatter plots of the mass ratio of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ vs. those of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$, and $\text{SiO}_2/\text{Al}_2\text{O}_3$ showing the upper and lower paleosol and unweathered samples of the Hidden formation from DeWolfe et al. (2009).

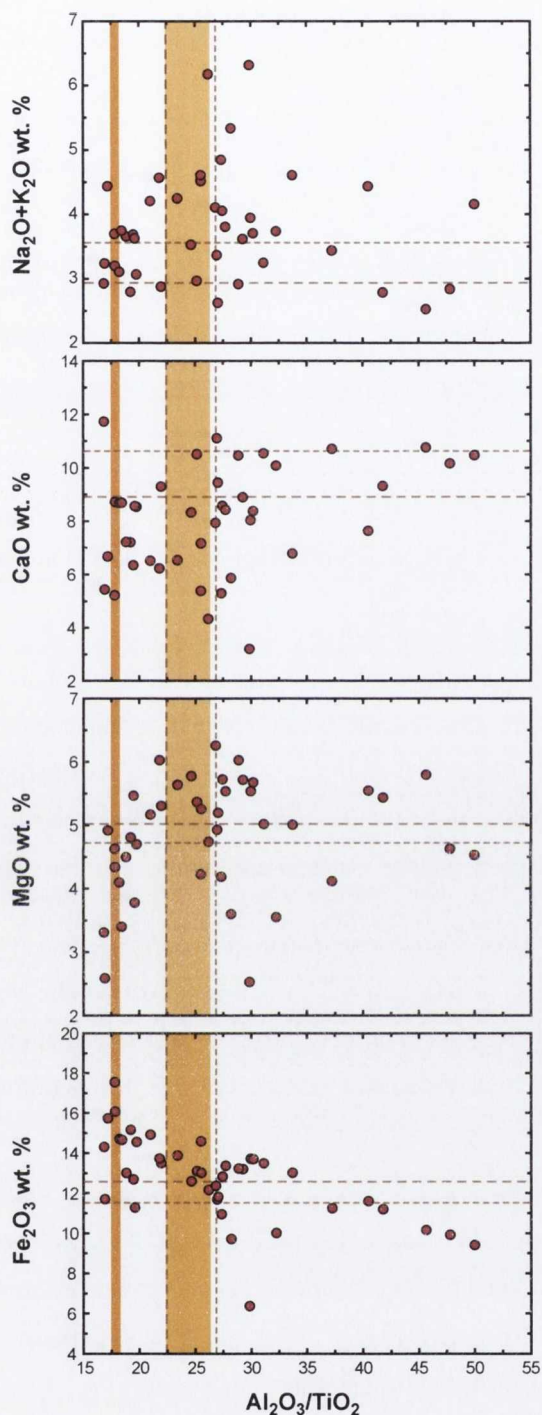


Figure S14: X-Y scatter plots of $\text{Al}_2\text{O}_3/\text{TiO}_2$ (mass ratio) against Fe_2O_3 wt.%, MgO wt.%, CaO wt.%, and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ wt.% for samples of the Hidden formation volcanic rocks from DeWolfe et al. (2009). Vertical bars represent the average $\pm 1\sigma$ SD $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of the inferred upper and lower lava flows originally present in the paleosol, whereas stippled lines (horizontal and vertical) represent the individual compositions of the two parent greenstone samples (FF021-FB1 and FF021-FB2).

In this study, Al was used as the immobile index element (i) and the parent rock was taken to be the mean greenstone composition reported in Table A1. The τ model has been applied successfully in other Precambrian paleosol studies (e.g., Driese 2004; Mitchell and Sheldon 2009; Driese et al. 2011).

A $\tau_{Al,j}$ value of 0 indicates no net loss or gain relative to the parent greenstone, whereas negative values represent a net loss (-1 being 100% loss) and positive values represent a net gain (1 being 100% gain).

In Figure S15, the $\tau_{Al,j}$ values for different groups of elements are plotted against depth for the profile. It should be noted that a lower concentration of elements in the parent rock of the upper flow of the profile will result in an overestimate of the degree of depletion.

The values for the least-mobile elements (Si, Ti, total Fe) are relatively constant in the profile aside from the offset related to the inherent difference of the two lava flows. The $\tau_{Al,Si}$ values are the most variable in the lower part of the paleosol as a result of the variability in the parent greenstone (e.g., quartz-filled amygdals).

The $\tau_{Al,j}$ values for the divalent elements (Ca, Mg, Mn, Fe^{2+}) scatter within the C horizon of the profile but are generally close to the parent rock, aside from Ca, which is depleted relative to the parent greenstone. Variability in the C horizon is interpreted to reflect pre-weathering seafloor alteration of the greenstone and deep subaerial weathering. In the B horizon, the values for the divalent elements begin to decrease in parallel with the loss of carbonate and chlorite. In the A horizon, the elements are highly depleted and remaining variability is related to spheroidal weathering.

The $\tau_{Al,j}$ values for Na and K are variable in the C horizon and, like Ca, the Na values are lower in the profile compared to the parent greenstone, reflecting the loss of albite. Within the B and C horizons, the values for both K and Na are correlated and increase towards the unconformity.

4.6 Retention factors

Retention factors (Φ) for each element were determined relative to the average parent greenstone composition as per Rye and Holland (2000). Retention factors provide a reasonably quantitative total element loss or gain in the profile, where a value of 1.0 indicates conservative behaviour, less than 1.0 indicates a net loss, and more than 1.0 indicates a net gain.

For the retention factor calculations, it was assumed that the parent greenstone and different sections of the paleosol had a constant density of 2.7 g/cm³ (Rye and Holland 2000; Utsunomiya et al. 2003; Murakami et al. 2011) and that Al was immobile. Note that the immobile element offset in the profile adds a minor degree of uncertainty to the assumption of a constant initial immobile element distribution. As in other studies (Rye and Holland 2000; Yang and Holland 2003), the paleosol was divided into several sections, with the first representing the depth between the parent greenstone at 1000 cm below the unconformity and the lowest sample in the paleosol profile (FF021H-LWB) at a depth of 515 cm. Each subsequent section, moving towards the unconformity, is taken as the depth between the sample below and the sample above with the concentration of the upper sample representing the section. The uppermost sample is taken as FF021A-002 with the depth taken as the base of the sample below and up to the unconformity at 0 cm (i.e., 11 cm). The corestone sub-samples at a depth of 340 cm (FF021C-98M/-98G) and the mineral band at 183 cm (FF021B-061) were excluded from the profile for the calculation.

Retention factors	
SiO ₂	1.15
TiO ₂	1.01
Al ₂ O ₃	1.00
Fe ₂ O _{3(T)}	1.06
FeO	0.89
MnO	0.69
MgO	0.89
CaO	0.23
Na ₂ O	0.25
K ₂ O	2.62
P ₂ O ₅	0.86

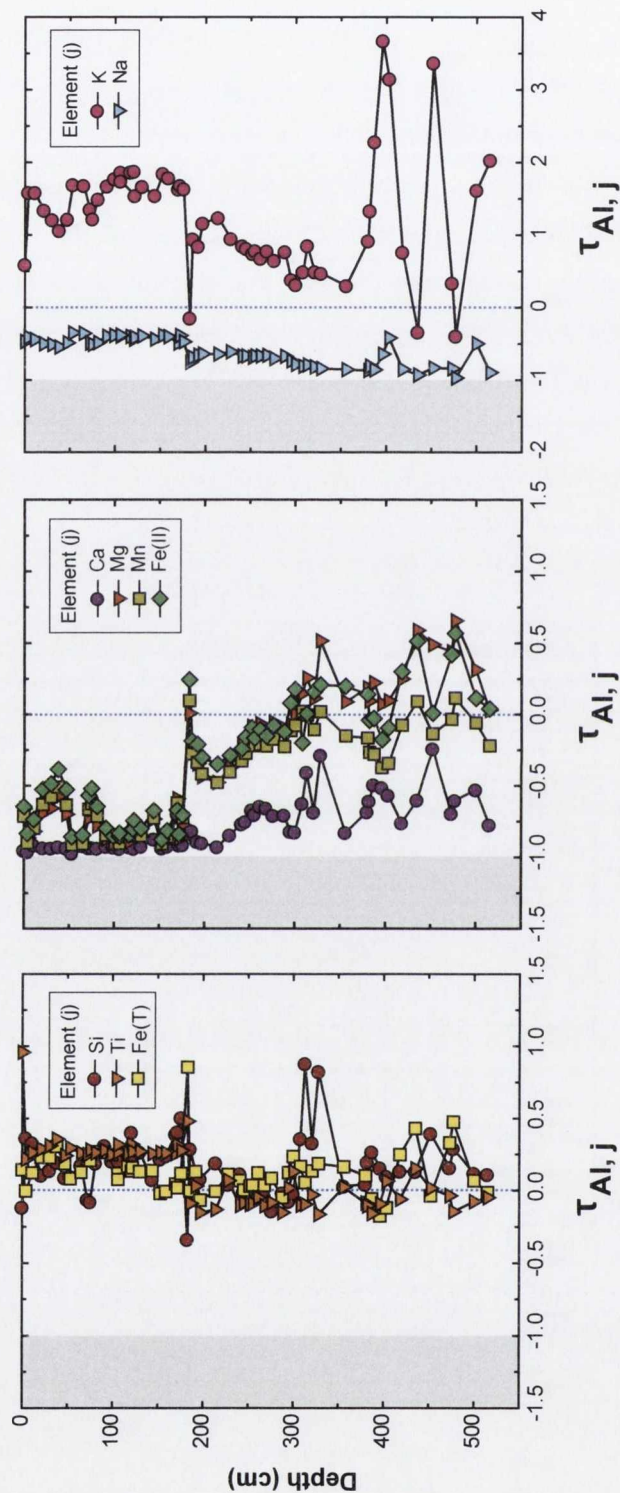


Figure S15: τ mass-balance profiles for the paleosol calculated using the composition of the average parent greenstone and assuming Al as an immobile element.

4.7 Fe-Mn-Ti-Al geochemistry

An O-type or M-type paleosol?

The re-interpretation of the Fe data from Holland et al. (1989) by Ohmoto (1996) was based on only one of the two originally studied profiles (Profile #2) comprised of 8 samples. In this profile, a depletion of $\Sigma\text{Fe}/\text{Ti}$ from the upper profile and an enrichment of Fe^{2+}/Ti lower in the profile are evident. This trend is the hallmark of a so-called M-type paleosol (Ohmoto 1996). In order for these trends to provide insight into the redox behaviour of Fe in the profile, however, it needs to be demonstrated that they are a function of the behaviour of Fe and not the normalising element (Ti).

In Figure S16 and S17, the molar Fe-Mn-Ti-Al geochemistry (Al/Ti, Fe/Ti, Fe/Al, Mn/Al) of the two profiles of Holland et al. (1989) are plotted. The most important observation is that the Fe/Al profile exhibits a different trend to the Fe/Ti profile. Notably, normalisation to Al removes many of the Fe “enrichments” and implies that the Fe/Ti trends are better explained as an artefact of local Ti depletion. Many of the fluctuations in the Fe/Ti ratio are also expressed in the Al/Ti ratio. Therefore, the smaller-scale heterogeneities in the original Fe-Ti oxide abundance of the greenstone produces some of the scatter in the Fe redox trends and needs to be considered, especially in the samples lower in the profile (Holland et al. 1989; Holland and Rye 1997).

One key feature of M-type paleosols, the depletion of Fe (ΣFe and Fe^{3+}), is evident in the uppermost sample of Profile #2 from Holland et al. (1989) regardless of the immobile element chosen for normalisation. It is possible that post-weathering fluids resulted in some Fe loss from the profile, but there appears to be no obvious enrichment of Fe^{2+} lower in the profiles to balance the loss. By contrast, in Profile #1 of Holland et al. (1989), there is a relatively constant to slightly increasing $\Sigma\text{Fe}/\text{Al}$ ratio in the upper profile. The contrast between profiles could indicate that Fe loss was a localised feature, but we view this as an unlikely explanation. As demonstrated with the new data in this study, spheroidal weathering and the reworking of regolith with Missi sediment may have had an influence on the Fe-Ti-Al chemistry. These variations are restricted to only the uppermost samples of some of the profiles and do not change the overall interpretation of the Fe geochemistry.

In summary, it is clear that Fe was almost quantitatively retained during pedogenesis and remained largely immobile during post-weathering alteration events. Thus, the Flin Flon paleosol is one of the oldest ‘true’ O-type paleosols discovered to date. Unlike Fe, however, Mn was lost from the profile, presumably as Mn^{2+} prior to oxidation.

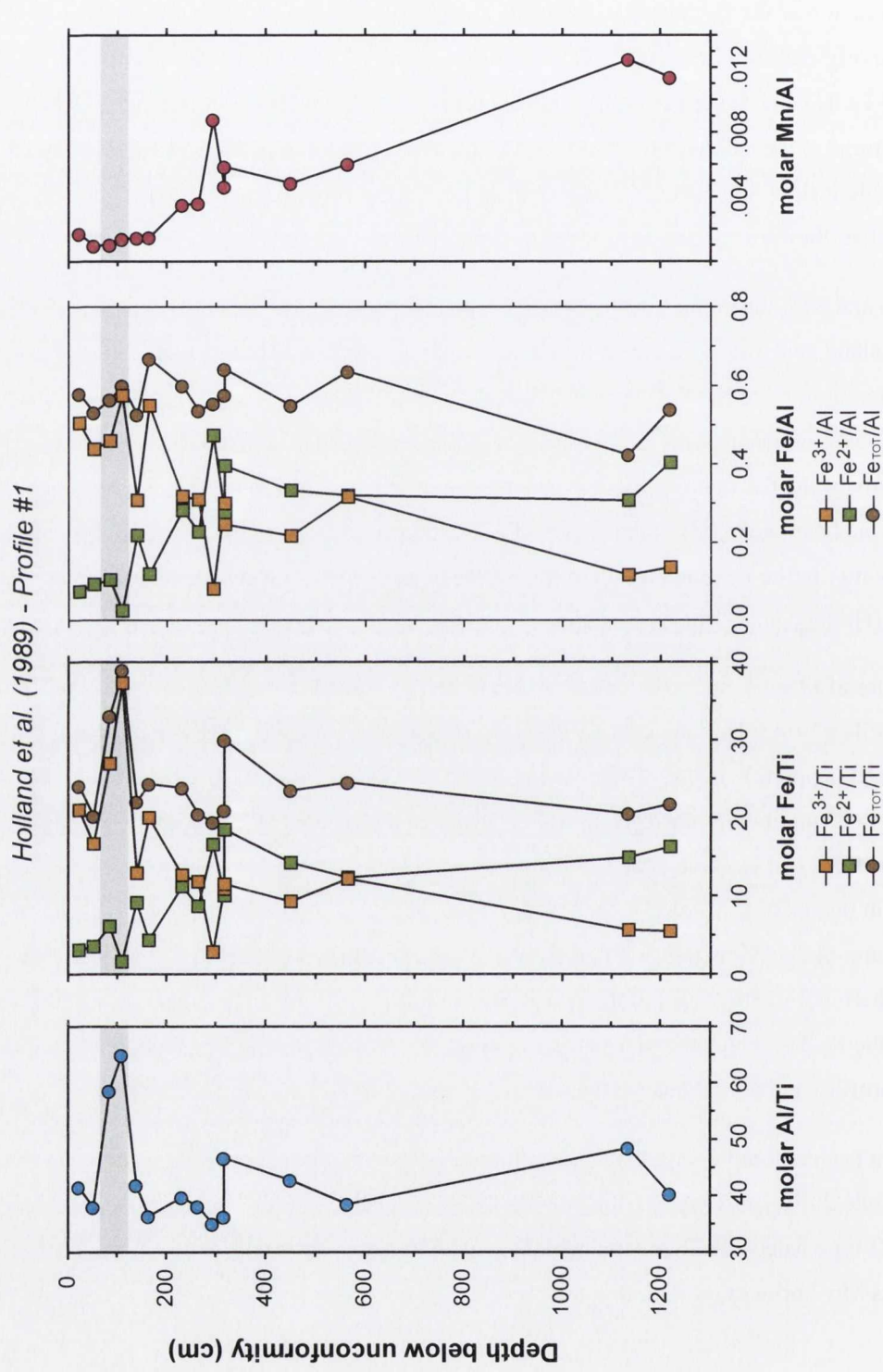


Figure S16: Molar Al/Ti, Fe/Ti, Fe/Al, and Mn/Al ratios for Profile #1 of Holland et al. (1989). Horizontal band draws attention to two samples with lower Ti concentration that creates excursions in normalised ratios.

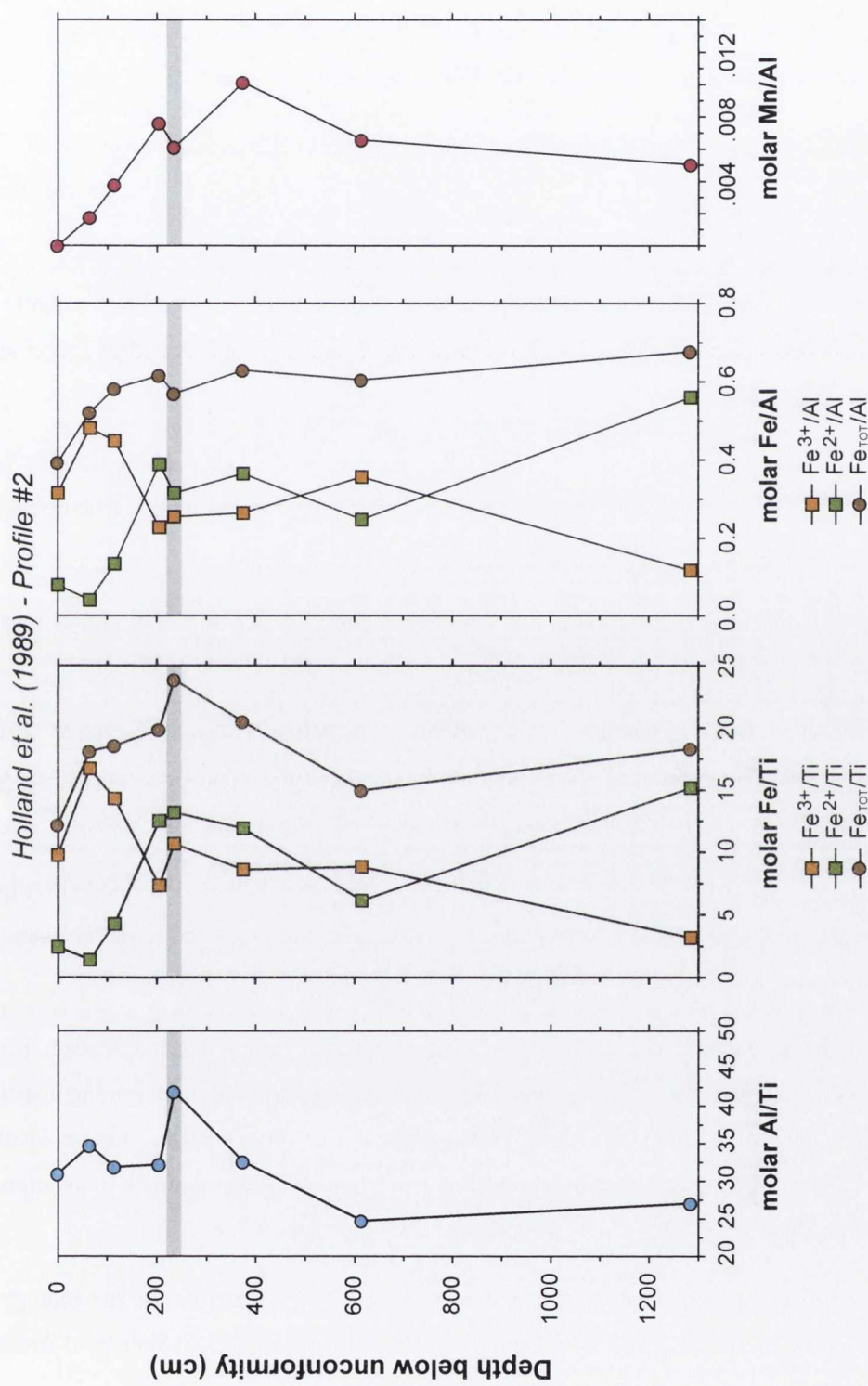


Figure S17: Molar Al/Ti, Fe/Ti, Fe/Al, and Mn/Al ratios for Profile #2 of Holland et al. (1989). Horizontal band draws attention to one sample with a lower Ti concentration that creates excursions in normalised ratios.

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Chapter 6: Paleosol Fe-Mn redox geochemistry, atmospheric oxygen evolution, and Cr isotopes

1. Fe redox and the Great Oxidation Event transition

Iron rapidly oxidises from Fe^{2+} to Fe^{3+} during weathering in the presence of O_2 , leading to the formation of Fe^{3+} -oxides at or very near the site of Fe^{2+} release from minerals during acid attack. The high O_2/CO_2 ratio of the modern atmosphere prevents the concentration of O_2 from being a limiting factor in soil Fe oxidation unless there is a high abundance of organic carbon or a textural or hydrological barrier to O_2 influx (for example in some clay-rich and water-logged soils). Thus, in ventilated soils Fe^{2+} oxidation proceeds to completion. All paleosols younger than 2.25 Ga show a near-complete retention of Fe from the oxidation of Fe^{2+} to Fe^{3+} during soil formation that is similar to modern weathering profiles (oxidised paleosols). These oxidised paleosols show near-constant total Fe/Al or Fe/Ti ($\Sigma\text{Fe}/\text{Al}, \text{Ti}$) ratios throughout the profile and a progressive upward decrease in $\text{Fe}^{2+}/\text{Al}, \text{Ti}$ with a proportional increase in $\text{Fe}^{3+}/\text{Al}, \text{Ti}$ (Figure 1c). This Fe topology is exemplified by the ca. 1.85 Ga Flin Flon paleosol (Figure 2c). In distinct contrast, all mafic paleosols older than ca. 2.25 Ga show an upward loss of Fe^{2+} from the profile with very limited to no evidence of Fe^{3+} formation (reduced paleosols). Instead, both the total $\Sigma\text{Fe}/\text{Al}, \text{Ti}$ and $\text{Fe}^{2+}/\text{Al}, \text{Ti}$ is depleted upwards towards the paleo-surface (Figure 1a). This Fe topology is exemplified by the ca. 2.45 Ga Cooper Lake paleosol (Figure 2a; Utsunomiya et al., 2003). The switch in Fe behaviour within the mafic paleosol record occurs approximately at the formation age of the ca. 2.25 Ga Hekpoort paleosols, which shows evidence of reductive as well as oxic Fe behaviour. In many mafic paleosols ≥ 2.25 Ga in age, it is clear that some of the Fe^{2+} (along with Mg) released from higher in the profile during soil formation was re-precipitated in Fe^{2+} -rich pedogenic smectite-group minerals at depth (now the chlorite zones). This Fe^{2+} redistribution is evident from higher $\text{Fe}^{2+}/\text{Al}, \text{Ti}$ and $\Sigma\text{Fe}/\text{Al}, \text{Ti}$ ratios in the chlorite zone than the underlying protolith and the overlying muscovite zone (Figure 1b). The temporal transition to full Fe retention in paleosols is expressed in Figure 2d where the $\%\Sigma\text{Fe}/\text{Al}$ and $\%\Sigma\text{Fe}/\text{Ti}$ from the protolith is plotted vs. age for all of the definite mafic paleosols. The ca. 2.25 Ga Drakenstein and 1.85 Ga Flin Flon paleosols are the first examples to show a limited $\Sigma\text{Fe}/\text{Al}, \text{Ti}$ close to that of the protolith. Near-complete retention of Fe continued throughout the Proterozoic and into the Phanerozoic in all aerated, non-lateritic soils.

