

Rhenium and osmium isotope and elemental behaviour accompanying laterite formation in the Deccan region of India

J. Wimpenny^{a,*}, A. Gannoun^{a,b}, K.W. Burton^{a,c}, M. Widdowson^a,
R.H. James^a, S.R. Gíslason^d

^a Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK

^b University of Oxford, Department of Earth Sciences, Parks Road, Oxford, OX1 3PR, UK

^c LMTG, Université de Toulouse, CNRS, IRD, OMP, 14 Av. E. Belin, F-31400 Toulouse, France

^d Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland

Received 5 November 2006; received in revised form 25 June 2007; accepted 29 June 2007

Available online 16 August 2007

Editor: R.W. Carlson

Abstract

This study presents major-, trace-element and Re–Os isotope data for two laterite profiles from the Deccan region in India. The first profile from Bidar developed upon Deccan basalt itself, the second from Goa formed on an Archean greywacke. Both profiles show the typical changes in mineralogy and chemistry accompanying laterite formation; from little altered parent rock at depth, to altered saprolite (depleted in mobile elements), to a highly altered, Si depleted, Fe-rich laterite capped by an iron-rich crust at the surface.

Rhenium and Os concentrations show a systematic enrichment with increasing degree of alteration, where the highest concentrations are found in the Fe-rich laterite crust. The level of Os enrichment is greater than that of Re, and as a consequence ¹⁸⁷Re/¹⁸⁸Os ratios are lower in the laterite than the parent rock. With time this leads to the development of ¹⁸⁷Os/¹⁸⁸Os ratios that are also less radiogenic than the parent rock, and this relationship holds irrespective of rock type or age or the time of laterite formation.

The marked enrichment of both Re and Os, and the patterns of change above and below the paleowater table, indicates that both elements are highly mobile. High Eh and low pH conditions facilitate Re and Os dissolution, and redistribution occurs via groundwaters, whereas with increasing pH (higher in the profile) both elements are scavenged out of solution and precipitate either as PGE-rich alloys or are strongly partitioned into oxides or oxyhydroxides. Nevertheless, the isotope and elemental data for both profiles suggests that at least some of the Re and Os must be externally derived, either from aeolian deposition or from the lateral movement of solute-laden groundwaters.

Given the high levels of Os in laterites, their extensive geographical coverage of the continents, and their active role in the surface water cycle, it seems likely that they will exert a significant influence on the continental flux of Os to the oceans, that will, in turn, be sensitive to tectonic or climatic change.

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Keywords: rhenium; osmium; laterite formation; basalt weathering

* Corresponding author. Tel.: +44 (0) 1908 655947; fax: +44 (0) 1908 655151.

E-mail address: j.b.wimpenny@open.ac.uk (J. Wimpenny).

1. Introduction

The continental crust is severely depleted in many platinum group elements (PGE: Ru, Rh, Pd, Os, Ir and Pt) relative to the Earth's core and mantle, and contains less than 0.01% of the terrestrial PGE budget (e.g. Esser and Turekian, 1993; Taylor and McLennan, 1995; Wedepohl, 1995; Schmidt et al., 1998; Peucker-Ehrenbrink and Jahn, 2001). This depletion, in part, reflects the siderophile and chalcophile behaviour of these elements, which means that they are highly concentrated in the Earth's metallic core (Wänke, 1981; Shirey and Walker, 1998), but also, in part, because some of these elements are compatible during silicate melting, and hence are preferentially retained in the residual mantle (Allegre and Luck, 1980; Shirey and Walker, 1998).

Osmium (Os) is a platinum group element that is related to rhenium (Re) through the beta decay of ^{187}Re to produce ^{187}Os . During partial melting Os behaves as a compatible element and is retained in the residue, whereas Re is moderately incompatible and enters the melt (Hauri and Hart, 1993; Shirey and Walker, 1998). Consequently, the Earth's crust (continental and oceanic) possesses high Re/Os (parent/daughter) ratios and develops radiogenic Os isotope compositions over time, relative to contemporaneous mantle. Under normal circumstances the Os isotope composition of the continental crust is controlled by the Re/Os ratio and age of a given rock type (Esser and Turekian, 1993). However, estimates for the average $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of the upper continental crust are variable, ranging from 1.4 to 1.9 (from loess (Peucker-Ehrenbrink and Jahn, 2001) and river sediments (Levasseur et al., 1999), respectively) while rivers themselves yield a global mean value of ~ 1.4 (Levasseur et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000a).

The behaviour of Re and Os during continental weathering is unusual because these elements are often highly concentrated in accessory phases or else in particular rock types. At the mineral scale in silicate rocks, a significant proportion of the Re and Os is located in phases present at trace levels (accessory phases) such as sulphide and PGE-alloys (Hart and Ravizza, 1996; Burton et al., 1999). It is these phases that control the Os isotope composition and elemental abundance of Re and Os in the whole-rock, and often their behaviour during weathering that determines the composition of waters and soils. Similarly, certain rock types such as organic-rich sediments are highly concentrated in Re and Os, possess very high Re/Os ratios, and thus with time develop highly radiogenic Os isotope compositions, relative to average continental

crust (Singh et al., 1999; Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002). Such sediments are also highly susceptible to weathering and readily release their radiogenic Os, and this weathering signal may strongly influence the marine Os isotope composition, despite comprising less than 1% of the continental crust (Peucker-Ehrenbrink and Hannigan, 2000). Notwithstanding, the concentration of Re and Os in accessory phases and particular rock types, under certain circumstances both elements may be highly mobile during weathering, and readily transported in natural waters (i.e. ground and river waters).

Laterites result from extreme weathering of the continental crust in tropical or sub tropical climates, they are estimated to cover $\sim 30\%$ of the exposed continental crust, and nearly 50% of continental drainage flows through laterite covered terrain (Tardy, 1997). Laterites are commonly over 20 m thick and can have thicknesses of up to 100 m (Brimhall et al., 1991). Laterite profiles generally show a progression from unaltered bedrock to increasingly altered rock above with an iron rich crust or duricrust at or close to the surface. Laterites are formed during continuous in situ weathering of bedrock (Schellmann, 1981; Widdowson and Cox, 1996; Tardy, 1997), which acts to strip away less resistant elements (such as silica, and the mobile elements Na, Mg, Ca) leaving secondary minerals enriched in Fe_2O_3 and Al_2O_3 . There is also some evidence to suggest that they are, at least in part, modified by external input and redistribution processes (Schellmann, 1981; Brimhall et al., 1991; Widdowson and Cox, 1996; Kisakurek et al., 2004) and that their formation may be initiated by changing weathering conditions (Dequincey et al., 2002).

It has long been known that laterite soils may be enriched in platinum group elements, located in PGE-rich alloys and associated sulphides and iron-oxides (e.g. Bowles, 1986). Early work suggested that these PGE-rich minerals were present as resistant phases residual from weathering of the parent rock (e.g. Cabri and Harris, 1975). However, it is now established that under the conditions prevalent in laterite soils (that is, low pH and high Eh) some platinum group elements may be taken into solution, transported and redeposited (Cabri and Harris, 1975; Bowles, 1986), consistent with textural evidence indicating that PGE-minerals in laterites have grown in situ (Mann, 1984; Bowles, 1986). Thus far there have been few published Re–Os isotope measurements for laterites. The data that have been obtained indicate a depletion of Re and enrichment of Os in the topsoil part of the profile, and consequently a relatively unradiogenic Os isotope composition, relative to the parent rock (Sharma et al., 1998). These results were taken to indicate that the weathering of

laterite soils will yield relatively unradiogenic Os which may control the composition of dissolved and aeolian material delivered to the oceans (Sharma et al., 1998).

This study presents major-, trace element, and Re–Os isotope and elemental data for two laterite profiles from a similar climatic regime, but having different parent-rock types, from Bidar and Goa in India. These results provide information on the distribution and mobility of Re and Os during laterite formation and groundwater movement, the consequences for the Os isotope evolution of laterites (compared to parent-rock types), and the implications for the behaviour of these elements during weathering in tropical and sub-tropical climates.

2. Geological setting and background

2.1. Geological setting

Two laterite profiles from the Deccan region have been studied here; the first is from Bidar in central India,

and the second is from Goa on the west coast (Fig. 1). Bidar is located near the present-day edge of the Deccan Traps Continental Flood Basalt Province (CFBP). The Deccan Traps were erupted during a $\sim 3\text{--}4$ Ma period straddling the Cretaceous–Tertiary boundary (e.g. Courtillot et al., 1988; Widdowson et al., 2000), onto a complex Archean–Proterozoic basement comprising part of the Dharwar craton (Chadwick et al., 2000). Today the Deccan Traps cover an area of over $500,000\text{ km}^2$, and have a maximum thickness of $\sim 2\text{ km}$ (Mitchell and Widdowson, 1991). Each lava package (or formation) has a distinct chemical and isotopic signature, reflecting different stages of the eruptive history (Widdowson and Mitchell, 1992). Of these different lavas the Ambenali formation is the most volumetric and geographically widespread (Widdowson et al., 2000), and forms the upper flow units that have been subsequently lateritised at Bidar (Kisakurek et al., 2004). The second profile at Goa developed on a Proterozoic greywacke that forms part of the Dharwar supergroup.