The presence of rip-up clasts with the same Fe chemistry as the underlying paleosol, re-precipitation of Fe^{2+} -bearing clays at depth, and the preservation of Fe^{3+} -oxides through the

younger metasomatic and metamorphic overprint in paleosols younger than 2.25 Ga all favour a pedogenic over a hydrothermal origin of Fe signatures. As such, the end of Fe^{2+} loss or redistribution and transition to Fe retention in Fe^{3+} -oxides in paleosols is widely accepted to be a primary pedogenic feature that records the increase in O_2 associated with the Great Oxidation Event (GOE). Nevertheless, Palmer et al. (1989) suggested that post-burial hydrothermal alteration cannot be ruled out as a factor in some paleosols with an upward loss of Fe. Ohmoto (1996) further challenged the preservation of primary pedogenic Fe signatures and suggested that all paleosols originally had Fe redox topologies similar to the oxidised paleosols described above and that cases of Fe loss, if not developed during hydrothermal alteration, resulted from subsequent reduction of Fe^{3+} -oxides by organic acids.

The alternative interpretation of Fe redox geochemistry by Ohmoto (1996) has two obvious and significant implications: 1) paleosol Fe geochemistry does not record an increase in paleo-atmospheric O_2 in the Paleoproterozoic and oxygenic photosynthesis had evolved to produce elevated and stable O_2 levels sufficient to form pedogenic Fe^{3+} -oxides as early as the Mesoarchean; and, 2) a significant and widespread terrestrial biomass capable of producing organic acids was established as early as the Archean and has been the driving force behind Fe mobilisation in soils since then. Multiple lines of evidence, including organic carbon in paleosols, do suggest the colonisation of terrestrial ecosystems by microbial life at least as far back as the Neoarchean (e.g., Watanabe et al., 2000; Rye and Holland, 2000a; see Beraldi-Campesi, 2013 for an overview), although the metabolism of these microbes and their quantitative role in generating organic acids capable of Fe mobilisation in Precambrian soils is uncertain (Rye and Holland, 1998). Holland and Rye (1997) and Rye and Holland (1998) also noted that the interpretation of Fe signatures in paleosols by Ohmoto (1996) relies on the use of candidate paleosols that did not meet all criteria for definite paleosol status (Chapter 4). Crowe et al. (2013) contributed to this debate with the study of the 2.96 Ga Nsuze paleosol. This paleosol has an Fe topology similar to other >2.25 Ga reduced mafic paleosols, although Crowe et al. (2013) infer an active oxidative weathering cycle from Cr isotope data. Thus, the preserved Fe topology is interpreted to have developed during a subsequent event of pedogenic Fe^{3+} -oxide reduction and Fe^{2+} re-distribution through which the Cr isotope signature of oxidation survived.

In summary, the alternative interpretations of Fe loss in Precambrian paleosols by some researchers invoke hydrothermal overprint or the influence of organic acids (Palmer et al., 1989; Ohmoto, 1996; Crowe et al., 2013). These scenarios are compatible with Archean atmospheric oxygenation. However, these interpretations are based on poorly constrained variables such as the necessity for expansive terrestrial biota, or require preferential preservation of some redox-sensitive element

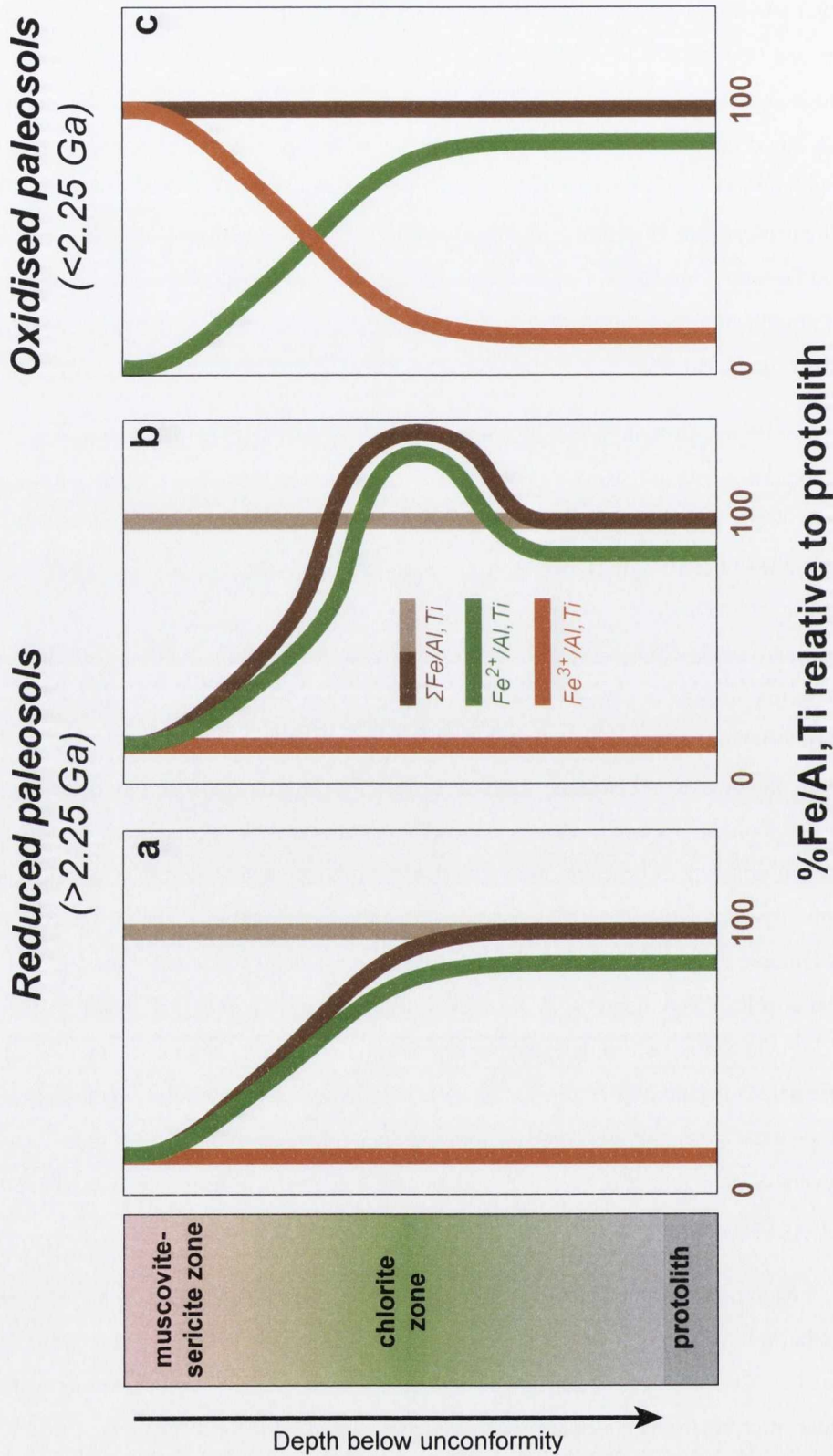


Figure 1: Idealised weathering behaviour of Fe under reduced (a,b) or oxidised (c) conditions, expressed as the molar ratio of Fe^{2+} , Fe^{3+} , and total Fe (ΣFe) normalised to Ti or Al. Reduced paleosols show upward loss of ΣFe and Fe^{2+} (a) sometimes with re-distribution of some Fe^{2+} at depth (b). Oxidised paleosols show complete oxidation of Fe^{2+} to Fe^{3+} with constant total Fe. The original Fe^{3+} in the protolith is assumed to be unaffected in both oxidised and reduced conditions.

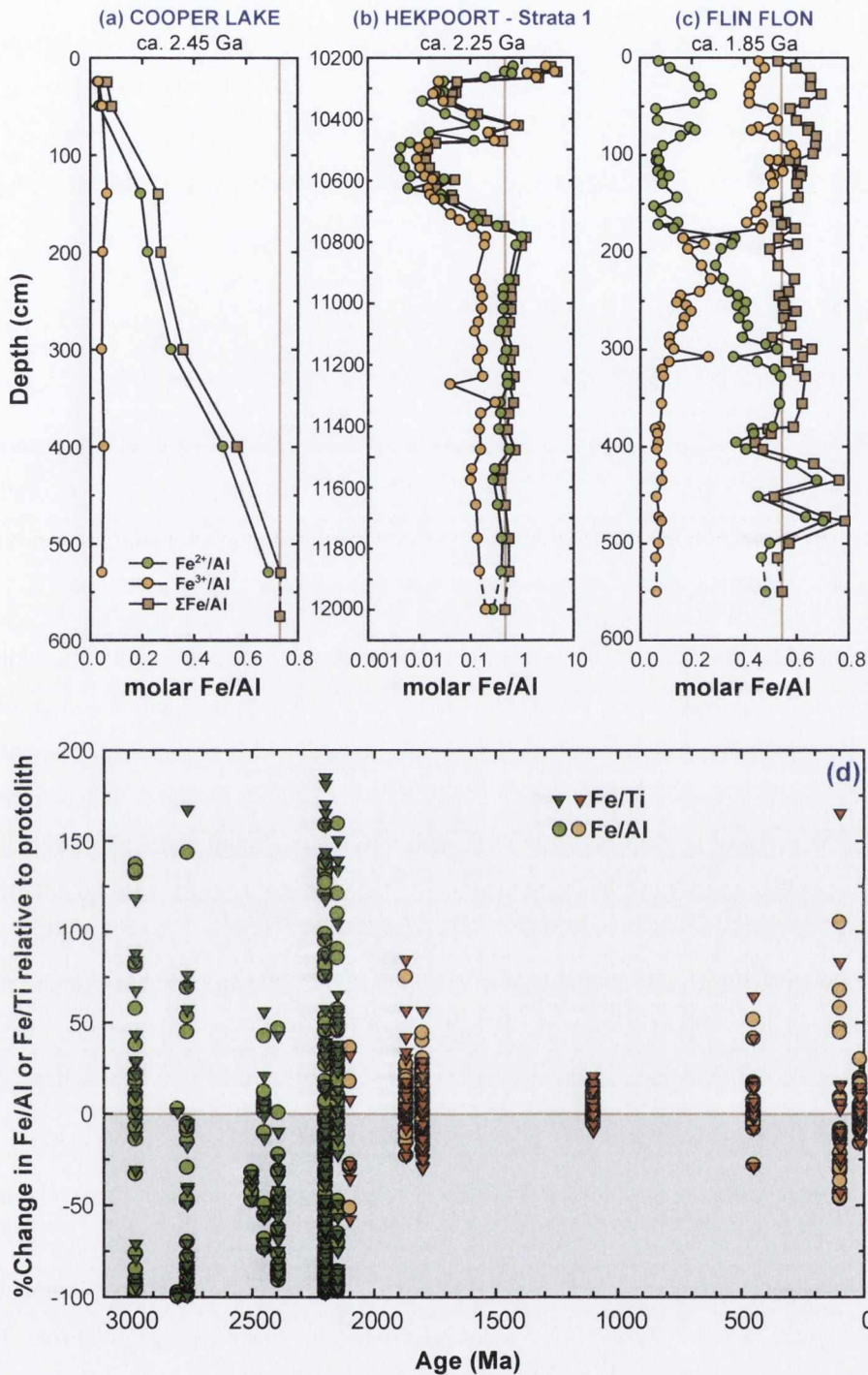


Figure 2: Fe redox chemistry, expressed in molar Fe/Al as per Figure 1, of a reduced paleosol (a: ca. 2.45 Ga Cooper Lake; Utsunomiya et al., 2003), a paleosol showing oxidised and reduced Fe behaviour (b: ca. 2.25 Hekpoort – Strata 1; Yang and Holland, 2003), and a fully oxidised paleosol (c: ca. 1.85 Ga Flin Flon paleosol; this thesis). The deepest sample in each profile represents the protolith value placed at an arbitrary depth. Note the log scale for the Hekpoort – Strata 1 profile. A compilation of molar $\Sigma\text{Fe}/\text{Al}$ (circles) and $\Sigma\text{Fe}/\text{Ti}$ (triangles) ratios in all definite mafic paleosols calculated as the percent deviation from the protolith (d). See Chapter 4 for the percent deviation calculation, plotting position (age), and data source of all paleosols in the compilation. Paleosols ≥ 2.25 Ga (green symbols) show loss of Fe or enrichment (as Fe^{2+}) expressed as significant percent deviations above and below the protolith value, whereas paleosols < 2.25 Ga show only minor deviation from the protolith due to more complete Fe^{2+} oxidation and retention as Fe^{3+} (orange symbols).

signatures over others (Cr vs. Fe). Clearly, re-examination of a primary vs. secondary origin of Fe depletion and redox topology in mafic paleosols is a key aspect of this debate deserving further attention. For the remainder of this thesis, however, the widely prevailing interpretation (Rye and Holland, 1998) that the Fe topologies of the (definite) mafic paleosols are primary with limited influence from terrestrial biota is adopted.

2. Role of texture, topography, and protolith composition on Fe oxidation

If the GOE was a protracted event that began at ca. 2.4 Ga with possible oxygen pulses even earlier, why then do mafic paleosols not show evidence of Fe oxidation until the formation of the ca. 2.25 Ga Hekpoort paleosols? In order to address this question, a brief comparison is necessary between mafic and felsic paleosols that formed between 2.45 and 2.25 Ga.

The Pronto (ca. 2.45 Ga; Gay and Grandstaff, 1980; Nedachi et al., 2005) and Ville Marie paleosols (ca. 2.3 Ga; Rainbird et al., 1990; Panahi et al., 2000) both developed on granitoid bedrock. They exhibit a more complex but generally more oxidised Fe topology compared to their near-contemporaneous mafic counterparts. The Ville Marie paleosols show evidence for Fe^{2+} oxidation at the tops of some profiles, but Fe^{2+} redistribution at depth. The sub-Huronian Pronto paleosol in the Elliot Lake area shows complete oxidation of Fe^{2+} to Fe^{3+} with quantitative Fe retention in some profiles and partial Fe^{2+} oxidation with some loss of total Fe in others. In the case of the Pronto paleosol, weathering was contemporaneous with the other sub-Huronian paleosols developed on mafic rocks in the area (i.e., Cooper Lake, Denison/Stanleigh Mine). Therefore the contrast in Fe oxidation behaviour cannot be explained by a fluctuation in atmospheric oxygen level between the time of their formation.

In an atmosphere with a lower O_2/CO_2 than present day, factors which limit O_2 availability in a soil are amplified and, in contrast to modern soils, the composition of the protolith becomes an important factor in Fe oxidation behaviour. The organic carbon content of most Precambrian paleosols appears to be minor and is often considered to have played a negligible role. Thus, the role of topography, texture, and protolith chemistry were the dominant factors for Fe oxidation. From the distribution of the sediment cover, it is possible to reconstruct the topography of the pre-Huronian landscape. In the Elliot Lake area granites were situated at paleotopographic highs and the greenstones primarily in paleotopographic lows (Figure 3), which would indeed have limited the drainage and promoted reducing conditions in the low-land soils (e.g., Gay and Grandstaff, 1980; Farrow and Mossman, 1992). Likewise, the clay content of the soil can limit drainage but the clay content of mafic and felsic sub-Huronian paleosols is often similar. It is thus concluded that

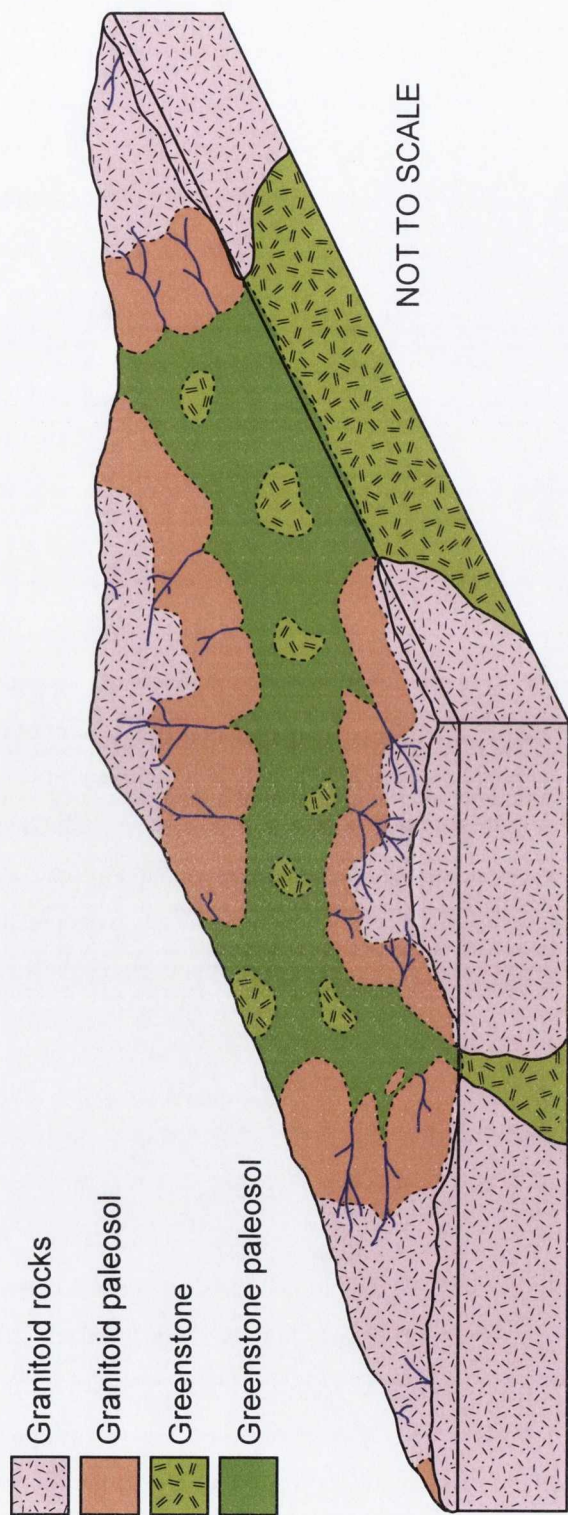


Figure 3: Schematic diagram of the topography of the Archean granite-greenstone terrane with the contemporaneous weathering profiles developed on each lithology, representing the sub-Huronian paleosols (modified from Goddard, 1987). Granites are situated at topographic highs and tend to develop more aerated soils, whereas greenstone is in topographic lows (e.g., valleys and floodplains) that would tend to develop more waterlogged (reducing) soils.

clay content and topographical effects alone cannot explain variable degrees of Fe oxidation in profiles developed side-by-side on different lithologies (Sutton and Maynard, 1993). These factors also cannot explain instances of Fe loss in soils with evidence for sufficient ventilation (Farrow and Mossman, 1992). The remaining factor, the composition of the protolith, indeed appears to explain the difference in Fe oxidation behaviour of the sub-Huronian paleosols and most other >2.25 Ga paleosols. When oxidative weathering is viewed as a two-stage process with the release of Fe^{2+} by carbonic acid attack as a preceding step to oxidation, loss of Fe is explainable if the amount and rate of Fe^{2+} released by acid attack outpaces the supply of O_2 available to oxidise it. Holland (1984) described this concept using the relative demand of O_2 over CO_2 for the complete weathering of a protolith, defined as the ratio R (DO_2/DCO_2), compared to the available O_2/CO_2 in a soil. The demand for O_2 in a protolith is controlled by its reductants such as Fe, Mn, S, and C, whereas the demand for CO_2 is controlled by the cations (Ca, Mg, K, Na) capable of reacting with carbonic acid. Only when the ratio of O_2/CO_2 supplied to a soil exceeds the value of R , can Fe oxidation go to completion and result in full Fe retention. In cases where R is greater than the ratio of O_2/CO_2 supplied to a soil, any Fe^{2+} released after the exhaustion of O_2 is apt to be removed from the soil in solution prior to oxidation. Since Fe is often the most abundant reductant in a protolith, Fe-rich rocks, such as basalt, have a high O_2/CO_2 demand (a high R value) and tend not to favour oxidation of Fe^{2+} unless the available O_2/CO_2 is very high. Conversely, more of the Fe^{2+} released from Fe-poor rocks (lower R value), such as granitoids, can be oxidised at lower O_2/CO_2 levels in a soil. This principle is described more completely elsewhere (Holland, 1984; Gay and Grandstaff, 1986; Holland and Zbinden, 1988; Pinto and Holland, 1988; Rye and Holland, 1998) and has been used to account for variations in pedogenic Fe oxidation behaviour between felsic and mafic protoliths in many Precambrian paleosols (e.g., Farrow and Mossman, 1988; Sutton and Maynard, 1993).

In summary, although there is a lag in the oxidation of Fe in mafic paleosols after the rise of O_2 during the GOE (ca. 2.4 Ga), there is evidence for soil Fe^{2+} oxidation in felsic paleosols formed between 2.45 Ga–2.25 Ga. The difference in oxidation behaviour is explained by the lower Fe concentration of granitoids and their tendency to form aerated soil profiles that enhance atmospheric O_2 supply. A greater level of soil oxidation of felsic paleosols between 2.45–2.25 Ga is also supported by the existence of Ce anomalies (Panahi et al., 2000; Nedachi et al., 2005; cf. Murakami et al., 2001). By contrast, Ce anomalies have yet to be reported for mafic paleosols >2.25 Ga. Future analysis of paleosols with a lithological contrast using new paleo-redox proxies should help to further understand the variable levels of soil oxidation in mafic vs felsic paleosols around the time of the GOE.

3. The ca. 2.25 Ga Hekpoort paleosols – the oldest laterite?

Temporally, the paleosols developed on the Hekpoort basalt occur at the transition from Fe loss to Fe retention in the mafic paleosol record (Figure 2) and they have received a great deal of attention due to their fascinating Fe geochemistry. However, interpretations have been widely diverging (Rye and Holland, 2000b; Beukes et al., 2002; Yang and Holland, 2003; Driese, 2004; Yamaguchi et al., 2007). The earliest studies of the paleosol (Rye and Holland, 2000b and references therein) from the Waterval Onder and Daspoort Tunnel localities and the Break Bank drill core (BB3, BB8, BB14) intersections had an Fe redox topology similar to reduced paleosols (Figure 1b). Rye and Holland (2000b) interpreted this to indicate that these were the youngest paleosols formed under a predominantly reducing atmosphere. When this was coupled with the oxidised paleosols developed on the Ongeluk lavas (Drakenstein paleosol; Wiggering & Beukes, 1990) and the Kuruman iron formation (Wolhaarkop paleosol; Holland & Beukes, 1990) which at the time was believed to be younger than the Hekpoort paleosols, it implied a substantial increase in atmospheric oxygen in the intervening period of time (ca. 2.2 and 2.0 Ga; Rye and Holland 1998, 2000b; Holland and Beukes, 1990). A subsequently discovered drill core intersection of the Hekpoort paleosol near Gaborone (Strata 1) by Beukes et al. (2002), however, forced a complete revision of this original interpretation; the Strata 1 profile is a more complete sequence that contains upper horizons enriched in $\text{Fe}^{3+}/\text{Al}, \text{Ti}$ not seen in the previous profiles. This complete sequence includes textural transitions and an overall Fe redox distribution resembling that seen in laterites (e.g., Widdowson, 2007), which develop in tectonically stable areas with prevalent tropical weathering conditions. Laterites also display evidence for enhanced leaching and element mobility from reactions with organic acids generated by the breakdown of vegetation, including Fe reduction and chelation. Beukes et al. (2002) thus interpreted that the Hekpoort lavas weathered under a highly oxic atmosphere with a substantial and continent-wide terrestrial biomass.

According to Beukes et al.'s (2002) view, the horizon of Fe^{2+} loss developed due to a deep water-table that promoted extensive lateral transport of Fe^{2+} independent from influence of the oxic atmosphere. These authors also revisited the stratigraphic correlations between the Hekpoort and Drakenstein and Wolhaarkop paleosols and concluded that they are preserved below one laterally equivalent unconformity with all units having formed between ca 2.22 and 2.18 Ga. This motivated a follow-up study by Yang and Holland (2003) on the complete Strata 1 profile of the Hekpoort paleosol (Fe/Al data from their study is shown in Figure 2b). Yang and Holland (2003) interpreted the Fe redox topology of this section as evidence for formation under a mildly oxygenated atmosphere (estimated at between 2.5×10^{-4} and 9×10^{-3} atm) where O_2 penetrated the upper part of the soil but conditions turned reducing below and into O_2 -devoid groundwater zone, where

liberated Fe^{2+} was transported vertically downwards and re-precipitated as a constituent of chlorite. The diverging interpretations of Yang and Holland (2003) and Beukes et al. (2002) are still a matter of debate (see Driese, 2004). More recent studies attempted to better to define whether the Fe mobility occurred in an open vs. closed system. Modern laterites with a pallid zone have often lost a substantial amount of their total Fe from lateral groundwater transport in an open system. The interpretation of Yang and Holland (2003) is a closed system, in which transport of Fe in groundwater is vertical and where all of the Fe lost from the sericite zone can be accounted for by enrichments in the mottled and chlorite zones. To address this, Yang and Holland (2003) applied a retention factor approach (see Rye and Holland 2000 for details) and calculated that very little net loss or gain of Fe occurred during development of the profile. Yamaguchi et al. (2007) also attempted to address this aspect of the Hekpoort paleosol with Fe isotope mass balance and concluded that groundwater-rock interaction instead resulted in substantial horizontal mobilisation of Fe^{2+} , a process consistent with lateritisation.

4. Mn behaviour and the lag in Mn-oxide formation

Manganese, like Fe, can oxidise from Mn^{2+} to Mn^{3+} or Mn^{4+} in the presence of O_2 . Unlike Fe, however, the oxidation of Mn^{2+} is kinetically sluggish (Morgan, 2005) unless biologically catalysed by Mn-oxidising bacteria (Diem and Stumm, 1977). Consequently, in many modern soils there is a greater potential for Mn to be re-distributed or lost as bivalent Mn even when Fe^{2+} is quantitatively oxidised (e.g., Middelburg et al., 1988; Nesbitt and Wilson, 1992; Nesbitt and Markovics, 1997). The mobility of Mn during Precambrian soil formation is well documented (Pinto and Holland, 1988; Maynard, 2014) and the chemical topology of Mn in most paleosols shows upward loss along with other mobile elements. Additionally, there is often Mn enrichment in the chlorite zone (Figure 1c). These patterns indicate that Mn^{2+} was transported downward in groundwater and re-precipitated in smectite-group minerals along with Mg and Fe^{2+} or in pedogenic carbonates. The three mafic paleosols that show different Fe oxidation topologies (Cooper Lake, Hekpoort Strata 1, Flin Flon; Figure 2) all show evidence for Mn depletion or re-distribution (Figure 4). Significantly, the ca. 2.25 Ga Hekpoort Strata 1 profile, interpreted as a possible laterite developed under high O_2 and the presence of significant terrestrial biota (Section 3), also shows a distinct upward loss of Mn apart from two features: 1) irregular enrichments in the chlorite zone from incorporation in smectite as described above; and, 2) a slight return to higher Mn concentrations in the upper ferricrete zone relative to the mottled zone below. However, a contribution from an allochthonous source cannot be ruled out higher in the section as the ferricrete is reworked. When plotted as a percent deviation from the protolith ($\%\text{Mn}/\text{Ti,Al}$), the mobilisation

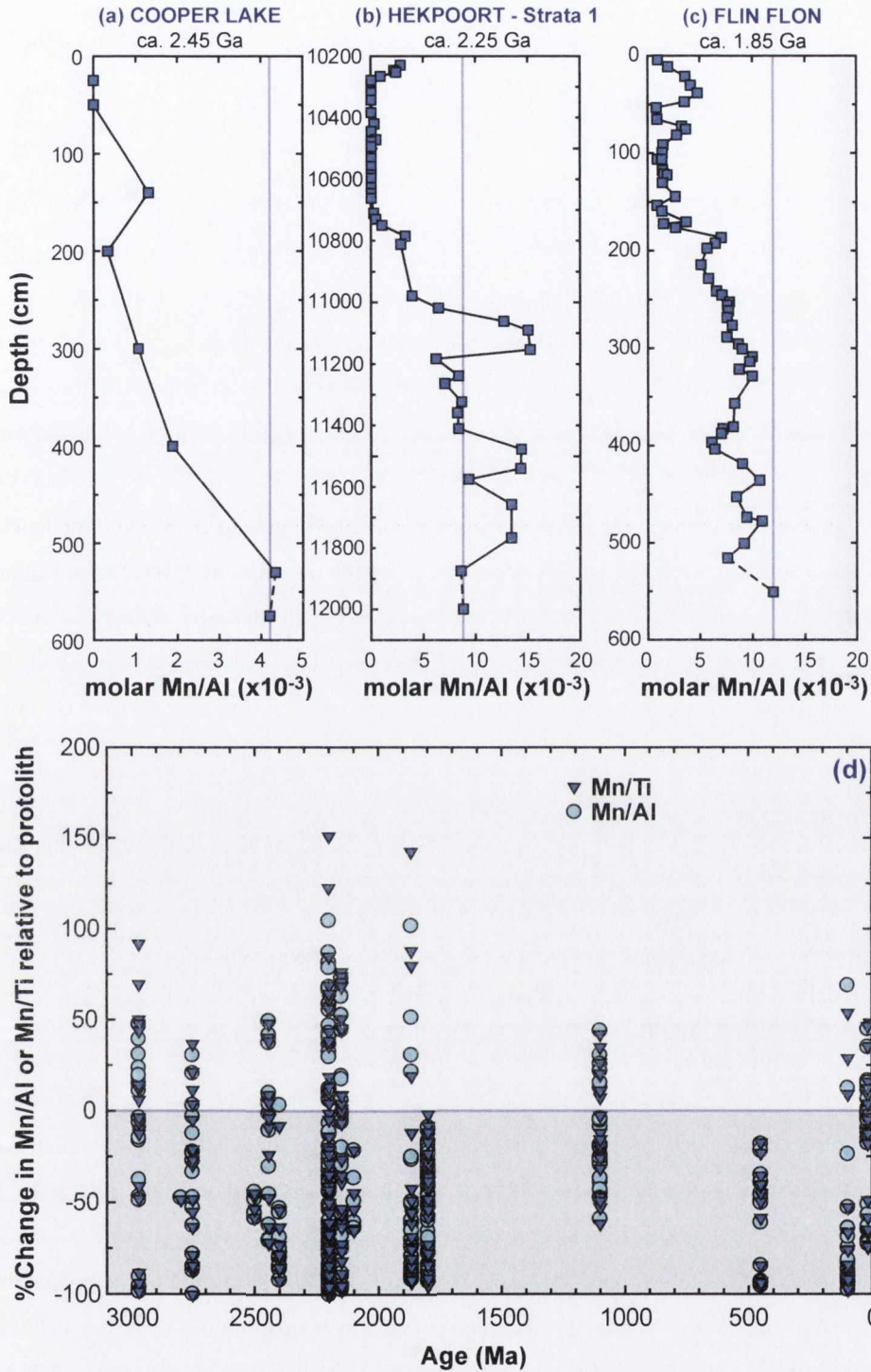


Figure 4: Mn chemistry, expressed in molar Mn/Al, of the same paleosols from Figure 2 (a-c). The Mn/Al decreases upwards in all three paleosols with enrichment in the lower horizon in the case of the Hekpoort – Strata 1 profile (b). A compilation of molar Mn/Al (circles) and Mn/Ti (triangles) ratios in all definite mafic paleosols calculated as the percent deviation from the protolith (d). See Chapter 4 for the percent deviation calculation, plotting position (age), and data source of all paleosols in the compilation. Loss or re-distribution of Mn is evident in all Precambrian paleosols, the ca. 0.45 Ga Arisaig paleosols, and even in the modern profiles, highlighting its different oxidation behaviour compared to Fe (Figure 2).

of Mn and high levels of depletion are evident in all mafic paleosols formed from 2.96 Ga to 0.45 Ga. Manganese therefore does not show the ca. 2.25 Ga temporal change in weathering behaviour as Fe does (Figure 2d vs. 4d).

Collectively, these results point to very little or no oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+} in Precambrian paleosols during and after the GOE, reflecting the larger thermodynamic barrier and slower kinetics of its oxidation relative to Fe, and, perhaps, the absence of soil microorganisms capable of catalysing the oxidation. Murakami et al. (2011), however, suggest that a gradual retention of Mn in paleosols occurred throughout the Paleoproterozoic culminating at ca. 1.85 Ga with Mn in the Flin Flon paleosol showing near full oxidation and retention. The analyses of the Flin Flon paleosol in this thesis do not support this claim; the Mn/Al ratio (Figure 3c) shows upward Mn loss and retention in the lower horizons of the paleosol can be explained almost entirely from sequestration as Mn^{2+} . Some support for the decoupling of terrestrial Mn and Fe oxidation comes from the geochemistry of Precambrian clastic sedimentary rocks. Shales show an increase in Fe oxidation state after ca. 2.3 Ga (Bekker and Holland, 2012), whereas Mn/Ti ratios in clastic sedimentary rocks show evidence for Mn loss throughout the Precambrian (Kump and Holland, 1992). It is important that the diverging Mn and Fe terrestrial redox cycles in the Paleoproterozoic may have substantial and underappreciated implications for the interpretation of other redox-sensitive trace metal cycles, most notably Cr, the subject of the following thesis chapter.

5. Chemical weathering indices and ternary plots

The utility of weathering indices to quantify the extent of weathering and the visualisation of trends in ternary plots were demonstrated as important strategies to studying chemical weathering in Chapters 2 and 6. Here, this is revisited again with a compilation of all definite mafic paleosols to highlight their similarities and differences with Phanerozoic weathering profiles and address the aforementioned trends of oxidised vs. reduced chemical weathering. The mafic paleosols are divided into three separate groups based on their age and corresponding Fe redox-behaviour as described above (i.e., Fe loss/redistribution or Fe retention): 1) paleosols older than 2.25 Ga showing Fe^{2+} loss or re-distribution; 2) paleosols younger than 2.25 Ga showing Fe retention due to ferric oxide formation; and, 3) the ca. 2.25 Ga Hekpoort paleosol that shows evidence for both Fe^{2+} loss and Fe^{3+} formation.

The most commonly applied index is the ‘chemical index of alteration’ (CIA; Nesbitt and Young, 1982).

$$\text{CIA} = [\text{Al}_2\text{O}_3 / \text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}] \times 100$$

The chemical index of alteration increases from an original unweathered value of ~50 for intermediate and felsic igneous rocks or 30-50 for mafic rocks (lower due to apportioning of some Ca to pyroxene) towards a value of 100 that indicates complete depletion of Ca, Na, and K relative to Al. Note that in this thesis CaO^* (silicate-hosted Ca only) is calculated in all profiles with correction for apatite but not carbonate due to the lack of data for carbonate-associated CO_2 in most studies. The CIA is projected into the Al_2O_3 – CaO^* – Na_2O – K_2O (A–CN–K) ternary plot. Mafic rocks plot very close to the A–CN join due to their low K content and their weathering trend follows a path along this join from the protolith away from the CN towards the A apex (Figure 5). The similar behaviours of Ca and Na in mafic paleosols compared to Phanerozoic profiles are anticipated to have resulted in an identical trend. However, it is apparent that the majority of paleosol samples plot to the right of the modern basalt weathering trend closer to the K apex. This deviation represents the ubiquitous addition of K experienced by paleosols during burial metasomatism/metamorphism. The K addition in Precambrian paleosols indicates that the calculated CIA value for paleosols underestimates the true extent of chemical weathering. The A–CN–K plot is therefore useful in determining the amount of K added to a paleosol whereby the projection of a line from the K apex through the sample to the point where it intersects the inferred primary chemical weathering trend (approximately parallel to the A–CN join) can determine the equivalent CIA position prior to K addition. To circumvent the issue of K metasomatism, many alternative weathering index approaches have been proposed, such as calculating the CIA minus K (CIA–K), which is equivalent to the ‘chemical index of weathering’ (CIW) proposed by Harnois (1988). This alternative approach of using the CIA–K or CIW is suitable for quantifying weathering intensity of profiles developed on low-K igneous rocks such as basalts, but is not suitable for those developed on rocks with a significant proportion of K-feldspar prior to weathering (Fedo et al., 1995). Instead, the ‘plagioclase index of alteration’ (PIA) can be applied (Fedo et al., 1995) in these cases.

$$\text{CIA-K or CIW} = [\text{Al}_2\text{O}_3 / \text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}] \times 100$$

$$\text{PIA} = [\text{Al}_2\text{O}_3 - \text{K}_2\text{O} / \text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O}] \times 100$$

The weathering behaviour of Fe and Mg, clearly of importance in mafic weathering profiles, has led to the development of other indices and ternary plots that incorporate these elements. Maynard (1992) proposed the Mg index (MgI) to quantify the loss of Mg relative to Al.

$$\text{MgI} = [\text{Al}_2\text{O}_3 / \text{Al}_2\text{O}_3 + \text{MgO}] \times 100$$

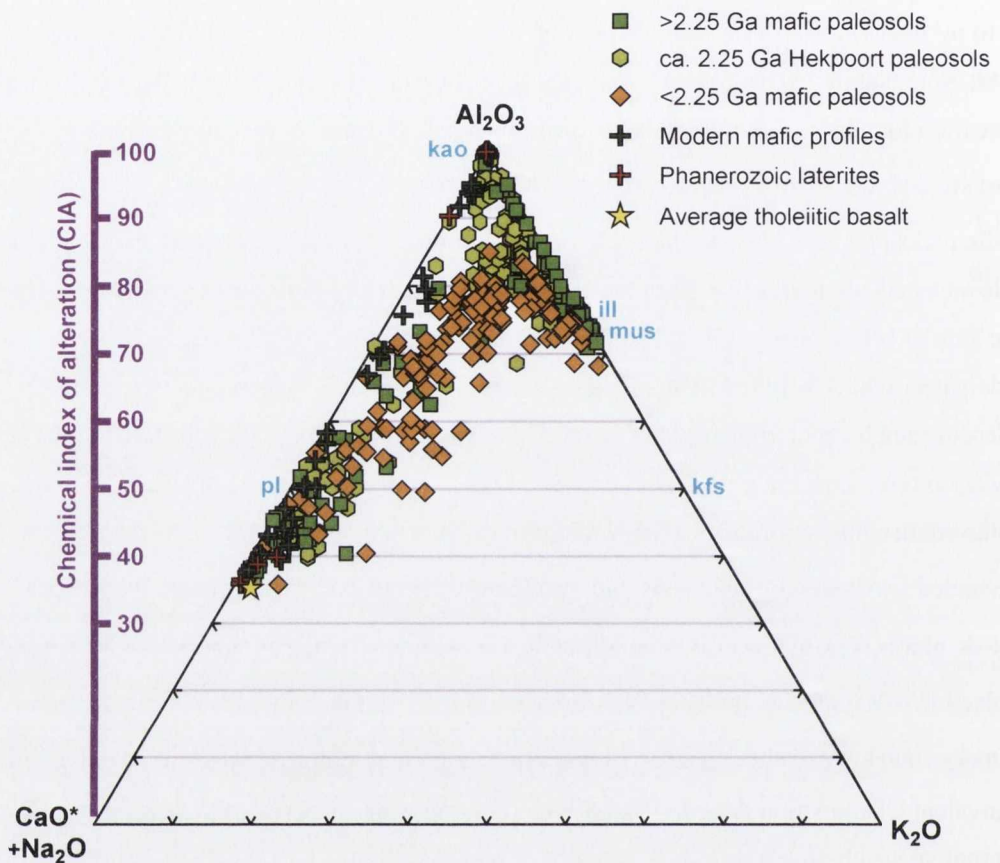


Figure 5: Ternary Al_2O_3 – $\text{CaO}^*+\text{Na}_2\text{O}$ – K_2O (A–CN–K) plot and accompanying chemical index of alteration (CIA) showing data from mafic paleosols, modern basalt profiles, Phanerozoic laterites, and an average tholeiitic basalt (Nockolds, 1954). Paleosols are divided into those >2.25 Ga (reduced), <2.25 Ga (oxidised), and the ca. 2.25 Ga Hekpoort paleosols. All data are from the compilation in Chapter 4. Modern basalt profiles and Phanerozoic laterites plot along a trend from the protolith towards the A apex close to the A–CN join. Precambrian mafic weathering profiles would have originally plotted along this same trend, but the paleosols now plot to the right, closer to the K apex due to the addition of K during metasomatism/metamorphism. The original CIA value prior to K addition can be determined by projecting a line from the K apex through the sample to the A–CN join. Positions of some minerals are also shown: pl (plagioclase), kfs (potassium feldspar), kao (kaolinite), ill (illite), mus (muscovite) to demonstrate the mineralogical progressions during chemical weathering.

The two ternary plots proposed by Nesbitt and Young (1989) and Nesbitt and Wilson (1992) – the $\text{Al}_2\text{O}_3\text{--CaO}^*+\text{Na}_2\text{O}+\text{K}_2\text{O--FeO}_T+\text{MgO}$ (A–CNK–FM, or ‘mafic’ plot) and the $\text{Al}_2\text{O}_3\text{--MgO}+\text{CaO}^*+\text{Na}_2\text{O}+\text{K}_2\text{O--FeO}_T$ (A–CNKM–F or ‘A–L–F’ plot, where ‘L’ refers to the labile/mobile elements Mg, Ca, Na, and K) – were further adapted in this thesis when formulating the new mafic index of alteration (MIA). Although predicting rock weathering trends in these plots is more difficult compared to the A–CN–K plot due to the incorporation of both mafic and felsic minerals with different weathering rates, they are nonetheless useful in illustrating mafic rock weathering trends. In Chapter 2 it was proposed that the A–CNK–FM is applied most effectively to reduced soils where Fe^{2+} is mobilised and behaves similarly to Mg, whereas the application of the A–L–F plot is more effective in oxidised soils exhibiting Fe conservation, such that they are ideally suited to comparing the geochemical trends of reduced vs. oxidised paleosols.

In the A–CNK–FM plot, modern basalt weathering profiles show an empirical trend from the position of the protolith away from the CNK apex towards the A–FM join representing Ca and Na loss from feldspar. Weathering of the mafic minerals would result in a vector away from the FM apex, although this is only likely to influence the bulk rock trend significantly if both Fe and Mg are mobile. Indeed, it is evident that reduced paleosols show a trend that extends further away from the FM apex due to the combined loss of Fe and Mg, exceeding the trend of oxidised paleosols and modern basalt profiles (Figure 6a) where only Mg is lost. Note that metasomatism (chiefly K addition) would pull the trend of these samples slightly back towards the CNK apex along this trend, such that the samples now plot between the composition of chlorite and illite/muscovite. If Fe is assumed to be mobile as Fe^{2+} and lost from a profile, the $\text{MIA}_{(R)}$ can be projected into the A–CNK–FM plot (Figure 6a).

$$\text{MIA}_{(R)} = [\text{Al}_2\text{O}_3 / \text{Al}_2\text{O}_3 + \text{MgO} + \text{Fe}_2\text{O}_{3(T)} + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}] \times 100$$

In the A–L–F plot, modern basalt weathering profiles show an empirical trend that follows a vector from the position of the protolith away from the L apex, without any significant deviation towards the A or F apices due to the conservation of both of Fe and Al as immobile elements (Figure 6b). All of the <2.25 mafic Ga paleosols overlap directly with the modern basalt profiles. Note that the magnitude of mobile element loss is underestimated since addition of K would pull the samples slightly back towards the L apex along the same vector. By contrast, mafic paleosols greater than 2.25 Ga in age show a trend further away from the vector representing Ca, Mg, and Na loss, due to the compounding effect of Fe^{2+} loss. The trend away from the F apex representing Fe

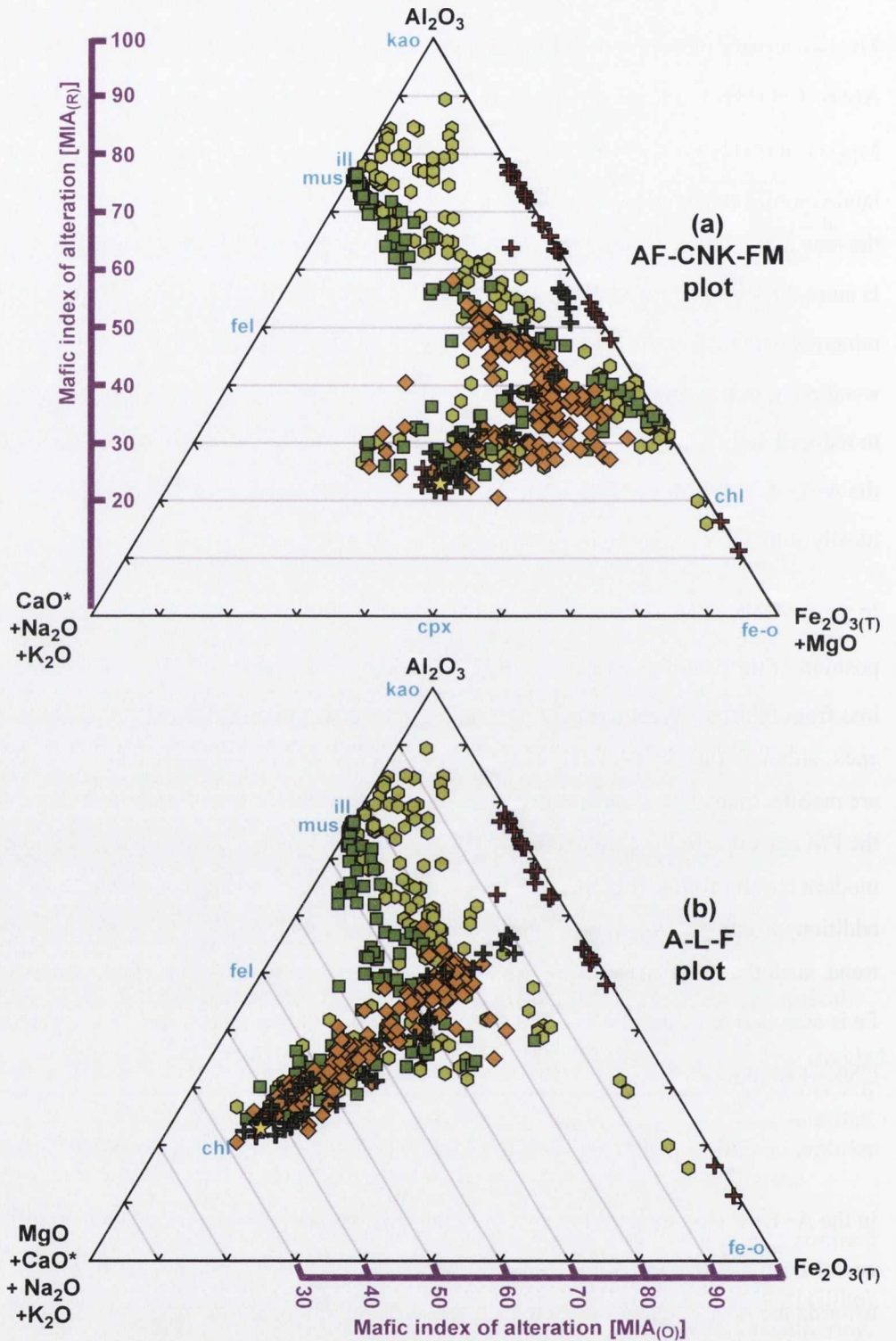


Figure 6: Ternary (a) Al_2O_3 – $CaO^*+Na_2O+K_2O$ – $MgO+Fe_2O_{3(T)}$ (A–CNK–FM) and (b) Al_2O_3 – $CaO^*+Na_2O+K_2O+MgO$ – $Fe_2O_{3(T)}$ (A–L–F) plots and accompanying mafic index of alteration (MIA). The A–CNK–FM plot and arrangement of MIA to include Fe as a mobile element $[MIA_{(R)}]$ are more suitable to studying reduced paleosols that show coupled Fe and Mg loss. The A–L–F plot and arrangement of MIA to include Fe as an immobile element $[MIA_{(O)}]$ is more suitable to studying oxidised paleosols and modern profiles that show Fe retention but Mg loss. The data and symbols are identical to Figure 5.

loss is pulled slightly back towards the L apex due to K addition. If Fe is assumed to be immobile along with Al, the alternative $MIA_{(O)}$ arrangement can be projected into the A–L–F plot (Figure 6b).

$$MIA_{(O)} = [Al_2O_3 + Fe_2O_{3(T)} / Al_2O_3 + MgO + CaO^* + Na_2O + K_2O] \times 100$$

The differences between oxidised and reduced paleosol trends is evident in both the A–L–F and A–CNK–FM plots and the accompanying MIA index introduced in this thesis is therefore very practical to estimate the degree of weathering experience by Precambrian paleosols. In reduced paleosols, the $MIA_{(R)}$ tracks the progression of chemical weathering better than the CIA-K, CIW, or MgI alone. By contrast, $MIA_{(O)}$ is insensitive to the chemical weathering progression of reduced paleosols and this alternative arrangement is instead useful for quantifying weathering intensity in oxidised paleosols. Further stable metal isotope studies will benefit from exploring how the degree of isotope fractionation varies with the degree of weathering quantified with the MIA indices.