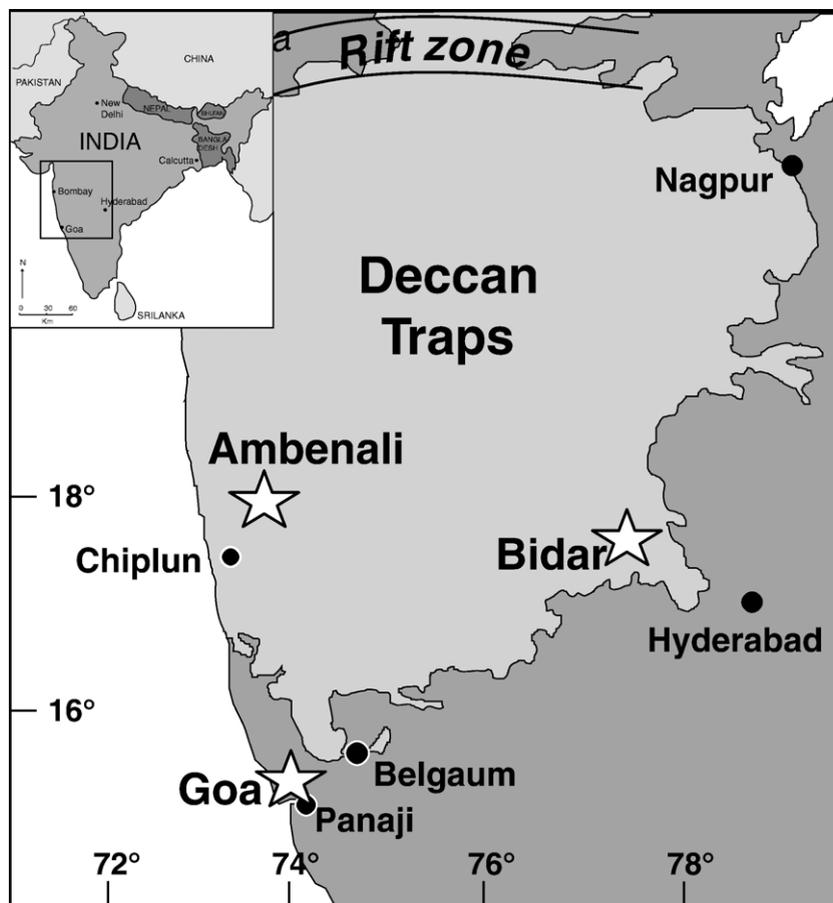


Fig. 1. Map showing the location of the two laterite profiles studied here. Bidar is in central India and the profile is located on the Ambenali formation of the Deccan Trap basalts, Goa is on the west coast of India and the profile is located on an Archean greywacke of the Dharwar Craton.