The final weathering index considered is the SiO_2 – Al_2O_3 – $Fe_2O_{3(T)}$ (S–A–F) ternary plot (Schellman, 1986) and accompanying ‘index of lateritisation’ (IOL; Chapter 2). This permits a quantification of the (chemical) definition of the term laterite applied to Precambrian paleosols.

$$IOL = 100 \times [(Al_2O_3 + Fe_2O_{3(T)}) / (SiO_2 + Al_2O_3 + Fe_2O_{3(T)})]$$

The use of the term laterite *sensu stricto* is somewhat contentious. It has been proposed that laterite should only be applied to *in situ* profiles that show an upward loss of Si and residual enrichment of Fe^{3+} -oxides (Widdowson, 2007; Chapter 2). The term bauxite or bauxitic profile is often used in place of laterite when residual Al enrichment exceeds that of Fe. The loss of Si is associated with the breakdown of kaolinite to gibbsite or dissolution of quartz to silicic acid and occurs at weathering intensities beyond those experienced by most saprolites where kaolinite is the end weathering product (kaolinitisation). Therefore, the traditional weathering indices (CIA, MIA) are ineffective at quantifying the intense leaching conditions associated with lateritisation. In Chapter 2 it was demonstrated how the IOL and S–A–F, can separate weathering reactions up to kaolinite (kaolinitisation) from those characterised by Si loss with subdivisions into ‘weakly’, ‘moderately’, and ‘strongly’ lateritised as calculated from the starting amount of Al in the protolith. This separation of weathering trends is demonstrated with the modern basalt profiles that plot within the field of kaolinitisation and the Phanerozoic laterites that plot within the separate lateritisation fields depending on their degree of alteration (Figure 7). In cases where Fe enrichment is associated with allochthonous Fe addition (e.g., in ferricretes) it is misleading to infer the intensity of alteration

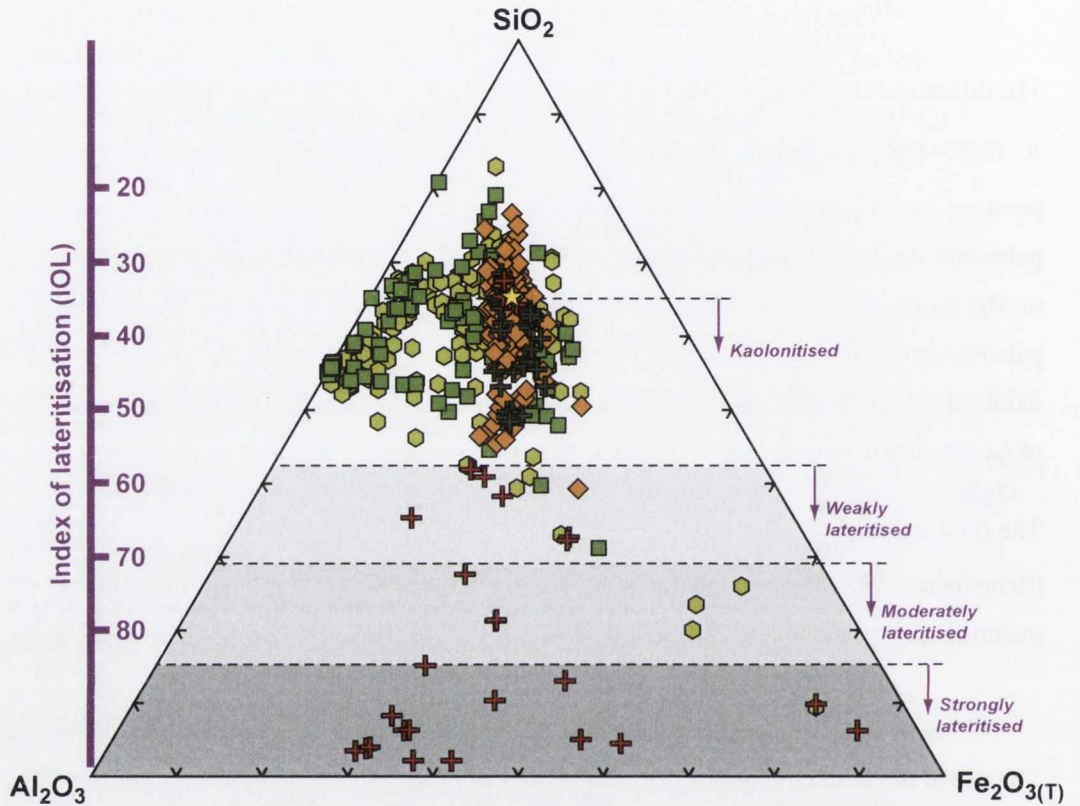


Figure 7: Ternary $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Fe}_2\text{O}_3(\text{T})$ (S–A–F) plot and accompanying index of lateritisation (IOL). This plot separates kaolinitisation (saprolites) from the more advanced chemical weathering trends of Si loss and Fe/Al enrichment associated with lateritisation/bauxitisation, although using the chemistry of a profile to identify a laterite requires geological constraints that Fe-enrichment is autochthonous. The data and symbols used in this plot are identical to Figure 5. The majority of mafic Precambrian paleosols plot within the field of kaolinitisation, although loss and re-distribution of Fe^{2+} complicates the position of reduced paleosols on the diagram. Of all of the oxidised mafic paleosols, only the samples from the upper horizons of the Hekpoort – Strata 1 profile plot within the fields of lateritisation. These samples, however, appear to violate the geological criteria of laterite based on their evidence for allochthonous Fe addition.

from the IOL and position of a sample on the S–A–F plot since it violates the definition of laterite given above.

When applied to the mafic paleosol record, it becomes clear that the term and definition of laterite is misleading in this context and its use should perhaps be avoided when describing Precambrian weathering. Firstly, nearly all of the mafic paleosol samples plot within the kaolinitisation field of the S–A–F plot indicating minimal Si loss. In the case of >2.25 Ga paleosols, trends in the S–A–F plot are obviously complicated by the mobilisation of Fe^{2+} , as evident by the two samples from the ca. 2.96 Ga Nsuze paleosol that plot within the weakly lateritised field from the enrichment of Fe^{2+} (36.7 and 20.1 wt. % $\text{Fe}_2\text{O}_{3(\text{T})}$) in the chlorite zone. Regardless all of the >2.25 Ga mafic paleosols violate the definition of laterite in terms of a lack of residual Fe^{3+} enrichment. In all of the oxidised, ≤ 2.25 Ga paleosols excluding Hekpoort Strata 1, only one (from the Drakenstein paleosol) plots outside of the kaolinitisation field into the weakly lateritised field.

The important conclusion from this analysis is that the oxidised Precambrian paleosols are far more comparable to modern non-lateritic weathering profiles such as Chhindwarra and Baynton. Only the Hekpoort Strata 1 profile remains as a possible laterite candidate (see the debate on the origin of the Fe chemistry in this paleosol, lateritisation or development under mildly oxygenated in Section 3). In the S–A–F diagram (Figure 7), 8 samples from this profile plot on a trend towards the F apex, with 3 in the ‘moderately’ lateritised and 1 in the ‘strongly’ lateritised field. The majority of these samples, however, are from the uppermost ferricrete horizon that is described with textural evidence for allochthonous Fe-enrichment (Beukes et al., 2002; Yang and Holland, 2003) such that these samples may not represent true loss of Si from *in situ* weathering processes. Overall, it is clear that of all of the documented mafic paleosols only the Hekpoort Strata 1 profile could possibly be considered a laterite in terms of Si-Fe-Al chemistry and the term would not be accurately applied to the other <2.25 Ga paleosols despite them showing Fe oxidation. Thus, the term laterite (over ‘oxisol’ for instance) should be avoided. The absence of bona fide ancient laterites may in itself have significance as it may reflect limited atmospheric O_2 concentrations and/or limited effects of organic acid from the fledging terrestrial biosphere.

6. Cr isotopes as a proxy for terrestrial oxidation

This brief review of the state of knowledge regarding paleosol redox chemistry from traditional geochemistry explains the need for information from additional proxies. In this respect, the discovery of Cr isotope fractionation in groundwater during Cr^{6+} reduction (Ellis et al., 2002) was

significant. It led to the proposal that redox reactions of Cr could have left isotopic signatures in the Precambrian surface environment with potential to fingerprint terrestrial oxidative weathering (Frei et al., 2009). Chromium has four stable isotopes (^{50}Cr , ^{52}Cr , ^{53}Cr , ^{54}Cr) and the isotope composition of natural materials is typically measured with the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio normalised to the NIST SRM979 standard and expressed in delta (δ) notation ($\delta^{53/52}\text{Cr}$).

$$\delta^{53/52}\text{Cr} = 1000 \times \{[(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{SRM979}}] - 1\}$$

Trivalent Cr is the predominant species in igneous rocks, hosted in oxides (chromite, ilmenite, magnetite, and spinel) or in Fe/Mg-bearing silicates (e.g., pyroxenes) with highest concentrations found in ultramafic and mafic rocks. The Cr isotope composition of Cr^{3+} -bearing minerals and igneous rocks is relatively constant with an average $\delta^{53/52}\text{Cr}$ of -0.124 ± 0.101 ‰ according to Schoenberg et al. (2008) or -0.079 ± 0.129 ‰ according to Farkaš et al. (2013).

The resistance of most Cr^{3+} -bearing minerals to chemical weathering reactions and the insolubility of Cr^{3+} at pH ranges typical of most surface environments, tends to lead to an overall immobile behaviour of Cr and its accumulation in soils. Nevertheless, under oxidising conditions some Cr^{3+} can be converted to Cr^{6+} . Importantly, this only occurs in the presence of Mn-oxides (Eary and Rai, 1987; Manceau and Charlet, 1992; Rai et al., 1989; Fendorf and Zasoski, 1992). Hexavalent Cr is more soluble and can be removed (predominantly as CrO_4^{2-}) from soils, although the presence of reductants (e.g., S, Fe^{2+} , and organic matter) along the pathway of aqueous Cr^{6+} transport from soils can induce back-reduction to Cr^{3+} . The oxidation of Cr (Frei et al., 2014) and its subsequent back-reduction (Ellis et al., 2002; Izbick et al., 2008; Berna et al., 2010) both appear to fractionate isotopes; the heavier isotopes of Cr are enriched in the soluble Cr^{6+} whereas the residual Cr^{3+} is enriched in the lighter isotopes. The predicted Cr isotope response of Cr redox reactions is ^{53}Cr -enrichment in the hydrosphere and ^{53}Cr -depletion in the solid reservoirs of residual Cr. Empirical measurements to date support this prediction, with river waters (Frei et al., 2014) and open seawater (Bonnand et al., 2013; Scheiderich et al., 2015) showing higher $\delta^{53/52}\text{Cr}$ and weathering profiles (Berger and Frei, 2014; Frei et al., 2014) showing predominantly lower $\delta^{53/52}\text{Cr}$ than igneous rocks, respectively.

Notwithstanding this promising emerging picture, readers are reminded that the Cr isotope system is still in its infancy with the Cr isotope composition of several reservoirs yet to be examined and some of the pathways of fractionation, such as Cr^{3+} oxidation, still poorly understood.

Nevertheless, the above model of Cr isotope fractionation has been applied as a proxy for Precambrian oxidative weathering (e.g., Frei et al., 2009; 2013, Crowe et al., 2013; Planavsky et al., 2014). Frei et al. (2009) suggested that ^{53}Cr -enriched signatures (relative to igneous

rocks/minerals) in iron formations record authigenic Cr initially sourced from Cr^{6+} formed in soils. Thus, a link was made between ancient soil formation, transport of soluble Cr into the ocean, and precipitation of the signal into the chemical sediment. The veracity of this chain of logic depends on several assumptions: 1) Oxidation of Cr^{3+} to Cr^{6+} by Mn-oxides in soils is the initial origin of all ^{53}Cr -enriched runoff; 2) at least some of the runoff survived as Cr^{6+} through transport from soils to the oceans; 3) Cr^{6+} was reduced by Fe^{2+} and co-precipitated with Fe^{3+} -oxyhydroxides quantitatively in the oceans (Døssing et al., 2011); and, 4) the Cr isotope composition of the Fe^{3+} -oxyhydroxides was transferred to the iron formation and survived undisturbed. Accordingly, the ^{53}Cr -enriched signature of iron formation throughout the Archean and Proterozoic, extending as far back as ca. 2.96 Ga, has been attributed to pulses of elevated paleo-atmospheric O_2 levels, sufficiently high to facilitate soil Mn-oxide formation (Frei et al., 2009; Crowe et al., 2013). Neoproterozoic and Phanerozoic Fe-rich sedimentary rocks are significantly more ^{53}Cr -enriched by comparison to earlier Proterozoic and Archean iron formation (Frei et al., 2009; Frei et al., 2013; Planavsky et al., 2014). This change was explained as a transition to more pronounced formation of Cr^{6+} in soils and/or a greater flux of Cr^{6+} to the oceans after the second rise of paleo-atmospheric oxygen, often referred to as the Neoproterozoic oxygenation event (NOE; Och and Shields-Zhou, 2012). A summary of the available Cr isotope data in Fe-rich marine sedimentary rocks is plotted in Figure 8a.

Two further studies (Konhauser et al., 2011; Planavsky et al., 2014) have addressed the elemental and isotopic composition of Cr in Fe-rich marine sedimentary rocks. Konhauser et al. (2011) used elemental Cr-Ti-Al systematics (Figure 8b) to show that marine authigenic Cr enrichment occurred in the early Proterozoic in the absence of any $\delta^{53/52}\text{Cr}$ excursions as reported by Frei et al. (2009). Thus, these authors questioned the prominence of the hypothesised terrestrial Cr^{6+} flux in the Archean and early Proterozoic and instead suggested that Cr^{3+} was the dominant species from terrestrial runoff, with an interval of extreme Cr^{3+} delivery near the GOE associated with acidic weathering conditions brought on by the destabilisation of crustal pyrite. Planavsky et al. (2014) further examined Cr isotope signatures in Fe-rich rocks throughout the Proterozoic leading into the Phanerozoic, finding minimal marine ^{53}Cr -enrichment prior to the NOE and also suggest a subdued flux of Cr^{6+} . Although Konhauser et al. (2011) and Planavsky et al. (2014) question the significance of the Cr isotope composition of early Proterozoic and Archean iron formation, the general model of Precambrian Cr cycling proposed by Frei et al. (2009) was still adopted.

From a mass balance perspective, Precambrian paleosols should record a ^{53}Cr -depletion as a consequence of oxidative Cr^{6+} release, similar to that observed in the Phanerozoic profiles measured (Berger and Frei, 2014; Frei et al., 2014). The Cr isotope compositions of two

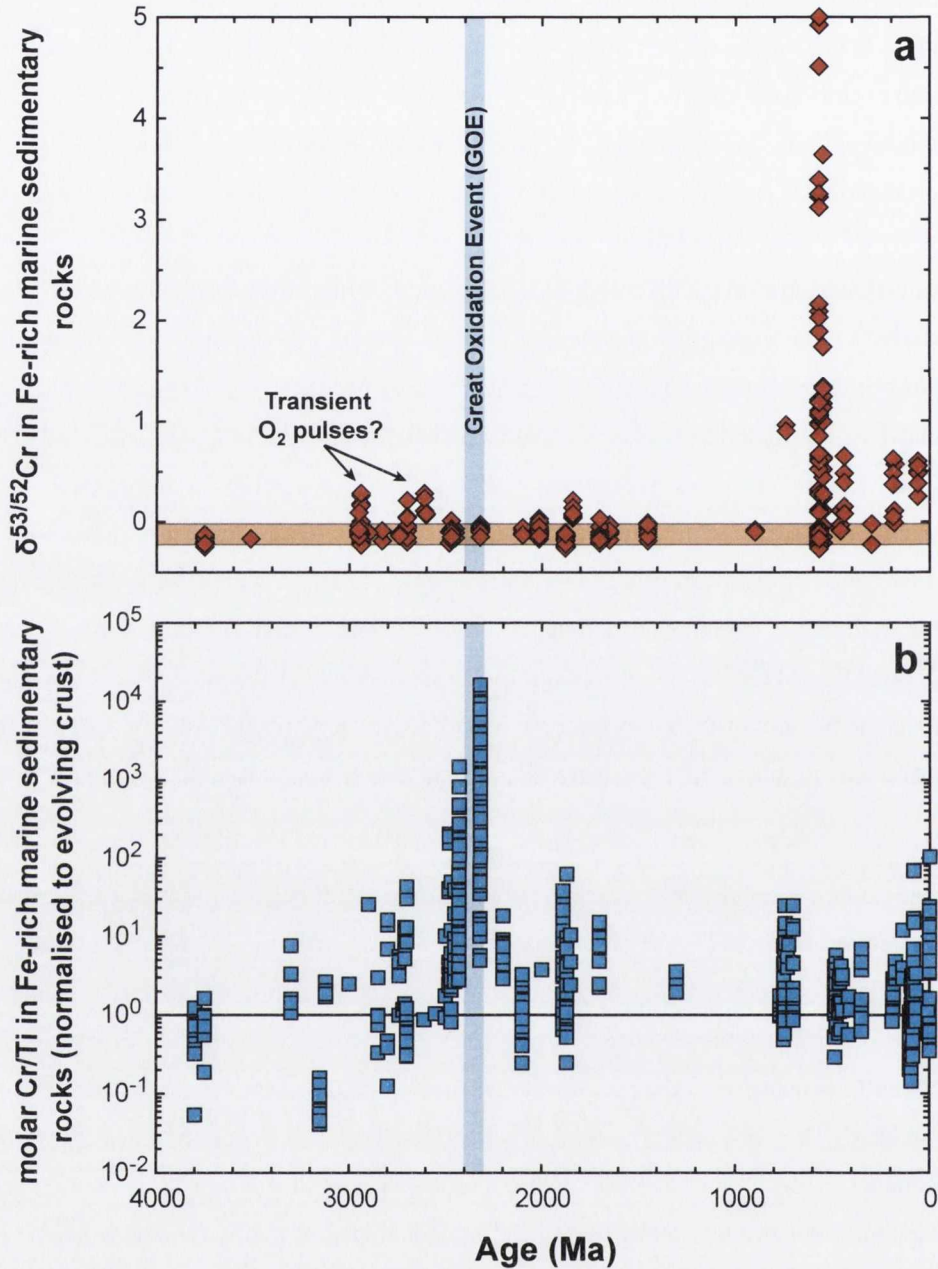


Figure 8: Compilation of Cr isotope (a) and elemental Cr-Ti (b) data for Fe-rich sedimentary rocks. Chromium isotope data are compiled from Frei et al. (2009), Frei et al. (2013); Crowe et al. (2013), and Planavsky et al. (2014) and the molar Cr/Ti ratio data are from Konhauser et al. (2011). The shaded horizontal band in (a) represents the average $\delta^{53/52}\text{Cr}$ of Cr^{3+} -bearing igneous rocks and minerals (-0.124 ± 0.101 ‰; Schoenberg et al., 2008). The ^{53}Cr -enriched signature ($\delta^{53/52}\text{Cr}$ higher than igneous average) in Archean iron formation has been interpreted as evidence for transient pulses of atmospheric O_2 through the inference of oxidative Mn-Cr cycling in soils. The elemental Cr/Ti data are presented normalised to the evolving Cr/Ti ratio in the crust as per the source of data (Konhauser et al., 2011). Extreme enrichments of Cr over Ti in the absence of ^{53}Cr -enrichment has been interpreted by Konhauser et al. (2011) as evidence for a Cr^{3+} dominated terrestrial flux questions the interpretation of oxidative Mn-Cr cycling of Frei et al. (2009).

Precambrian paleosols measured to date, the ca. 2.96 Ga Nsuze paleosol (Crowe et al., 2013) and a ca. 1.9 Ga paleosol (Frei and Polat, 2013), provide some support for this through the preservation of a ^{53}Cr -depleted signature. Thus, an active Mn-Cr redox couple is still implied from the Cr isotope data based on the current model of Frei et al. (2009). The analysis of Fe and Mn redox chemistry in this chapter, scrutinising the data from all *bona fide* paleosols, however, shows that several proxies for terrestrial oxidation are in contradiction. Soil oxidation is not recorded in the Fe redox chemistry of any definite >2.45 Ga paleosol and is also in apparent contradiction with the Mn signature preserved in all Precambrian paleosols. Further work is required to test the link between the terrestrial and marine reservoirs of Cr isotopes and better establish whether a ^{53}Cr -depleted signature in paleosols is a response unique to Cr^{3+} oxidation by Mn-oxides. This is necessary before accurate inferences about Mn-Cr in soils can be made from Cr isotopes and applied to reconstruct oxygenation events in the Precambrian.

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Chapter 7: Chromium isotope fractionation during oxidative mafic rock weathering: implications for fingerprinting paleoatmospheric oxygen

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Manuscript in preparation

Abstract

Chromium concentration, $\delta^{53/52}\text{Cr}$, and major element data are used to investigate the oxidative weathering progression of two mafic substrates temporally separated by ca. 2 Ga: a Quaternary (saprolite) basalt profile (Deccan Traps, Chhindwara, India) and the ca. 1.85 Ga Flin Flon paleosol (Manitoba, Canada). The primary objective is to better resolve the Cr isotope signatures of modern basaltic weathering environments and test the extrapolation of modern Cr isotope systematics to oxidative weathering reactions in ancient paleosols. The Flin Flon paleosol is key to testing the Cr isotope fingerprint of Precambrian oxidative weathering since it formed well after the Great Oxidation Event and exhibits near-complete oxidation of Fe(II) to Fe(III).

Minimal Cr mobility and $\delta^{53/52}\text{Cr}$ variation (-0.190 ‰ to -0.013 ‰) is observed in the Chhindwara profile, with the overall $\delta^{53/52}\text{Cr}$ range being nearly invariant within analytical uncertainty and within the range of the average igneous Earth reservoirs. These Cr isotope data are interpreted as the result of limited Cr(III) release from primary magmatic oxide minerals that would be available for oxidation by Mn oxides. Thus, despite the inference of oxidative weathering from Fe, Mn, and redox-sensitive trace elements (e.g., Ce, U), oxidation of Cr(III) to Cr(VI) is not recorded by the Cr isotope composition of the profile.

In the Flin Flon paleosol, the protolith greenstone and deepest weathering horizon exhibit negative $\delta^{53/52}\text{Cr}$ ratios (-0.151 to -0.229 ‰) comparable to igneous Earth inventory values. By contrast, substantial isotopic fractionation is observed in the overlying horizons which are influenced by oxidative subaerial weathering with significant ^{53}Cr -enrichment predominating ($\delta^{53/52}\text{Cr}$ up to +2.375 ‰). Only one sample is ^{53}Cr -depleted ($\delta^{53/52}\text{Cr}$: -0.381 ‰) relative to the greenstone protolith ($\delta^{53/52}\text{Cr}$: -0.230 ‰). Importantly, the Cr chemistry of the paleosol does not appear to be influenced by post-weathering events of metasomatism and metamorphism or the seafloor alteration event that preceded subaerial weathering. The depletion of the lighter isotopes of Cr in the Flin Flon paleosol is inconsistent with an oxidative Mn-Cr cycle comparable to modern soils. Coupled with evidence for Mn loss, presumably a result of insufficient O_2 levels in the regolith to

form many Mn-oxides, the ^{53}Cr -enrichment is interpreted to reflect the preferential loss of isotopically light Cr(III) from the profile. An isotopic effect of Cr(III) incorporation into pedogenic Fe(III)-oxides could also be a contributing factor. Regardless of which process exerted the dominant control on the $\delta^{53/52}\text{Cr}$ variation, a loss of light Cr isotopes from the profile is required and the capture of Cr with this isotope signature lower in the profile could account for ^{53}Cr -depleted areas at depth.

If the elemental and isotopic results from the Flin Flon paleosol do indeed provide evidence for the loss of Cr(III) during weathering and it can be extrapolated beyond this case, it has wider ramifications for better understanding the Precambrian Cr cycle. Most significantly, a ^{53}Cr -depleted signature in Precambrian paleosols may not uniquely fingerprint paleoatmospheric oxygen. This would have further implications for the interpretation of marine Cr signatures in deep time by suggesting that the soluble Cr flux to the oceans may not have been exclusively isotopically heavy as assumed to date. Alternative models for hydrothermal Cr flux and detrital Cr derived from the erosion of mafic or ultramafic substrates with ^{53}Cr -enriched characteristics are conceivable, and thus need to be considered as factors modifying the Cr chemistry of marine chemical sediments.

1. Introduction

The aqueous behaviour of Cr at the Earth's surface is strongly dependent on its redox state as either Cr(III) or Cr(VI) and redox transformations between these two states are accompanied by a mass-dependent fractionation of Cr isotopes (Ellis et al., 2002). As a result, Cr isotopes can be applied to trace the fate of soluble Cr(VI) in the environment (e.g., Izbicki et al., 2008; Berna et al., 2010; Wanner et al., 2012; Economou-Eliopoulos et al., 2014; Jamieson-Hanes et al., 2014) and are being explored as a proxy for Cr redox reactions on the ancient Earth surface (Frei et al., 2009, 2014; Crowe et al., 2013; Planavsky et al., 2014). Stable Cr isotope fractionation is typically expressed in delta notation as the per mil difference relative to the NIST SRM979 standard ($\delta^{53/52}\text{Cr}_{\text{SRM979}} = [(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{SRM979}}] - 1$), hereafter abbreviated as $\delta^{53/52}\text{Cr}$. Chromium(III)-bearing rocks and minerals define a relatively constant $\delta^{53/52}\text{Cr}$ range [-0.124 ± 0.101 ‰ (Schoenberg et al., 2008) or -0.079 ± 0.129 ‰ (Farkaš et al. 2013)] and only a limited number of reaction pathways have yet been isolated that result in Cr isotope fractionation from these igneous reservoir values: (i) during partial reduction of soluble Cr(VI) to Cr(III) in natural waters by Fe(II), sulphides, or organic matter (Ellis et al., 2002; Izbicki et al., 2008); (ii) during oxidative Cr cycling in soils (Frei et al., 2009; Frei et al., 2014); and, (iii) during the seafloor alteration of ultramafic rocks (Farkaš et al. 2013).

Element oxidation in soils involves a complex chain of reactions beginning with release from primary minerals during acid attack, sorption onto sites where partial oxidation can occur, and subsequent release from the site of oxidation. The oxidation of Cr(III) to Cr(VI) on the surfaces of Mn oxides is thought to be the stage at which Cr isotope fractionation occurs in soils (Crowe et al., 2013; Frei et al., 2014), although the preceding stage of acid dissolution is known to induce fractionation in other stable metal isotopes such as Fe (e.g., Brantley et al., 2004; Chapman et al., 2009; Kiczka et al., 2011) and this has yet to be thoroughly tested for Cr. Regardless of the exact mechanisms inducing Cr fractionation in soils, the end-product is soluble Cr(VI) with an isotopically heavy (^{53}Cr -enriched) signature that is transferred to rivers and seawater (Frei et al., 2014; Bonnand et al., 2013; Scheiderich et al., 2015) and the isotopically light Cr (^{53}Cr -depleted) signatures in soils relative to the associated bedrock (Berger and Frei, 2014; Frei et al., 2014) suggests that a corresponding pool of residual Cr(III) develops at the site of oxidative weathering.

When this model for Cr cycling is extrapolated to the ancient Earth, Cr isotope excursions in marine chemical sediments (Frei et al., 2009, 2011, 2013) and paleosols (Frei and Polat, 2013; Crowe et al., 2013) have been interpreted as evidence for the operation of a surficial Mn-Cr redox cycle resembling that in modern soils. Accordingly, Cr isotopes have been applied as tracer of Precambrian atmospheric O_2 fluctuations (Frei et al., 2009) and used to infer episodes of

atmospheric oxygenation well in advance of the Great Oxidation Event (GOE) at ca. 2.4-2.3 Ga (Crowe et al., 2013), the latter of which are important in establishing the first appearance of oxygenic photosynthesis on the early Earth (Lyons et al., 2014). However, the assumption that atmospheric O₂ levels were high enough to form Mn oxides in soils was challenged by Konhauser et al. (2011) and Planavsky et al., (2014). These authors instead suggest that the atmospheric O₂ levels prior to the increase in levels in the Neoproterozoic (e.g., Och and Shields-Zhou, 2012) inhibited Mn oxide formation in soils and that the terrestrial runoff may have been dominated by Cr(III) rather than Cr(VI). Thus, alternative sources of Cr isotope fractionation would be required to explain the $\delta^{53/52}\text{Cr}$ signature of Archean and early Proterozoic Fe-rich sedimentary rocks.

This study investigates the Cr chemistry of two oxidative mafic rock weathering profiles, a Quaternary saprolite profile (Deccan Traps, India) representative of a sub-recent weathering regime and the classic 1.85 Ga Flin Flon paleosol (Canada). The aim is to place new empirical constraints on the cycling of Cr in both modern and ancient oxidative weathering environments. The Flin Flon paleosol, having formed after the initiation GOE, exhibits near-complete oxidation of Fe(II) to Fe(III) (Babechuk and Kamber, 2013; Holland et al., 1989; cf. Ohmoto, 1996) and is thus ideally placed for testing the applicability of Cr isotopes to fingerprinting paleoatmospheric O₂ in earlier Proterozoic and Archean (pre-GOE) weathering profiles. The new results are considered in combination with Cr, Mn and Fe data from other mafic paleosols to discuss the land-derived flux of Cr on the early Earth.

2. Weathering profiles

2.1 Chhindwara, Deccan Traps, India (Quaternary profile)

This weathering profile spans across two identifiable basalt flows in the Deccan Traps, exposed in a quarry east of Chhindwara (22° 04.213' N, 79° 01.393' E). Its structure and chemical composition are described in detail by Babechuk et al. (2014). The upper flow (ChQB) is fully exposed and capped with a thin (~20 cm) topsoil, whereas only the upper 215 cm of the lower flow (ChQA) is exposed (Figure 1; Babechuk et al., 2014). Two samples from the centre of the upper flow represent the (least-weathered) protolith (ChQB9d and ChQB12). Overall, the saprolitic profile has progressed to a stage of intermediate weathering intensity, with chemical index of alteration (CIA) values of 35-80 and oxidative mafic index of alteration values [MIA_(O)] values of 38-71 (Figure 1a). The immobile elements show evidence of discrete change in the bulk chemistry of the juxtaposed flows, but their overall similar composition permits the treatment of most elemental trends as the result of a single weathering progression throughout. The elevated, mesa-like

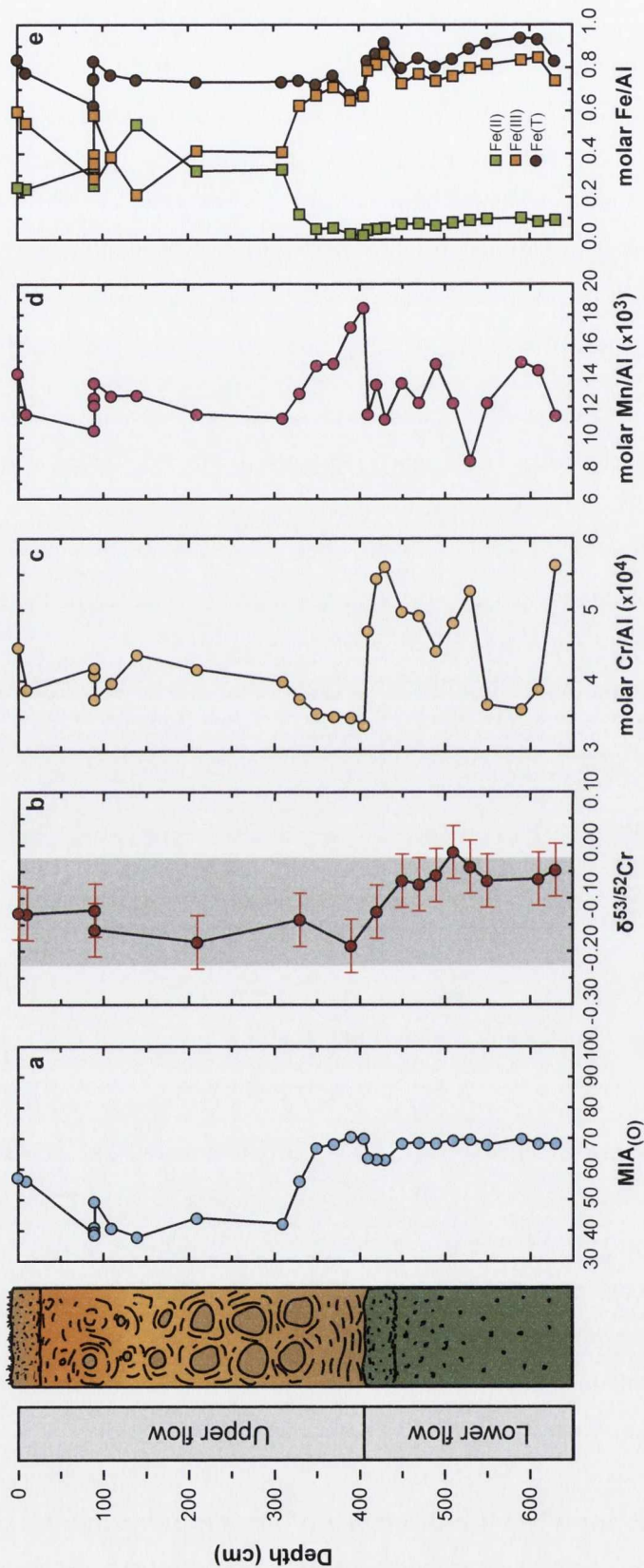
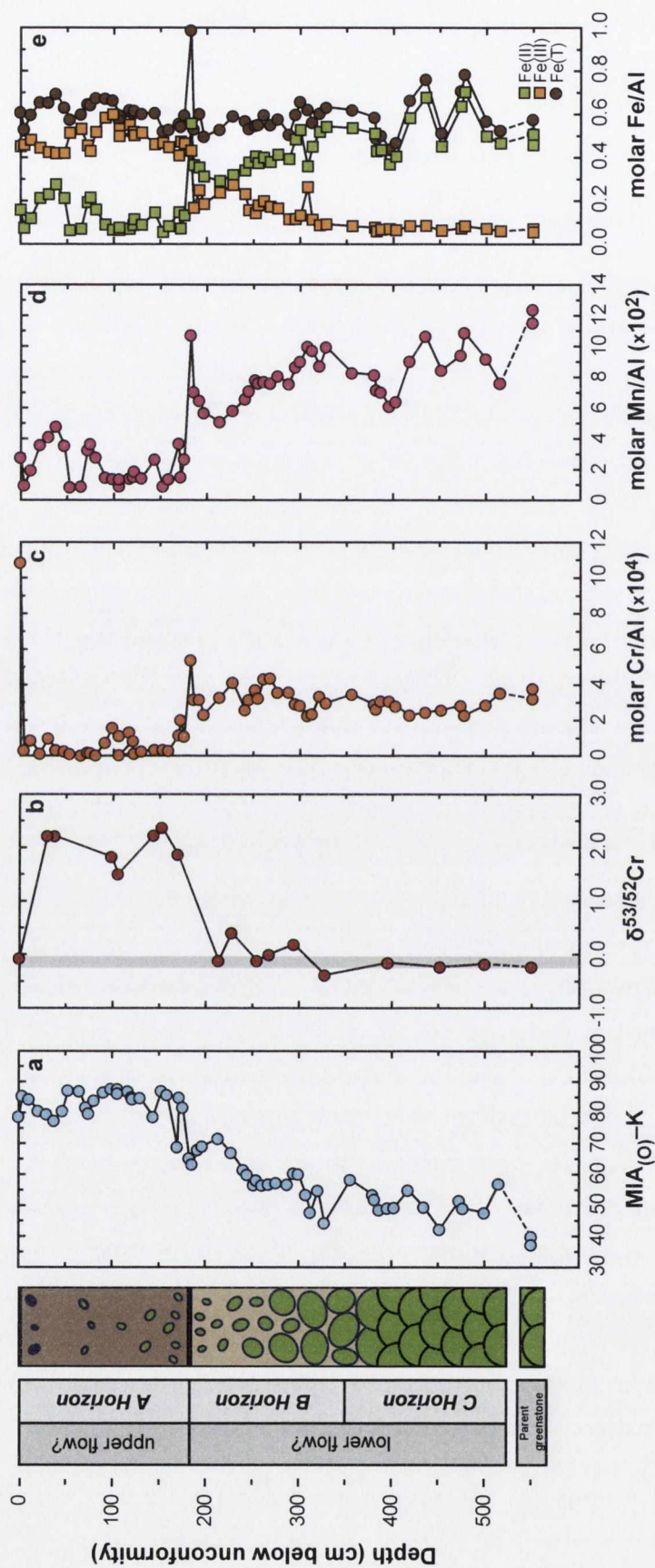


Figure 1: Chhindwara profile: (a) Mafic index of alteration for oxidative weathering [$\text{MIA}_{(\text{O})}$]; (b) Cr isotope ($\delta^{53/52}\text{Cr}$); and molar (c) Cr, (d) Mn, and (e) Fe ratios normalised to Al and plotted against depth below the soil surface. Profile sketch from Babechuk et al. (2014). The contact between the two flows (ChQA and ChQB) is illustrated. Samples ChQA 9a-d at a depth of 90 cm represent a corestone transect from centre (9d) to rim (9a). The uppermost three samples in the lower flow (ChQA10-ChQA12) constitute the porous, paleo flow-top. The grey bar in (a) represents the range in Cr isotope values of the average igneous inventory ($-0.124 \pm 0.101 \text{ ‰}$) from Schoenberg et al. (2008). The $\text{MIA}_{(\text{O})}$ is a weathering index using moles of element oxide that calculates the loss of Na, Ca, Mg, and K relative to Fe and Al; for further details of the calculation see Babechuk et al. (2014).

topography of the area isolates the profile from protracted groundwater interaction, leaving only the transformation from the magmatic to pedogenic mineralogy and the incorporation of eolian dust as plausible means of changing the Cr isotope composition in the profile from that of the protolith.

2.2 Flin Flon paleosol, Manitoba, Canada (1.85 Ga profile)

The Flin Flon paleosol is developed on a hydrothermally seafloor-altered pillow-lava greenstone that is associated with an intra-oceanic arc sequence on the western edge of the Trans Hudson Orogen (Lucas et al., 1996; DeWolfe et al., 2009a, 2009b). Subsequent to pedogenesis, the profile was partially eroded and overlain by continental (alluvial-fluvial) sandstones and conglomerates belonging to the Missi Group (Stauffer, 1990) and metamorphosed to sub-greenschist to greenschist facies during regional deformation. The geology, geochemistry, and mineralogy of an exposure of the Flin Flon paleosol was studied in detail by Holland et al. (1989) and revisited recently by Babechuk and Kamber (2013), who employed high-density sampling. Based on textural and mineralogical characteristics of the paleosol, Babechuk and Kamber (2013) divided the profile into three horizons (A, B, and C). The C horizon is the zone of deep, groundwater-saturated weathering where the profile retains most of the characteristics of the protolith greenstone (colour, induration, variability in the modal abundance of Fe-Ti oxides) and only the most mobile (Ca, Na) are depleted relative to the protolith greenstone. The B horizon is defined by the first signs of oxidative subaerial weathering (e.g., chlorite-rich corestones bounded by hematite-rich rindlets) that is evident through a colour change from green to bluish-maroon, and is characterised by the progressive upward depletion of Ca, Mg, Fe(II), and Mn. The transition into the A horizon is marked by a very sharp boundary above which the paleosol is consistently maroon in colour (apart from small, green corestones), carbonate is virtually absent, and the mobile elements [Ca, Mg, Fe(II)] are substantially depleted. The upward loss of mobile elements can be traced with the oxidative mafic index of alteration [$MIA_{(O)}$] since the Fe(II) is converted near-quantitatively to Fe(III), similar to oxidised modern weathering profiles. An immobile element concentration and ratio (e.g., Al/Ti) offset is evident between the upper (A) horizon and the lower (B and C) horizons that marks a probable pre-weathering lithological boundary preserved in the paleosol (Babechuk and Kamber, 2013). The (least-weathered) protolith composition is represented by two samples, FF021-FB1 and FF021-FB2, taken from approximately 1000-1200 cm below the unconformity. Post-weathering metasomatism of the profile is evident through the upward increase of Na and K in correspondence with the amount of illite and further by white micas (muscovite/paragonite).



3. Materials and Methods

3.1 Elemental analysis

Samples from the Chhindwara profile (n=27; Babechuk et al., 2014) and Flin Flon paleosol (n=61; Babechuk and Kamber, 2013) were powdered in an agate mill and analysed for their trace element composition at Laurentian University (LU, Sudbury, Ontario) and Trinity College Dublin (TCD, Dublin, Ireland). The method of Eggins et al. (1997) was followed, incorporating modifications described in Kamber (2009) and Babechuk et al. (2010). For analysis, 100 mg of sample powder was digested with HF-HNO₃ (4:1) in closed, Savillex Teflon® beakers at ~160 °C for 72-90 hours. These were then evaporated, concentrated HCl (1 mL) was introduced to liberate any residual metals associated with organic material, and then evaporated once more. Final conversion using two 1 mL aliquots of concentrated HNO₃ was performed and the nitrate residue product was dissolved in a 20 % HNO₃ stock solution. Approximately 4 % of this stock was gravimetrically diluted to produce a 2 % HNO₃ solution with an internal standard mixture containing ⁶Li, Rh, Re, Bi, and ²³⁵U for solution quadrupole ICP-MS analysis. This was performed on a Thermo Scientific XSeriesII at LU and a Thermo Scientific iCap-Qs at TCD. Measurements on the latter instrument were repeat analyses of one batch of samples (23 of 61) that were undertaken due to detector-associated instability evident for some elements in the XSeriesII data from LU. In this case, stock solutions prepared at LU were transported to TCD in their Savillex beakers, with an intermittent storage interval of ca. 22 months prior to the repeat analysis. The separate measurements produced identical concentrations of Cr in solution, indicating that these data were not affected by detector instability or long-term acid storage.

During the experimental sessions in both laboratories, sample unknowns were preceded by blanks, calibration (USGS rock standard W-2a) and quality control standards (USGS rock standards BCR-2 and BIR-1), and bracketed with monitor samples (one every 5-7 unknowns) for external drift correction (Eggins et al., 1997). The internal standard and external drift corrected data were calibrated using a W-2a Cr concentration of 92790 ppb. Precision and accuracy are monitored using the long-term reproducibility of concentrations in mafic USGS rock standards (e.g., Kamber, 2009; Babechuk et al., 2010; Marx and Kamber, 2010). For Cr, the estimated precision is approximately 3 % (2σ RSD).

3.2 Cr isotope analysis

The Cr concentration and Fe(II)/Fe(III) topology (determined by potentiometric titration; Babechuk and Kamber, 2013) of both profiles was used to guide selection of samples for Cr isotope analysis. A calculated mass of powder to yield sufficient chromium for isotope analysis (5-

10 µg) and an adequate amount of the ^{50}Cr - ^{54}Cr double spike solution were mixed in Teflon® beakers. Sample digestion was achieved with a HF-HNO₃ mixture, followed by HCl addition and final uptake in HNO₃ similar to the element analysis protocol described above. Chromium was separated following a three-step method to remove the matrix and minimise isobaric interferences (^{54}Fe , ^{50}Ti , and ^{50}V). Full details of the ^{50}Cr - ^{54}Cr double spike calibration, chemical separation of Cr, and data processing are described in Schoenberg et al. (2008). One batch of samples, however, was treated with a different laboratory protocol, again using a three-step method to purify chromium from the sample matrices (Yamakawa et al. 2009). This method first separates Fe from all other elements including Cr by anion exchange chromatography. Chromium purification from all other elements is then accomplished in two further separation steps using cation exchange chromatography. Two samples (ChQA7 and FF021A-009), one from each profile, were treated with both methods and yield identical results (Tables 1 and 2).

Chromium isotope analyses were performed on a ThermoFisher Scientific NeptunePlus MC-ICP-MS using medium- or high-resolution (Weyer and Schwieters, 2003) in four separate analytical sessions at the University of Tuebingen, Germany. For the isotope measurements, approximately 0.5 to 1 µg of sample chromium was aspirated using the instrument's standard spray chamber yielding Cr signal intensities in sample unknowns ranging from approximately 1 to 5 V for ^{52}Cr using $10^{11} \Omega$ resistors, depending on analyte concentration and instrumental resolution mode. The Cr isotope ratios were corrected for isobaric interferences by monitoring the ^{49}Ti , ^{51}V and ^{56}Fe beams. Instrumental mass bias, Cr isotope ratios, and the Cr concentrations were calculated from the double spike deconvolution method described in Schoenberg et al. (2008).

In accordance with other Cr isotope studies, the $^{53}\text{Cr}/^{52}\text{Cr}$ ratios are reported in delta notation, normalised to NIST SRM979 for inter-laboratory comparison using the average value for the standard during each individual analytical session. For simplification, $\delta^{53/52}\text{Cr}$ are expressed in ‰ (per mil). The repeated measurement of SRM979 (internally normalised) and the in-house Merck Cr(III) standard returned average $\delta^{53/52}\text{Cr}$ values and 2 standard deviations of $0.000 \pm 0.020 \text{ ‰}$ ($n=31$) and $-0.433 \pm 0.027 \text{ ‰}$ ($n=18$), respectively, over the combined analytical sessions, in good agreement with other studies following the same method (Schoenberg et al., 2008; Zink et al., 2010). The reproducibility of $\delta^{53/52}\text{Cr}$ in natural samples is conservatively estimated as 0.05 ‰ (Schoenberg et al., 2008), which is the value used in all plots of Cr isotope data. Full procedural duplicates on samples from both profiles were performed to further assess the external reproducibility. Full procedural blanks for Cr ranged from 24 to 28 ng for the first and 0.6 ng for the second chromium purification procedure, respectively, and were negligible relative to the total amount of digested sample chromium.

The Cr concentrations calculated from the MC-ICP-MS analysis and the externally calibrated SQ-ICP-MS method in this study agree very well ($r^2=0.999$).

4. Results

Aluminium is used as the immobile, normalising element in this study to assess relative gains and losses of Cr, Mn, and Fe. Elemental abundance and Cr isotope data are reported for the Chhindwara profile and the Flin Flon paleosol in Tables 1 and 2, respectively. The mafic index of alteration for oxidative weathering [$MIA_{(O)}$; Babechuk et al. (2014)], molar Cr-Mn-Fe-Al data, and $\delta^{53/52}\text{Cr}$ are presented for the Chhindwara profile in Figure 1 and for the Flin Flon paleosol in Figure 2.

4.1 Chhindwara profile

Apart from the surficial soil material, the weathering intensity of the upper flow increases at the finer-grained and banded section at its base; this is evidenced by a sharp increase in pedogenic phyllosilicates and oxides. The oxidation of Fe(II) to Fe(III) increases from the centre of corestones outwards, towards the soil surface, and downwards towards the base of the flow, as evident by the decrease in Fe(II)/Al and corresponding increase in Fe(III)/Al on Figure 1e (Babechuk et al., 2014). The Cr concentrations in the protolith samples are 60.5 ppm (ChQB9d) and 58.7 ppm (ChQB12) and the Cr concentrations vary from 77.6 to 55.0 ppm in the remaining samples of the upper flow. The increase in weathering intensity at the base of the flow is accompanied by lower Cr/Al ratios and increasing Mn/Al ratios (samples ChQB5-ChQB1; Figure 1). By contrast, the lower flow, is more highly and consistently weathered, exemplified by the higher degree of Fe(II) oxidation and more constant Fe(II)/Fe(III) ratio, and exhibits an offset in Cr/Al, Mn/Al, and Fe/Al ratios. The Cr concentration ranges from 56.8 to 94.2 ppm and the Mn/Al and Cr/Al ratios are more variable within the flow and broadly antithetic.

The $\delta^{53/52}\text{Cr}$ values of the weathering profile are nearly invariable within measurement uncertainty and are within the range of the average igneous Earth (Schoenberg et al., 2008). The upper flow, ranging from -0.123 to -0.190 ‰, defines an average of -0.150 ± 0.06 ‰ (2SD), with the base (ChQB2) exhibiting the most isotopically light $\delta^{53/52}\text{Cr}$ value (-0.190 ‰). In general, the $\delta^{53/52}\text{Cr}$ values of the lower flow are offset relative to the upper flow, similar to the element ratios, towards heavier values that range from -0.013 to -0.125 ‰.

Table 1: Chhindwara weathering profile

Sample	Notes	Depth (cm)	Cr (ppm) <i>Q-ICP-MS</i>	Cr (ppm) <i>MC-ICP-MS</i>	$\delta^{53/52}\text{Cr}_{\text{SRM979}}$	2SE	MnO wt. %	FeO wt. %	Fe ₂ O ₃ (T) wt. %
ChQB11	Soil	Upper flow	77.58	75.44	-0.128	0.028	0.30	5.20	19.92
ChQB10	Soil	Upper flow	67.19	65.74	-0.130	0.027	0.24	4.97	18.16
ChQB9a	Corestone	Upper flow	55.53	56.70	-0.160	0.029	0.25	4.71	17.20
ChQB9b	Corestone	Upper flow	57.14				0.23	6.58	15.42
ChQB9c	Corestone	Upper flow	56.16				0.22	7.20	15.23
ChQB9d	Corestone; Parent rock	Upper flow	60.54	60.01	-0.123	0.030	0.20	6.55	13.36
ChQB8		Upper flow	54.96				0.23	7.00	15.60
ChQB12	Parent rock	Upper flow	58.73				0.23	9.75	15.07
ChQB7		Upper flow	62.16	61.99	-0.183	0.025	0.22	6.18	15.73
ChQB6		Upper flow	57.57				0.21	6.17	15.40
ChQB5		Upper flow	62.74	60.50	-0.141	0.023	0.26	2.42	16.82
ChQB4		Upper flow	64.84				0.31	1.10	17.14
ChQB3		Upper flow	63.87				0.31	1.18	17.97
ChQB2		Upper flow	68.07	67.52	-0.190	0.027	0.38	0.60	16.74
ChQB1		Upper flow	63.61				0.39	0.47	16.40
ChQA12		Lower flow	72.01				0.20	0.82	16.23
ChQA11		Lower flow	77.68	76.97	-0.125	0.014	0.22	0.85	15.91
ChQA10		Lower flow	79.52				0.18	0.92	16.57
ChQA9		Lower flow	83.47	82.54	-0.067	0.015	0.25	1.38	16.59
ChQA8		Lower flow	80.59	79.70	-0.074	0.019	0.22	1.37	17.04
ChQA7		Lower flow	74.25	75.29	-0.057	0.013	0.27	1.24	16.50
ChQA7rep				75.65	-0.066	0.023			
ChQA6		Lower flow	79.39	79.93	-0.013	0.016	0.22	1.47	16.97
ChQA5		Lower flow	84.05	83.03	-0.041	0.015	0.15	1.64	17.65
ChQA4		Lower flow	56.77	57.82	-0.067	0.016	0.21	1.71	17.59
ChQA3		Lower flow	56.80				0.26	1.81	18.39
ChQA2		Lower flow	60.46	60.11	-0.064	0.018	0.25	1.51	18.21
ChQA1		Lower flow	94.17	95.19	-0.047	0.017	0.21	1.71	17.18

*Major element data and MIA values were reported previously in Babechuk et al. (2014)

Al ₂ O ₃	TiO ₂	MIA ₍₀₎	ΣFe/Al	Fe ²⁺ /Al	Fe ³⁺ /Al	Mn/Al	Cr/Al
wt. %	wt. %		molar	molar	molar	molar	molar
15.17	3.32	57	0.83843	0.24324	0.59520	0.01421	0.00045
14.92	2.78	56	0.77716	0.23638	0.54079	0.01156	0.00039
13.22	2.33	50	0.83073	0.25282	0.57792	0.01359	0.00037
13.11	2.31	41	0.75101	0.35615	0.39486	0.01261	0.00041
13.03	2.24	40	0.74631	0.39211	0.35421	0.01213	0.00041
13.69	2.36	39	0.62312	0.33951	0.28361	0.01050	0.00042
12.98	2.35	41	0.76739	0.38268	0.38471	0.01273	0.00040
12.93	2.23	38	0.74418	0.53508	0.20910	0.01278	0.00044
13.70	2.23	44	0.73312	0.32010	0.41302	0.01154	0.00042
13.39	2.32	42	0.73435	0.32698	0.40738	0.01127	0.00040
14.48	2.55	56	0.74169	0.11859	0.62310	0.01290	0.00037
15.14	2.67	67	0.72285	0.05156	0.67130	0.01472	0.00035
14.99	2.59	68	0.76544	0.05586	0.70958	0.01486	0.00035
15.85	2.72	71	0.67436	0.02686	0.64750	0.01723	0.00035
15.16	2.58	70	0.69073	0.02200	0.66873	0.01849	0.00034
12.44	2.27	64	0.83304	0.04677	0.78626	0.01155	0.00047
11.72	2.43	63	0.86678	0.05146	0.81531	0.01349	0.00054
11.53	2.52	63	0.91761	0.05662	0.86099	0.01122	0.00056
13.23	3.04	68	0.80067	0.07402	0.72665	0.01358	0.00050
12.86	2.91	69	0.84605	0.07560	0.77045	0.01229	0.00049
13.08	2.91	68	0.80546	0.06727	0.73818	0.01483	0.00044
12.87	2.92	69	0.84192	0.08105	0.76087	0.01228	0.00048
12.66	3.10	70	0.89018	0.09192	0.79825	0.00852	0.00053
12.28	3.03	68	0.91460	0.09881	0.81579	0.01229	0.00037
12.50	3.10	70	0.93937	0.10275	0.83662	0.01495	0.00036
12.46	3.03	68	0.93316	0.08600	0.84717	0.01442	0.00039
13.19	2.97	68	0.83166	0.09200	0.73966	0.01144	0.00056

Table 2: Flin Flon paleosol

Sample	Notes		Depth (cm)	Cr (ppm)	Cr (ppm)	$\delta^{53/52}\text{Cr}_{(\text{SRM979})}$	2SE	MnO
				Q-ICP-MS	MC-ICP-MS			wL %
FF021A-001	A horizon	Upper flow?	0	200.10	197.63	-0.070	0.030	0.07
FF021A-002	A horizon	Upper flow?	4	4.92				0.02
FF021A-003	A horizon	Upper flow?	11	13.21				0.04
FF021A-005	A horizon	Upper flow?	21	2.24				0.08
FF021A-007	A horizon	Upper flow?	30	16.01	15.60	2.219	0.024	0.09
FF021A-009	A horizon	Upper flow?	38	5.34	5.19	2.220	0.026	0.10
FF021A-009 rep					5.36	2.218	0.030	
FF021A-010	A horizon	Upper flow?	47	4.46				0.08
FF021A-011	A horizon	Upper flow?	53	2.18				0.02
FF021A-014	A horizon	Upper flow?	65	0.69				0.02
FF021A-016/017	A horizon	Upper flow?	72	3.63				0.08
FF021A-018	A horizon	Upper flow?	75	3.42				0.09
FF021A-020	A horizon	Upper flow?	81	0.89				0.06
FF021A-023	A horizon	Upper flow?	91	11.13				0.03
FF021A-027	A horizon	Upper flow?	99	25.12	24.50	1.829	0.037	0.03
FF021A-030	A horizon	Upper flow?	106	18.09	18.06	1.505	0.029	0.02
FF021A-035	A horizon	Upper flow?	117	20.55				0.03
FF021A-037	A horizon	Upper flow?	121	12.20				0.03
FF021B-039	A horizon	Upper flow?	106	1.01				0.03
FF021B-043	A horizon	Upper flow?	122	2.14				0.04
FF021B-046	A horizon	Upper flow?	130	4.05				0.03
FF021B-049	A horizon	Upper flow?	144	6.01	5.91	2.230	0.033	0.06
FF021B-052	A horizon	Upper flow?	153	5.73	5.80	2.375	0.030	0.02
FF021B-054/055	A horizon	Upper flow?	159	4.84				0.03
FF021B-057	A horizon	Upper flow?	170	16.47	16.01	1.873	0.033	0.07
FF021B-058	A horizon	Upper flow?	172	29.53				0.03
FF021B-059	A horizon	Upper flow?	176	15.17				0.05
FF021B-061			183	95.96				0.26
FF021B-062	B horizon	Lower flow?	186	46.36				0.14
FF021B-063/064	B horizon	Lower flow?	192	50.51				0.14
FF021B-065	B horizon	Lower flow?	197	39.09				0.13
FF021B-067	B horizon	Lower flow?	214	52.13	52.27	-0.110	0.020	0.11
FF021C-071	B horizon	Lower flow?	228	67.51	65.77	0.406	0.024	0.13
FF021C-072B	B horizon	Lower flow?	241	40.63				0.14
FF021C-074	B horizon	Lower flow?	245	52.50				0.16
FF021C-076	B horizon	Lower flow?	252	59.47				0.17
FF021C-077	B horizon	Lower flow?	255	53.26	54.03	-0.112	0.035	0.17
FF021C-079	B horizon	Lower flow?	261	70.16				0.17
FF021C-080	B horizon	Lower flow?	268	71.90	70.89	0.001	0.024	0.17
FF021C-081	B horizon	Lower flow?	276	61.84				0.19
FF021C-082/083	B horizon	Lower flow?	288	59.20				0.17
FF021C-084	B horizon	Lower flow?	295	49.83	47.37	0.187	0.037	0.20
FF021C-085/086	B horizon	Lower flow?	300	46.40				0.20
FF021C-088/089	B horizon	Lower flow?	308	30.04				0.18
FF021C-090	B horizon	Lower flow?	313	25.01				0.14
FF021C-092	B horizon	Lower flow?	321	45.24				0.16
FF021C-095	B horizon	Lower flow?	328	30.76	29.03	-0.381	0.028	0.14
FF021C-101	C horizon	Lower flow?	356	55.40				0.18
FF021D-102	C horizon	Lower flow?	380	44.43				0.17
FF021D-103	C horizon	Lower flow?	382	37.89				0.14
FF021D-104	C horizon	Lower flow?	387	45.05				0.13
FF021D-106	C horizon	Lower flow?	396	44.52	44.66	-0.151	0.031	0.12
FF021D-108	C horizon	Lower flow?	403	41.85				0.13
FF021E-110	C horizon	Lower flow?	418	33.67				0.18
FF021E-113	C horizon	Lower flow?	435	33.86				0.20
FF021E-116	C horizon	Lower flow?	452	31.48	29.84	-0.229	0.027	0.14
FF021E-120	C horizon	Lower flow?	473	39.75				0.18
FF021E-121	C horizon	Lower flow?	477	29.48				0.19
FF021F-LWB	C horizon	Lower flow?	500	41.41	40.59	-0.174	0.017	0.18
FF021H-LWB	C horizon	Lower flow?	515	54.62				0.16
FF021-FB1	Parent greenstone		1000-1200	45.96				0.24
FF021-FB2	Parent greenstone		1000-1200	55.62	54.70	-0.230	0.026	0.23

*Major element and MIA values were reported previously in Babechuk and Kamber (2013)

Chapter 7

FeO	Fe ₂ O ₃ (T)	Al ₂ O ₃	TiO ₂	MIA _(O) -K	ΣFe/Al	Fe ²⁺ /Al	Fe ³⁺ /Al	Mn/Al	Cr/Al
wt. %	wt. %	wt. %	wt. %		molar	molar	molar	molar	molar
4.03	17.25	18.05	1.55	79	0.610207	0.158432	0.451775	0.002787	0.001087
1.53	12.18	14.61	0.78	85	0.532307	0.074311	0.457996	0.000984	0.000033
2.43	13.72	14.62	0.81	84	0.599200	0.117943	0.481257	0.001966	0.000089
4.77	16.40	15.94	0.90	81	0.656933	0.212346	0.444587	0.003607	0.000014
5.08	16.08	15.67	0.90	80	0.655213	0.230043	0.425170	0.004128	0.000100
5.82	16.31	14.96	0.89	77	0.696126	0.276061	0.420064	0.004804	0.000035
4.82	16.01	16.16	0.88	81	0.632580	0.211651	0.420929	0.003558	0.000027
1.50	15.12	16.73	0.95	87	0.577060	0.063622	0.513438	0.000859	0.000013
1.54	14.83	15.75	0.87	87	0.601210	0.069383	0.531826	0.000913	0.000004
4.77	17.81	17.53	0.96	82	0.648705	0.193086	0.455619	0.003280	0.000020
5.34	17.78	17.62	0.99	80	0.644305	0.215055	0.429249	0.003671	0.000019
3.44	16.28	15.36	0.85	84	0.676750	0.158921	0.517829	0.002807	0.000006
1.83	15.25	14.44	0.81	87	0.674323	0.089929	0.584394	0.001493	0.000076
1.43	15.99	15.35	0.84	88	0.665128	0.066106	0.599022	0.001405	0.000160
1.42	14.50	15.51	0.86	88	0.596927	0.064967	0.531961	0.000927	0.000114
1.49	14.63	15.03	0.83	87	0.621514	0.070346	0.551167	0.001434	0.000134
1.73	13.28	14.00	0.81	85	0.605669	0.087686	0.517983	0.001540	0.000085
1.65	14.02	15.59	0.90	86	0.574205	0.075102	0.499103	0.001383	0.000006
2.46	14.76	15.26	0.85	85	0.617586	0.114392	0.503194	0.001884	0.000014
1.87	14.09	14.91	0.83	85	0.603391	0.088998	0.514393	0.001446	0.000027
3.31	15.37	16.16	0.89	79	0.607292	0.145345	0.461947	0.002668	0.000036
1.22	12.87	15.71	0.87	87	0.523080	0.055106	0.467974	0.000915	0.000036
1.81	12.91	15.56	0.86	86	0.529763	0.082544	0.447220	0.001386	0.000030
2.83	11.88	13.60	0.75	69	0.557754	0.147660	0.410095	0.003699	0.000119
1.43	12.12	14.21	0.82	85	0.544595	0.071410	0.473186	0.001517	0.000204
2.49	12.52	13.40	0.75	82	0.596575	0.131859	0.464716	0.002682	0.000111
13.68	26.98	17.41	1.13	65	0.989483	0.557573	0.431910	0.010733	0.000540
7.33	11.89	14.25	0.57	63	0.532761	0.365009	0.167752	0.007061	0.000319
7.73	14.64	15.49	0.70	68	0.603469	0.354114	0.249356	0.006495	0.000320
7.22	12.80	16.41	0.61	69	0.498043	0.312207	0.185836	0.005693	0.000234
6.37	12.86	15.48	0.59	72	0.530439	0.292000	0.238439	0.005107	0.000330
7.20	14.85	16.00	0.75	67	0.592614	0.319321	0.273293	0.005839	0.000414
7.32	13.64	15.26	0.60	62	0.570723	0.340385	0.230337	0.006593	0.000261
8.59	13.54	16.18	0.65	60	0.534325	0.376729	0.157596	0.007107	0.000318
8.94	13.44	15.61	0.62	57	0.549746	0.406396	0.143350	0.007827	0.000374
8.44	13.88	16.02	0.64	58	0.553213	0.373847	0.179366	0.007626	0.000326
8.93	14.83	15.83	0.66	57	0.598171	0.400299	0.197872	0.007718	0.000435
8.60	13.89	16.05	0.63	57	0.552577	0.380223	0.172354	0.007612	0.000439
9.85	15.32	16.91	0.68	57	0.578470	0.413340	0.165130	0.008075	0.000359
8.94	12.82	16.13	0.60	57	0.507480	0.393294	0.114186	0.007574	0.000360
11.31	15.59	16.59	0.74	60	0.600019	0.483761	0.116258	0.008664	0.000295
11.84	16.44	15.93	0.79	60	0.658948	0.527412	0.131536	0.009023	0.000286
6.55	12.62	12.94	0.51	54	0.622717	0.359188	0.263529	0.009997	0.000228
6.55	9.11	10.33	0.41	48	0.563097	0.449941	0.113156	0.009740	0.000237
9.62	12.48	13.16	0.56	55	0.605514	0.518721	0.086793	0.008738	0.000337
7.70	10.00	10.09	0.37	44	0.632811	0.541519	0.091292	0.009972	0.000299
11.81	15.17	15.60	0.70	58	0.620907	0.537205	0.083702	0.008292	0.000348
10.79	13.78	14.97	0.60	54	0.587750	0.511463	0.076287	0.008161	0.000291
8.49	10.74	14.01	0.55	52	0.489476	0.430015	0.059461	0.007182	0.000265
8.15	10.46	13.27	0.49	49	0.503299	0.435814	0.067485	0.007040	0.000333
7.32	9.69	14.08	0.56	49	0.439427	0.368912	0.070515	0.006125	0.000310
8.33	10.72	14.56	0.68	49	0.470109	0.405974	0.064135	0.006417	0.000282
11.75	14.92	14.31	0.59	55	0.665725	0.582657	0.083068	0.009040	0.000231
12.87	16.09	13.47	0.68	49	0.762700	0.677993	0.084707	0.010671	0.000246
7.58	9.59	11.89	0.53	42	0.514994	0.452378	0.062616	0.008462	0.000260
12.29	15.23	13.70	0.58	52	0.709814	0.636569	0.073245	0.009442	0.000284
12.41	15.43	12.53	0.47	49	0.786285	0.702805	0.083480	0.010898	0.000231
9.89	12.56	14.06	0.57	48	0.570387	0.499143	0.071244	0.009201	0.000289
9.91	12.45	15.08	0.63	57	0.527149	0.466323	0.060826	0.007625	0.000355
9.95	12.59	13.92	0.62	40	0.577500	0.507222	0.070278	0.012391	0.000324
9.25	11.51	14.32	0.53	37	0.513213	0.458367	0.054846	0.011543	0.000381

4.2 Flin Flon paleosol

The behaviour of Mn and Fe in the profile displayed in Figure 2 was described in Babechuk and Kamber (2013). Briefly, Mn is lost upwards in the profile and Mn in the B and C horizons is hosted predominantly in chlorite and carbonate, both indicative of loss and re-distribution as Mn(II). Iron shows upwards oxidation and near-complete retention in the profile (constant total Fe/Al).

The Cr concentration in the two protolith greenstone samples, FF021-FB1 and FF021-FB2, is 46.0 and 55.6 ppm respectively. The $\delta^{53/52}\text{Cr}$ of the latter sample is -0.230‰ , near to the range of the average igneous inventory proposed by Schoenberg et al. (2008). The Cr concentration in the C horizon of the paleosol ($>350\text{ cm}$ depth) is heterogeneous about an average value of $41\pm16\text{ ppm}$ (2SD, $n=13$). Three samples from this horizon (FF021D-106, FF021E-116, FF021F-LWB) have consistent $\delta^{53/52}\text{Cr}$ values with an average of $-0.185 \pm 0.08\text{‰}$ (2SD). The overlying B horizon is much more variable in its Cr concentration and $\delta^{53/52}\text{Cr}$ values, ranging from 25 to 72 ppm and -0.381‰ to $+0.406\text{‰}$, respectively. The Cr concentration and $\delta^{53/52}\text{Cr}$ of the two lower horizons (B and C) exhibit a crude correlation and both of these parameters independently correlate with concentration variations of the high field strength elements (e.g., Ti).

In the A horizon, Cr concentrations are significantly lower relative to the underlying paleosol, ranging from 29.5 ppm to 0.69 ppm, with two samples excluded – the uppermost sample (FF021A-001) and the Cr enriched band in the paleosol that separates the A and B horizon (FF021B-061). Two offset sampling zones in the A horizon show slight variation in Cr concentration at equivalent depths. The paleosol in this horizon exhibits a high and consistently positive $\delta^{53/52}\text{Cr}$ signature ($+1.62$ to $+2.22\text{‰}$), with an average of $+2.04 \pm 0.62\text{‰}$ (2SD, $n=7$). The uppermost sample of the profile, FF021A-001, appears to be a mixture of the paleosol and overlying Missi Group sediment based on the enrichments of elements associated with detrital minerals, including Cr (200 ppm). Isotopically, this sample contrasts with the paleosol immediately underlying with a $\delta^{53/52}\text{Cr}$ of -0.070‰ . Most importantly, these values are entirely dissimilar to those reported for modern oxidative weathering substrates, and constitute the most highly fractionated values yet measured in a regolith.

5. Discussion

5.1 Cr behaviour during modern oxidative weathering and delivery to the hydrosphere

Manganese oxides [Mn(III) or Mn(IV)] represent the only significant oxidant of Cr(III) in soils (e.g., Eary and Rai, 1987; Manceau and Charlet, 1992; Rai et al., 1989; Fendorf and Zasoski, 1992; Cooper, 2002). Chromium(III) sorbs to the surfaces of Mn oxides where it is converted, through still poorly understood mechanisms, to soluble Cr(VI). This redox transformation ultimately promotes the mobility of Cr from soils (e.g., Becquer et al., 2003; Mills et al., 2011; Garnier et al., 2013) and into groundwater and runoff (e.g., Ball and Izbicki, 2004; Oze et al., 2007). Subsequent to Cr(VI) formation, retention of this species in weathering profiles may be promoted by adsorption on Fe (oxyhydr)oxides (e.g., Becquer et al., 2003; Fandeur et al., 2009). The availability of Cr(III) in a soil prior to oxidation is often a strong function of the protolith mineralogy. When Cr(III) is hosted in magmatic oxides (e.g., Cr-spinel, chromite, magnetite) it has a greater retention during chemical weathering due to the resistance of these oxide to chemical weathering, as observed in Cr-spinel dominated soils (Oze et al., 2004). By contrast, when Cr(III) is hosted in silicates (e.g., pyroxene, Cr-chlorite) the potential for Cr(VI) generation is enhanced due to the greater weathering susceptibility of these minerals.

Oxidation of the Chhindwara basalt during weathering is well-established through the colour progression and substantial increase in Fe(III)/Fe(II). The increase in Mn/Al towards the base of the upper flow also points to an accumulation of Mn oxides. Further, both positive and negative Ce anomalies occur in the profile indicating that the Fe and Mn oxides influenced the redox cycling of other elements (Babechuk et al., 2014). Despite these hallmark features of oxidative weathering, the Cr isotope composition and Cr/Al ratios in the profile change only minimally. The topologies of Mn/Al and Cr/Al in the profile are broadly antithetic (Figure 1) and could hint at the formation of Cr(VI) and its subsequent depletion in areas of Mn enrichment. The most ^{53}Cr -depleted sample (ChQB2: $\delta^{53/52}\text{Cr}$ of -0.190) does occur within an area of apparent Cr depletion and Mn enrichment, consistent with the loss of Cr(VI), although this sample is still within the error of other samples in the same flow. Overall, the minimal variation in $\delta^{53/52}\text{Cr}$ and Cr/Al in the Chhindwara profile demonstrates that Cr(III) oxidation was either inhibited, or minimal, at the range of recorded chemical weathering intensity. Given a lack of obvious reducers [e.g., free Fe(II), sulphide] in the profile capable of back-reducing generated Cr(VI), this minimal oxidation is most likely attributed to limited release of Cr(III) from magmatic oxide minerals during chemical attack. Thus, the chemical resistance of the Cr(III)-bearing minerals limits the soluble Cr(III) available for oxidation by Mn oxides and inhibits Cr isotope fractionation or the isotopic effect of this process is masked by the much greater pool of remaining Cr(III) in the magmatic minerals.

Higher magnitude Cr isotope fractionation is reported in top soils or weathering profiles that have reached higher degrees of chemical alteration (Berger and Frei, 2014; Frei et al., 2014), indicating that specific soil types or horizons with enhanced formation of Mn oxides and Cr(III) release apparently are more significant in generating Cr(VI) and inducing Cr isotope fractionation. These more advanced weathering profiles are often strongly influenced by organic acids generated by the decay of vegetation and are associated with climate conditions favouring intense leaching. These observations are relevant to the Precambrian paleosol record since the roles of soil biota in redox processes and true lateritic weathering conditions in these paleosols are equivocal (Rye and Holland, 1998; Beukes et al., 2002; Yang and Holland, 2003).

The chemical weathering of the Chhindwara profile is superimposed on two separate lava flows that are demarked chemically with an offset in immobile element ratios (Babechuk et al., 2015). An offset in Cr/Al and $\delta^{53/52}\text{Cr}$ also corresponds to the lava flow boundary and suggests that these ratios also record a subtle difference in the protolith chemistry. If correct, these data would indicate that small natural Cr isotopic differences in magmatic sources, which so far remain undetected, might exist.

5.2 Element and isotope behaviour of Cr in the Flin Flon paleosol

5.2.1 Pre- and post-subaerial weathering events

In addition to hydrothermal alteration of the protolith prior to weathering, the profile that developed on the greenstone was also buried, metasomatised, and subjected to sub-greenschist to greenschist-facies metamorphism. Before pedogenesis can be accepted as a driver of Cr behaviour in the paleosol, these alternative events must be evaluated.

Late metamorphic fluid interaction is evident by the presence of euhedral tourmaline in some paleosol localities along the contact with the overlying Missi Group (Holland et al., 1989). However, these fluids do not appear to influence the chemical systematics of the studied profile below a depth of 30 cm (Babechuk and Kamber, 2013).

The most notable response of the paleosol to burial diagenesis and metasomatism was re-introduction of the alkali elements (Holland et al., 1989; Babechuk and Kamber, 2013), together with an unusual phosphorus enrichment in the A horizon (Babechuk and Kamber, 2013). The latter feature is relevant since this is where the most isotopically heavy Cr compositions occur. However, an absence of correlation between the indicator elements (Na, K, P) and the Cr concentration or the $\delta^{53/52}\text{Cr}$ value suggests that Cr was not directly influenced by these post-burial events. Additionally, the B horizon is unaffected by the apparent P enrichment, yet exhibits $\delta^{53/52}\text{Cr}$ fractionation

(including ^{53}Cr -enrichment) that further suggests that different events controlled the chemistry of each element.

If ^{53}Cr -enrichment was generated during metasomatism, which is often basin-wide (e.g., Young et al., 2001), the signature might be expected in the overlying Missi Group as well as the paleosol. This can be tested using the uppermost sample (FF021A-001) that preserves a physical mixing of regolith and sediment during Missi deposition (Babechuk and Kamber, 2013). This sample has a significantly higher Cr concentration and isotopically lighter $\delta^{53/52}\text{Cr}$ composition closer to the igneous inventory. This indicates that any metasomatic influence had a negligible effect on Cr isotope systematics or it was masked by detrital, Cr-bearing heavy minerals. Diagenetic influence upon $\delta^{53/52}\text{Cr}$ fractionation can be discounted on similar grounds.

Only the ca. 1.85 Ga subaerial weathering and preceding seafloor alteration events remain as the source of Cr isotope fractionation in the paleosol. Mineralogical and chemical evidence for a patchy Fe-Ti oxide distribution are consistent with seafloor alteration of the greenstone prior to subaerial exposure (Holland et al., 1989; Babechuk and Kamber, 2013) and this event could have also influenced Cr. For example, Cr(III) could be redistributed from pyroxene and the oxides into phases such as chlorite (e.g., Schandl and Wicks, 1993; Oze et al., 2004; Barnes, 2000; Merlini et al., 2009). A recent study by Farkaš et al. (2013) demonstrated that intense seafloor alteration (e.g., serpentinisation) of ultramafic rocks led to ^{53}Cr -enrichment, indicating that Cr redistribution during seafloor alteration can promote isotope fractionation. However, the C horizon of the paleosol displays a relatively limited range in $\delta^{53/52}\text{Cr}$ comparable to that of the protolith greenstone and suggests that despite the potential for mineralogical re-distribution the Cr isotope composition was unaffected.

The immobile element chemistry of the profile suggests that the subaerial weathering is superimposed on two lava flows (Babechuk and Kamber, 2013). Accordingly, the lower Cr concentration in the A horizon could be related, at least in part, to magmatic fractionation prior to eruption of the successive lava flow. From an isotopic perspective, however, there are no documented magmatic mechanisms that might result in such a substantial $\delta^{53/52}\text{Cr}$ variation between successive lava flows.

The observations collectively point to a negligible effect of post-weathering alteration on the Cr chemistry and that the ^{53}Cr -enrichment is linked to the subaerial weathering event as opposed to the preceding seafloor alteration. In this regard, it is not surprising that the most extreme fractionation is restricted to those paleosol horizons that have been subject to the oxidative weathering that attacked Fe(II)-bearing phases in the greenstone that are likely to host the available

Cr. It is also worth noting that in most previous studies of Proterozoic paleosols, the preserved Cr chemistry is regarded as pedogenic, along with the other transition metals, despite the overprinting effects of subsequent alteration (e.g., Yang and Holland, 2003). We therefore feel confident in promulgating the hypothesis that the $\delta^{53/52}\text{Cr}$ variability, including extreme ^{53}Cr -enrichment, was generated during the pedogenesis event.

5.2.2 *A model for Cr cycling in the Flin Flon paleosol*

The Flin Flon paleosol has unusual ^{53}Cr -enriched isotope compositions that are incomparable to modern oxidative weathering profiles. Nevertheless, this Cr isotope signature is argued to be pedogenic in origin and influenced by three predominant factors: (i) lower atmospheric O_2 levels during regolith development; (ii) the protolith greenstone mineralogy; and, (iii) and the prevailing pH conditions.

The loss or redistribution of Mn in the paleosol is a key observation for interpretation of the Cr chemistry. The loss of Mn is correlated with Ca and Mg (Holland et al., 1989; Babechuk and Kamber, 2013) and evident through a strong inverse correlation between Mn/Al ratios and the weathering indices such as $\text{MIA}_{(\text{O})-\text{K}}$ ($r^2=0.876$; see Figure 2). Manganese is soluble only in reduced [Mn(II)] form, thus implying that the observed behaviour of Mn in the paleosol results from it being hosted in easily weathered minerals and that dissolved O_2 and/or pH levels and leaching rates were not conducive to substantial Mn oxide formation. This behaviour of Mn has been attributed to the reaction kinetics and required activation energy of oxidation (e.g., Morgan, 2005; Pinto and Holland, 1988) that make the oxidation of Mn(II) more difficult and less kinetically favourable than Fe(II). Unless there was an alternative oxidant of Cr(III), a limited availability of Mn oxides would inhibit the formation of Cr(VI) during pedogenesis. The Cr isotope data are also inconsistent with the known isotope effect of Cr(VI) formation in modern soils, as will be discussed below. Although direct evidence of the ancient Cr redox state is unavailable for this and other Precambrian paleosols, the remaining discussion is necessarily predicated on the assumption that Cr was not oxidised (at least significantly) and, consequently, that factors other than simply $p\text{O}_2$ were required to promote its release and isotope fractionation during pedogenesis.

The Al-normalised topology of elemental Cr parallels those of Fe(II), Mn, and Mg in the paleosol. However, the presence of a separate flow in the upper part (A horizon) of the paleosol makes it difficult to attribute the Cr-depletion unambiguously to depletion during pedogenesis. Nevertheless, the lateral variation at equivalent depths in the A horizon provides independent evidence that Cr was mobilised at least on smaller scale. As noted previously, some Cr may have

redistributed to silicates during seafloor hydrothermal alteration. The greater susceptibility of silicate- versus oxide-hosted Cr to chemical attack may, therefore, be a relevant factor in promoting Cr release. Regardless of the Cr(III)-bearing phase in the protolith, the liberation and transport of Cr(III) requires not only low Eh, but also acidic solutions ($\text{pH} < 5$; see Richard and Bourg, 1991 and Fendorf, 1995 for reviews), since at near-neutral to alkaline pH, Cr(III) is rapidly hydrolysed and attenuated by Fe or Al oxides and oxyhydroxides (Charlet and Manceau, 1992) or smectites (Corker et al., 1991). These pH conditions may have been met purely through a higher atmospheric CO_2 at the time weathering. The intense leaching of Ca and Mg and near-complete absence of carbonate in the Cr-depleted A horizon and the presence of a static pH/hydrological boundary at the sharp transition to the B horizon (Babechuk and Kamber, 2013) with secondary carbonate accumulation textures in the lower horizons could support this scenario. Further, the substantially greater abundance of Cr in the lower horizons, comparable to protolith levels, indicates that its mobility was hindered in the less-weathered and carbonate-bearing (higher pH) zones.

Fractionation of Cr isotopes from the protolith composition is restricted to the A and B horizons that are influenced by oxidative weathering (e.g., oxidation of Fe(II) and presence of hematite) and the most extreme and ^{53}Cr -enriched isotope compositions in the paleosol occur in the A horizon which is the most highly oxidised, mobile-element depleted, and lowest Cr concentrations (Figure 3). These observations appear to implicate oxidative chemical weathering, but not Cr oxidation, directly or indirectly, as the main processes releasing Cr and fractionating its isotopes. Arguably, during oxidative weathering, the liberated Fe(II) was oxidised and retained as Fe(III)-oxides, whereas Cr(III) and Mn(II) were both removed from the profile in their reduced state. The preferential incorporation of isotopically heavy Cr(III) into Fe(III)-oxides could have also contributed to Cr isotope fractionation, especially in view of the high Fe/Cr ratio in the profile (Konhauser et al., 2011). Regardless, the generation and removal of ^{53}Cr -depleted Cr is required. Importantly, this isotope effect is opposite to that in modern oxidative profiles showing loss of Cr(VI). Only one sample (FF021C-095), from near the transition from the B to C horizon, has a significantly negative $\delta^{53/52}\text{Cr}$ ratio of -0.381‰ that would be consistent with oxidation of Cr(III) to Cr(VI). It is also feasible, however, that this sample sequestered ^{53}Cr -depleted fluid that was released from higher in the profile or the surrounding greenstone.

Collectively, the internal $\delta^{53/52}\text{Cr}$ systematics of the profile can be interpreted without necessitating Cr(VI) formation by Mn oxides and may instead indicate that Cr(III) was released from more acidic areas of the profile with some being potentially sequestered at depth. The ^{53}Cr -enriched compositions in the Flin Flon paleosol are one of the most unusual and significant findings of this

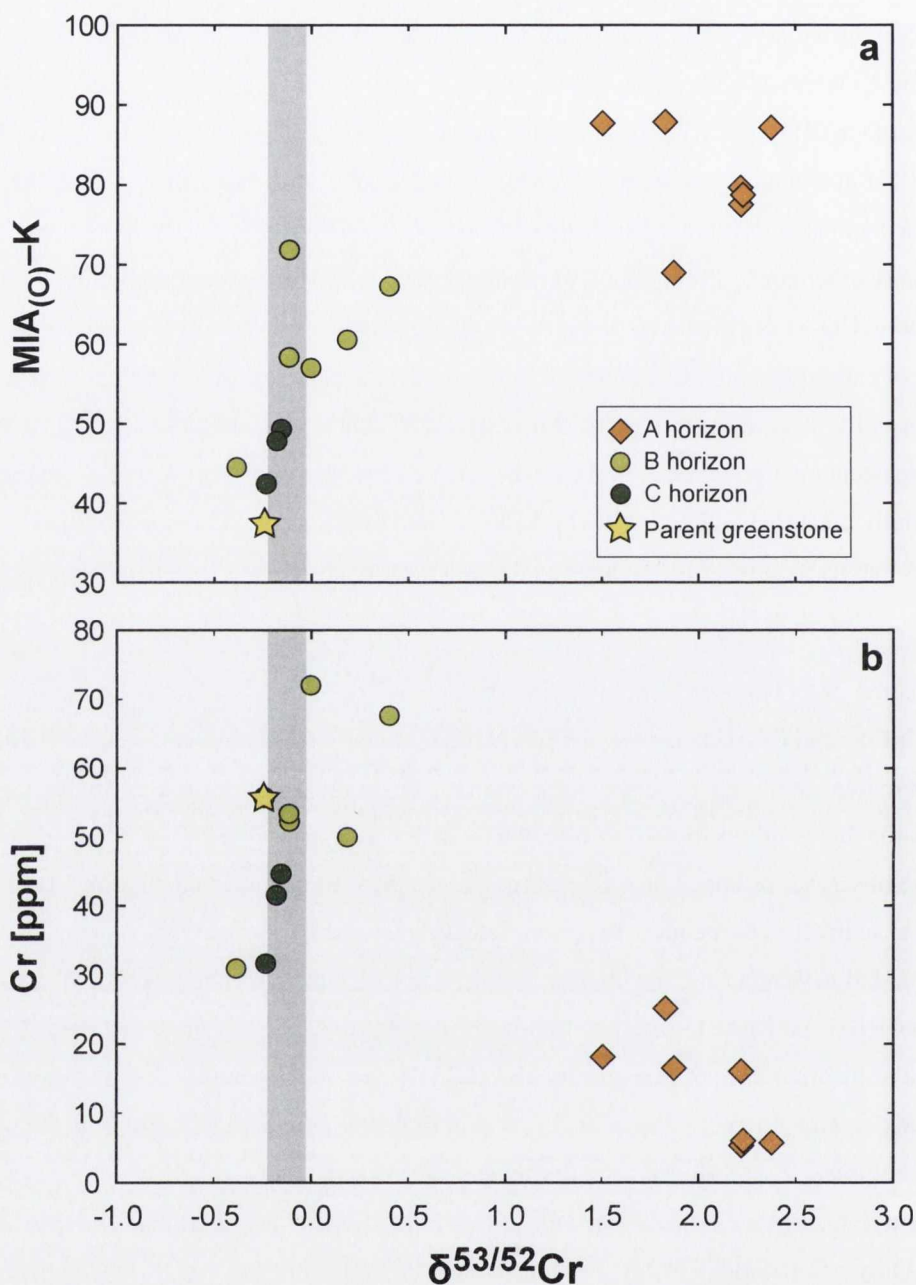


Figure 3: $\delta^{53/52}\text{Cr}$ in the Flin Flon paleosol plotted against: (a) the mafic index of alteration for oxidative weathering without K [$\text{MIA}_{(\text{O})-\text{K}}$] (loss of Ca, Mg, and Na relative to Al and Fe on a molar basis: Babechuk et al., 2014) and (b) Cr concentration (ppm). Relative to the protolith greenstone (represented by a star), the deeply weathered C horizon does not exhibit significant $\delta^{53/52}\text{Cr}$ fractionation. Within the remainder of the paleosol, however, which has experienced oxidative weathering, ^{53}Cr -enriched signatures dominate the paleosol with the exception of one ^{53}Cr -depleted sample in the B horizon. Substantially ^{53}Cr -enriched values (highly positive $\delta^{53/52}\text{Cr}$) are present in the most oxidised A horizon. Note that the uppermost sample (FF021A-001), which is influenced by the overlying Missi Group, is excluded from the graphs.

study. The leaching of Cr(III) during chemical weathering is not predicted to result in isotope fractionation and thus not to contribute to the Cr isotope signatures developed during oxidative weathering (Schauble et al., 2004; Frei et al., 2014). Here, attention is drawn to the study of Farkaš et al. (2013). These authors demonstrated that highly altered (e.g., serpentinised) ultramafic rocks and derivative secondary Cr-rich minerals were significantly ^{53}Cr -enriched. To account for these signatures, Farkaš et al. (2013) proposed two possible explanations: (i) complex seafloor redox cycling of Cr where Cr(VI) is generated at specific stages of serpentinisation and partially back-reduced to Cr(III) before incorporation into secondary minerals; or, (ii) the preferential release of weaker Cr(III)-bonds that leaves the residual Cr isotopically heavy. In view of the apparent absence of an operational Mn-Cr redox cycle in the Flin Flon paleosol, the ^{53}Cr -enriched compositions may provide substantiating evidence that preferential liberation of isotopically light Cr(III) is possible.

5.3 Precambrian Cr cycling and implications for inferring paleo-atmospheric O_2

5.3.1 Cr-Mn-Fe oxidation in Precambrian paleosols

The application of Cr isotopes to fingerprint paleo-atmospheric oxygen in the Precambrian hinges upon the assumption that Cr was cycled through soil oxidation processes involving Mn oxides comparable to present day. Whether or not Cr isotope signatures in Precambrian rocks, including pre-GOE paleosols (e.g., the Mesoarchean ca. 3.0 Ga Nsuze paleosol: Crowe et al., 2013), is explainable entirely through this process needs to be better established. This is particularly important in view of the widely accepted interpretation that Fe and Mn geochemistry show very little evidence for soil oxidation prior to ca. 2.4 Ga.

In the mafic paleosol record, Fe is lost or redistributed as Fe(II) in paleosols older than ca. 2.25 Ga (e.g., Yang et al., 2002; Utsunomiya et al., 2003; Rye and Holland, 2000), whereas paleosols younger than ca. 2.25 Ga show near-quantitative Fe(II) oxidation and retention of Fe(III) in pedogenic oxides (e.g., Zbinden et al., 1988; Holland et al., 1989) similar to present day oxidised soils. The behaviour of Fe in mafic paleosols older than 2.25 Ga is widely regarded to reflect reducing weathering conditions under a low- O_2 atmosphere that inhibited Fe oxidation (see Rye and Holland, 1998 and Murakami et al., 2011), although others have attributed the loss of Fe to overprinting effects of organic acids, reducing groundwater, or metamorphic fluids (Palmer et al., 1989; Ohmoto, 1996; Crowe et al., 2013). The latter interpretation is permissive of atmospheric O_2 levels high enough to form Fe(III)-oxides during the weathering event. By contrast to Fe, Mn is depleted from all documented Precambrian mafic paleosols (e.g., Holland et al., 1989; Macfarlane et al., 1994; Babechuk and Kamber, 2013). Murakami et al. (2011) suggested that the retention of

Mn in paleosols increased systematically throughout the Proterozoic along with Fe due to increasing oxidation in soils associated with rising pO_2 levels, culminating with near-complete oxidation in the Flin Flon paleosol. This claim, however, is not supported by chemical and mineralogical distribution of Mn in the Flin Flon paleosol that indicates mobility and retention occurred predominantly in its reduced [Mn(II)] state. Direct evidence for Mn oxide formation during Precambrian weathering is lacking at present. Independent of the documented loss of Mn in paleosols, clastic sedimentary rocks show a similar divergence in degree of Mn oxidation relative to Fe. Shales show greater retention of Fe relative to Ti after the GOE (Bekker and Holland, 2012), whereas Mn is lost relative to Ti in even post-GOE shales (Kump and Holland, 1992). Collectively, these observations indicate that Mn oxidation at the surface is less intricately linked to the level of atmospheric O_2 than Fe.

The understanding of Cr cycling in Precambrian paleosols is currently hindered by the lack of studies that report elemental data for Cr. In Figure 4a, the molar Cr/Ti ratios in all bona fide mafic paleosols (meeting all criteria of Rye and Holland, 1998 to be considered a definite paleosol), normalised to the protolith, are compiled. Despite the incomplete record of Cr record in these mafic paleosols, a striking trend is the prevalent loss of Cr in those formed both before and after the GOE. The loss of Cr in these paleosols is well beyond the magnitude of depletion observed in modern saprolitic basalt profiles (Figure 4a) developed under present day oxidising conditions. Several of the paleosols that show Cr loss also contain zones of Cr enrichment. Different mechanisms have been proposed to explain the elemental Cr distribution in paleosols, some invoking oxidation and others not. In order to better unravel the Precambrian Cr cycle, it is necessary to better establish whether Cr mobility requires formation of Cr(VI) such that areas of enrichment can be attributed to back-reduction to Cr(III), or whether Cr can be mobilised as Cr(III) without oxidation and redistributed to other paleosol zones (e.g. incorporation of Cr(III) in smectites). To account for trends of enrichment and depletion in the Strata 1 section of the Hekpoort paleosol, Yang and Holland (2003) inferred Cr mobilisation as both Cr(III) and Cr(VI). Konhauser et al. (2011) previously cited the loss of Cr in the sub-Huronian (ca. 2.45 Ga) Denison Mine paleosol as evidence for intense Cr(III) mobilisation due to low pH, sulphuric-acid driven weathering related induced by the destabilisation of the continental sulphide reservoir. However, we find it probable that the chemistry of the Denison Mine paleosol is a unique case and thus of questionable relevance to infer global weathering conditions. This paleosol is known to have an unusual immobile element geochemistry (Maynard, 1992; Rye and Holland, 1998) seemingly related to the seafloor-alteration mineral assemblage of the protolith greenstone. For this reason, the paleosol is often not used for paleoatmospheric reconstructions. Further, other sub-Huronian paleosols of an equivalent age (e.g., Cooper Lake paleosol: Sutton and Maynard, 1993;

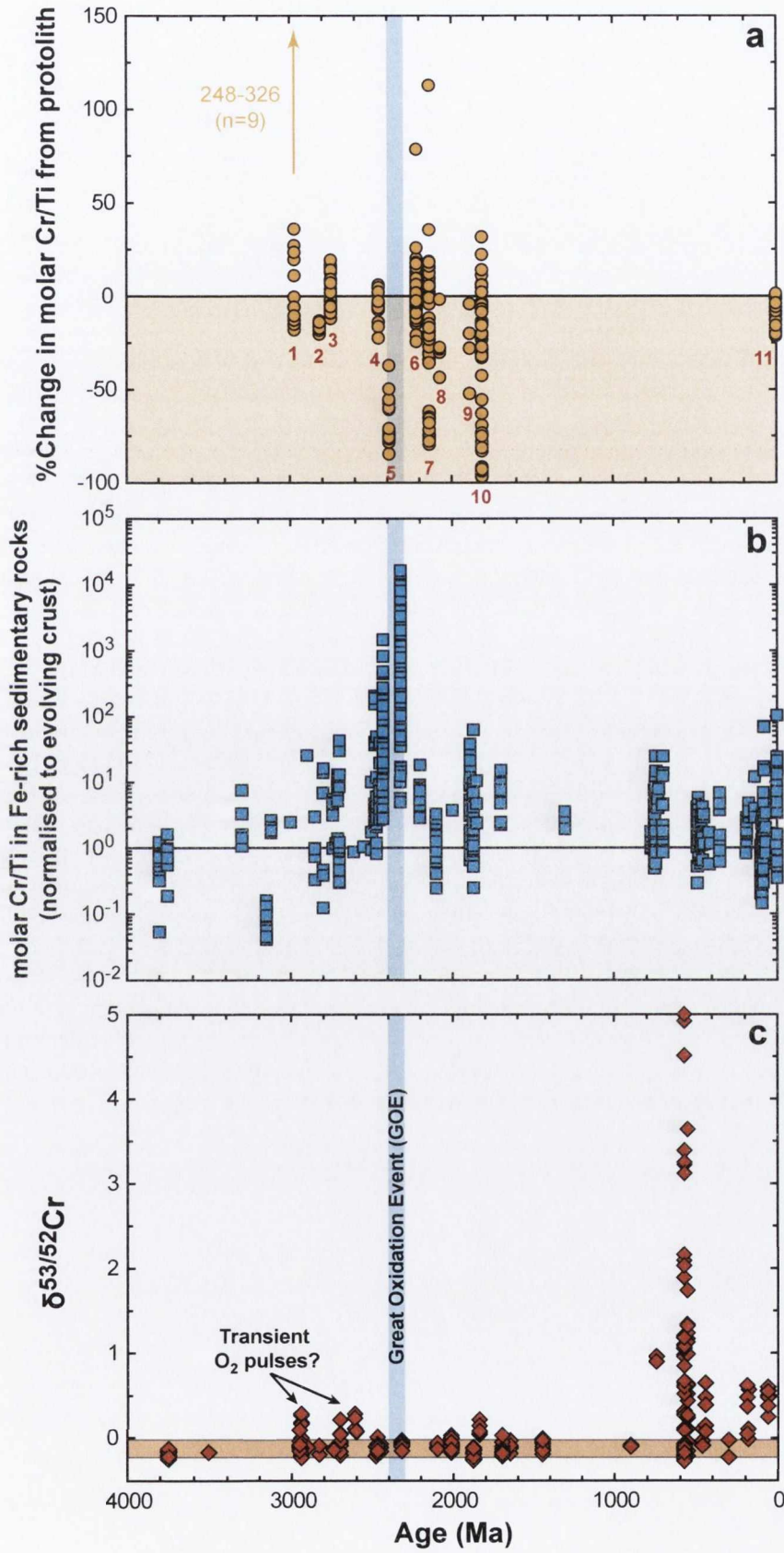


Figure 4 (previous page): Summary of Cr geochemistry in paleosols (a) and Fe-rich sedimentary rocks (b,c) through geological time. Paleosol data is presented as the % change in Cr/Ti relative to the protolith, $\{[(\text{Cr}/\text{Ti}_{\text{paleosol}} - \text{Cr}/\text{Ti}_{\text{protolith}})]/\text{Cr}/\text{Ti}_{\text{protolith}}\} \times 100$, such that values of 0 represent no change from the protolith, positive indicates gain of Cr relative to Ti, and negative values represent loss of Cr relative to Ti. For some paleosols, data from separate studies are plotted together and in other instances they are separated. The original sources of data for each time-point are identified by the numbers below each cluster in the figure and are as follows: 1) Nsuze (Crowe et al. 2013); 2) Mt. Roe #1 (Macfarlane et al., 1994); 3) Mt. Roe #2 (Macfarlane et al., 1994; Yang and Holland, 2002); 4) Quirke II (Prasad and Roscoe, 1991, 1996); 5) Cooper Lake (Sutton and Maynard, 1993; Utsunomiya et al., 2003); 6) Hekpoort (Rye and Holland, 2000); 7) Hekpoort – Strata 1 (Beukes et al., 2002; Yang and Holland, 2003); 8) Drakenstein (Wiggering and Beukes, 1990); 9) Flin Flon (Holland et al., 1989); 10) Flin Flon (This study); 11) Modern basalt profiles (Nesbitt and Wilson, 1992; This study). Note that in this figure Cr is normalised to Ti instead of Al in paleosols to allow comparisons with the marine sedimentary rock record. The compilation of molar Cr/Ti ratios in Fe-rich sedimentary rocks is taken from Konhauser et al. (2011) and presented normalised to evolving crustal values as per the original study. The compilation of $\delta^{53/52}\text{Cr}$ in Fe-rich sedimentary rocks is taken from Frei et al. (2009), Crowe et al. (2013), and Planavsky et al. (2014). Excursions towards $\delta^{53/52}\text{Cr}$ higher than the average igneous reservoir of Cr (Schoenberg et al., 2008: -0.124 ± 0.101 ‰, shown as a horizontal band) are interpreted as authigenic enrichments of Cr(VI) generated initially in soils. Significantly, subtle excursions occur before the timing of the Great Oxidation Event (GOE, marked by a vertical band at 2400-2300 Ma), which are interpreted as transient pulses of O_2 by Frei et al. (2013) and Crowe et al. (2013).

Utsunomiya et al., 2003) do not show the same depletion of Cr. Nevertheless, the study of Konhauser et al. (2011), among others (e.g., Reinhard et al., 2009) point out that the significantly higher CO₂ levels of the Precambrian atmosphere (e.g., Sheldon, 2006) may have led to more acidic rain and river waters that could enhance mobility of Cr(III) without needing to invoke low pH from sulphuric acid. Furthermore, many mafic paleosols are developed on greenstone that suffered seafloor-alteration prior to subaerial weathering and it may follow that this partitioned Cr into silicates that helped promote mobilisation of Cr in its reduced state, similar to modern serpentine soils (e.g., Oze et al., 2007).

In the ca. 3.0 Ga Nsuze paleosol (Crowe et al., 2013), extreme enrichment of Cr in the upper sericite horizon was interpreted to result from post-weathering interaction of the regolith with oxidised Cr(VI)-bearing groundwater that was reduced to Cr(III) within the upper zone of the paleosol. However, from their presented data, we note that the uppermost Cr enriched horizon has a contrasting immobile element ratio to the underlying paleosol (e.g., Al/Ti) and that the Cr enrichment is often accompanied by enrichments in Ti and K. These chemical systematics can also be explained by variations in the protolith chemistry or the introduction of an allochthonous component (e.g., mixing of the regolith with overlying conglomerate) influencing the chemistry of Cr and other elements (e.g., U).

The combination of element and Cr isotope chemistry should help to better understand the mechanisms of Cr mobilisation in Precambrian paleosols, but at present there is evidence that mobilisation of Cr(III) is feasible and our proposal that the Flin Flon paleosol elemental and isotope chemistry of Cr can be explained under this model should be considered and tested on other paleosols. The wider ramification of this hypothesis is that negative $\delta^{53/52}\text{Cr}$ excursions in paleosols may not uniquely fingerprint the presence of an operational Mn-Cr redox cycle and thus high levels of paleo-atmospheric oxygen. This is particularly important to explore as an alternative for pre-GOE paleosols where the chemistry of Mn and Fe both point to anoxic weathering conditions (e.g., Crowe et al., 2013). The proposal of Cr isotopes recording oxidation of Cr(III) to Cr(VI) by Mn oxides as far back the Mesoarchean is only reconcilable if the chemistries of Fe and Mn are systematically overprinted in paleosols.

5.3.2 Potential implications for Cr isotopes in ancient sedimentary rocks

The interpretation of $\delta^{53/52}\text{Cr}$ in Fe-rich Archean and Proterozoic rocks as recording fluctuations in paleoatmospheric O₂ requires that a flux of Cr(VI) to the oceans occurred (Frei et al., 2009; Crowe et al., 2013), whereas Konhauser et al. (2011) drew the conclusions from Cr-Ti-Al systematics in that authigenic enrichment of Cr in these rocks may have been dominantly in the form of Cr(III)

prior to the second rise of atmospheric O₂ in the Neoproterozoic. This is based on the premise that substantial authigenic enrichment occurred in the early Proterozoic without accompanying fractionations in the Cr isotope composition (Figure 4b,c). Riverine Cr at present can have a highly variable Cr(III)/Cr(VI) ratio with Cr(III) dominating in some cases (e.g., Comber and Gardner, 2003; Yusof et al., 2007). It would not be surprising to suspect a much higher Cr(III)/Cr(VI) ratio in the Precambrian riverine Cr flux due to a much higher atmospheric CO₂/O₂ that could drive the liberation of Cr(III) and its transport in lower pH waters (Konhauser et al., 2011). Our study of the Flin Flon paleosol appears to support the feasibility of Cr(III) flux from land, strengthening the likelihood of a non-uniformitarian Cr cycle operating at the ancient Earth surface, even after the GOE. The ⁵³Cr-enriched compositions of the paleosol requiring a loss of ⁵³Cr-depleted Cr(III) from the profile, however, is additionally relevant in that it suggests that the riverine Cr isotope composition was not necessarily on par with crustal values or uniquely ⁵³Cr-enriched as assumed in past studies (Konhauser et al., 2011; Crowe et al., 2013). Whether the generation of aqueous Cr with a ⁵³Cr-depleted isotope signature was indeed widespread and whether it could have escaped the regolith and survived through riverine transport and then be transferred to open marine waters, however, remains unconstrained at present. Apart from aqueous Cr in the form of continental runoff, the physical erosion of isotopically heavy substrates could transfer positive $\delta^{53/52}\text{Cr}$ values to solutions or particles delivered to the hydrosphere (Farkaš et al., 2013). It is also worth noting that each of these scenarios assumes Cr is derived from land prior to incorporation in BIF and the alternative scenario of Cr fractionation and release from hydrothermal activity on the seafloor remains to be more rigorously tested given that non-redox induced Cr isotope fractionation may be feasible.

6. Conclusions and areas of future study

This study documents the cycling of Cr in two oxidative mafic weathering profiles, a Quaternary saprolite profile and the ca. 1.85 Ga Flin Flon paleosol, using a combination of elemental Cr-Mn-Fe and $\delta^{53/52}\text{Cr}$ chemistry.

In the Quaternary saprolite profile, there is limited chromium mobility and isotope fractionation, despite the pervasive oxidising weathering conditions inferred from Fe, Mn, Ce, U (Babechuk et al., 2014, 2015). Thus, Cr is held predominantly within its Cr(III)-bearing minerals without significant generation and liberation of Cr(VI) or this process is masked by the residual Cr(III) with an igneous Cr isotope signature. By contrast, the ca. 1.85 Ga paleosol profile is significantly ⁵³Cr-enriched, indicating that loss of isotopically light Cr in weathering fluids occurred.

Importantly, this is the opposite behaviour to that observed in modern profiles measured to date. The depletion of Mn from the profile indirectly suggests that Cr(VI) formation was minimal or absent and, thus, that Cr(III) was the mobilised species. By comparison with the altered ultramafic rocks measured by Farkaš et al. (2013), this isotopic signature may be explained by the preferential weathering of weaker Cr(III)-O bonds, perhaps promoted by acidic conditions, and the specific Cr-hosting mineralogy of the protolith. Analysis of elemental data in other paleosols reveals that Cr loss as Cr(III) from land may have been the more prevalent process on the early Earth, as proposed previously by Konhauser et al. (2011). Further corroboration is required and the factors controlling the fate of Cr in other paleosols warrant further investigation.

This study of the Flin Flon paleosol study provides new evidence that the decoupling of soil Fe oxidation from Mn oxidation has significance for the interpretation of Cr isotope data. Our study demonstrates that Cr cycling and isotope fractionation in ancient weathering profiles may be more complex than previously assumed. In addition to atmospheric O₂, profile-specific factors such as hydrology, pH, and mineralogy are likely to be important in driving Cr mobility and isotope fractionation. Specifically, our results draw attention to the need to more fully evaluate the potential for Cr mobility and isotope fractionation during chemical weathering in the absence of Mn oxides. The isotopic composition of the Flin Flon paleosol could, conceivably, be a unique case in the rock record; accordingly, it would be premature to extrapolate our results to the wider Precambrian Earth system. Nevertheless, the possibility of a non-uniformitarian Cr cycle in the Precambrian is strengthened by these data and may imply that $\delta^{53/52}\text{Cr}$ signatures in paleosols and marine chemical sediments are not necessarily a unique fingerprint of paleoatmospheric oxygen. A re-evaluation of whether or not Cr redox changes are necessary to fractionate Cr isotopes is required.

The over-arching theme of the study is that inferring oxidative weathering conditions from Cr isotope data alone may not be warranted and that alternative pathways of Cr isotope fractionation need to be explored in the specific mineralogical and hydrological context of a weathering profile. Likewise, caution should be used when inferring redox processes in paleosols without converging lines of evidence and especially well-established parameters such as Fe valence. Insight could be provided from the *in situ* speciation of Cr and Mn in altered substrates and indeed may be necessary to understand better the redox cycling of both elements in deep time. Leaching experiments of Cr from different minerals (e.g., Cr-silicates vs. Cr-spinels) under varying pH and O₂ conditions may further unravel the mechanisms that promote the liberation of Cr, and better constrain the cause of ⁵³Cr-enrichment in altered substrates. Finally, detailed studies of well-

defined and mono-lithological weathering catchments in different climatic regimes should help in better constraining mass balances of elemental and isotopic Cr cycling from land to sea.

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Chapter 8: Synthesis

Mafic rocks, despite being a volumetrically minor constituent of the presently exposed land surface, contribute significantly to atmospheric CO₂ consumption through their denudation by chemical weathering and erosion (Louvat and Allègre, 1997; Dessert et al., 2003; Navarre-Sitchler and Brantley, 2007). Throughout all stages of Earth history, carbonation (CO₂-consuming) reactions have driven mafic rock weathering, whereas oxidation only became a significant reaction after the Great Oxidation Event (GOE) transition (ca. 2.3-2.4 Ga). Nevertheless, transient episodes of atmospheric oxygenation as far back as the Mesoarchean (ca. 2.96 Ga) have been proposed based on indirect records for terrestrial oxidative weathering (e.g., Frei et al., 2009; Crowe et al., 2013). Evidence in paleosols – the most direct archives of terrestrial weathering – for the presence of free oxygen in the Archean atmosphere is sparse or equivocal. The scarcity of *bona fide* paleosols in the Precambrian rock record, their complicated preservation history, and the very limited number of studies applying modern geochemical techniques (e.g., high-precision trace element and isotope analysis) conspire to obscure the full picture of oxidative Precambrian chemical weathering. This thesis has advanced the state-of-the-art via the study of oxidative mafic rock weathering profiles spanning from Paleoproterozoic (ca. 1.85 Ga) to Quaternary in age. The approach of this thesis was to combine rigorous field sampling with traditional methods (major element and Fe-speciation), modern high-quality trace element geochemistry, and novel isotope geochemistry. The resulting data and analysis have revealed new and important insights into profile development during oxidative weathering. In summary, the main contributions and conclusions of the thesis are:

1) Quantification of weathering intensity in mafic rock profiles benefits from the use of major element weathering indices that incorporate Fe and Mg. This thesis introduces a new such index, the mafic index of alteration (MIA), whereby the loss of Ca+Na+K+Mg±Fe relative Al±Fe is quantified. This index can be visualised in previously established ternary plots. The MIA can be adapted to study reduced weathering [MIA_(R)] that dominated at the surface prior to the oxygenation of the atmosphere or the oxidative weathering [MIA_(O)] that prevailed after and is thus ideally suited to the study Precambrian paleosols. Accurate quantification of the chemical weathering progression with major element indices (e.g., considering Fe mobile in reduced weathering profiles) can aid in linking trace element and isotope information to specific stages of mineralogical evolution in a weathering profile.

2) The rare earth elements are re-affirmed as a powerful tracer of pedogenic processes. Changes in the Y/Ho, Sm/Nd, and Eu/Eu* ratios have potential to track the progressive weathering of basalt, as demonstrated by the chemical evolution of the saprolitic Chhindwarra profile. These features are important when assessing the complementary record of eroded sediment and dissolved load of elements transferred to the hydrosphere. In the case of Y/Ho, fractionation in weathering profiles resulting in preferential retention of Ho appears to be consistent with the enrichment of Y over Ho in river waters (e.g., Lawrence et al. 2006; Leybourne and Johannesson, 2008) but establishing Sm/Nd and Eu/Eu* mass balances awaits further work.

3) Several high field strength elements (Nb, Ta, Zr, Hf, Th) other than the traditionally measured Al and Ti can help fingerprint pre-weathering variation in the protolith (e.g. separate lava flows) as well as the incorporation of allochthonous material (e.g. dust). Using high-precision data it is possible to recognise even small variations that arose during inter-flow exposure whereas long-term addition and downward winnowing during prolonged lateritisation is more easily seen even in data of standard quality. Radiogenic isotope information (e.g., Nd) is ideally coupled to this type of analysis since it can independently confirm the addition of an allochthonous component, help calculate the fraction of dust in a profile (Kurtz et al., 2001), and, with additional climatic constraints, aid in provenancing the dust source.

4) A limitation of the present database of weathering profiles is that many studies have focussed on the most complex end-product of severe weathering (laterites) and far fewer studies are dedicated to active saprolitic weathering, yet the majority of ancient paleosols did not progress to the laterite stage. Thus, there is need for better understanding the behaviour of interesting elements in saprolites. This is particularly true for Mo and W, two elements of known bioessential importance for specific microbial metabolisms. The new data from the Chhindwarra profile shows $W > Mo$ mobility, an expected result based on the crustal vs. marine mass imbalance of Mo/W (e.g. Kashiwabara et al., 2013). Addressing the mechanistic causes of the contrasting mobility of these two elements will require far more detailed work, but the preliminary results of this study suggest that the chemical weathering behaviour of these elements might be more relevant to their oceanic inventories than previously believed and that changes in this weathering behaviour in geological time may be linked to the evolution of some microbial metabolisms.

5) The ca. 1.85 Ga Flin Flon paleosol is confirmed as one of the oldest mafic paleosols that exhibits full Fe^{2+} to Fe^{3+} oxidation and retention of Fe in Fe^{3+} -oxides. By contrast, elemental Mn geochemistry indicates very minimal $Mn^{3+}/^{4+}$ -oxide formation. The high sampling density employed in this thesis revealed an offset in Al/Ti ratio assumed to be lava flow boundary in the profile upon which the subaerial weathering was superimposed.

6) In view of the contradictory paleo-redox conditions inferred from the Fe-Mn-Cr geochemistry of *bona fide* mafic paleosols, Cr isotope analysis was performed on the Chhindwara (saprolitic) profile and the Flin Flon paleosol. The very limited Cr mobility and small Cr isotope fractionation in the Chhindwara profile suggests that Cr was predominantly retained in the primary magmatic oxides and that the isotopic signal preserved in these minerals masked any ^{53}Cr -depleted signatures potentially generated by residual Cr^{3+} after partial oxidation to Cr^{6+} during breakdown of more labile Cr-bearing phases. Thus, despite the presence of highly oxidative weathering conditions, factors such as mineralogy and intensity of weathering can exert primary control on the Cr isotopic budget of modern weathering profiles. Importantly, the absence of a Cr isotopic signal in this case could erroneously be mistaken as weathering under anoxic conditions.

7) By contrast to the Chhindwara profile, Cr isotope fractionation of the Flin Flon paleosol is extreme and dominated by ^{53}Cr -enrichment. This cannot be explained with the current understanding of Cr cycling. At present, I interpret this finding as the signature of preferential leaching of the lighter isotopes of Cr^{3+} during chemical weathering (i.e., without oxidation by Mn-oxides, for which there is only very limited evidence) coupled possibly with preferential sorption of the heavy isotopes of Cr^{3+} onto or incorporation into Fe-oxides. This interpretation of Cr isotope signatures breaks from the limited conventional understanding of Cr behaviour. It will require further testing and cannot, at present, be extrapolated beyond the Flin Flon paleosol. Regardless of the true explanation for the unexpected isotope ratios, the new results indicate that Cr isotope fractionation may have multiple (possibly Cr^{3+} -specific) origins. If this finding is substantiated, it will require a revision of the uniformitarian interpretation of Cr isotope signatures in other Precambrian rocks (Crowe et al., 2013).

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