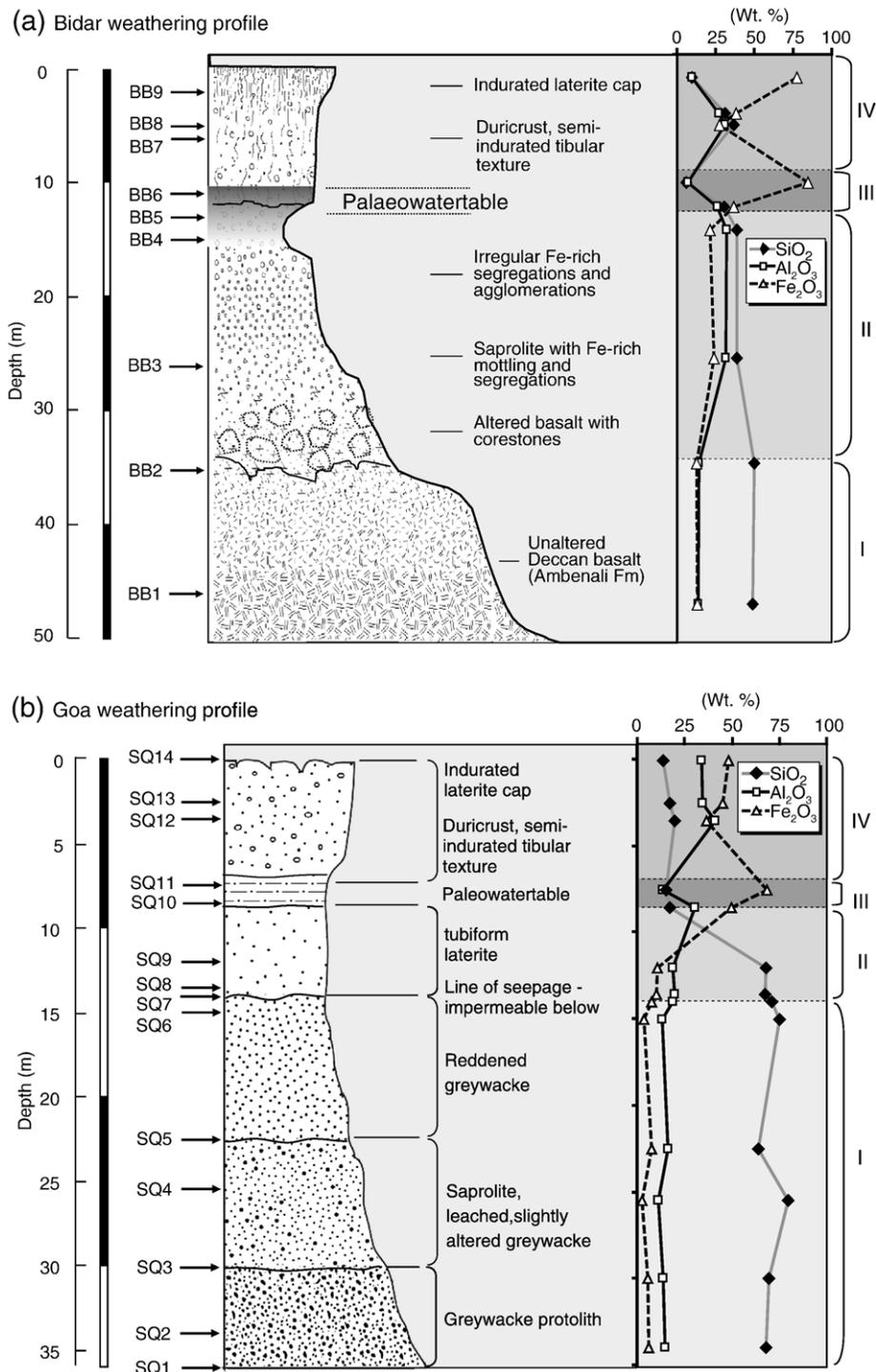


Fig. 2. Schematic profiles of the studied laterites at (a) Bidar and (b) Goa. Both profiles show progression from unaltered rock at the base to increasingly altered rock towards the surface, and both have a hard indurated iron cap at the surface and a distinct paleowatertable horizon. Zones I–IV illustrate the progressive lithological changes within the laterite. Zone I — unaltered or little altered bedrock, Zone II — high alteration bedrock/laterite (saprolite), Zone III — paleowatertable, Zone IV — Fe rich laterite cap (see text). Includes major element profiles that are characterised by a general decrease in Si, and relative enrichment in Fe and Al contents. This pattern of chemical change is interrupted at the paleowatertable where there is considerable enrichment of Fe, and depletion of both Si and Al.

During the later stages of eruption of the Deccan Traps, northwest drift of India, across the equator (Klootwijk and Peirce, 1979), exposed the Deccan (CFBP) to intensive weathering leading to the development of deep weathering profiles capped by a regional laterite (Widdowson and Cox, 1996). At the Bidar site, this major period of laterite formation was brought to a close between 55 and 45 Ma (Schmidt et al., 1983), when regional uplift raised the laterite above the watertable (Widdowson, 1997), possibly as a result of the collision of India and Asia, thereby preserving this ancient weathering profile. In contrast, the site at Goa did not experience this uplift, and paleomagnetic data suggests that laterite formation occurred during the late Tertiary, ~20 Ma, and is ongoing today.

The profile at Bidar extends to a depth of ~50 m where unaltered basalt is located (Fig. 2). In the region of the Bidar profile the Ambenali formation represents the uppermost flow units of the Deccan, constructed at the highest elevations, and not overlain by later eruption. Consequently, any extraneous groundwater influence from different lithologies at higher levels can be discounted. Rather, the huge lateral extent and thickness of the Ambenali formation suggests that the majority of elements mobilised and transported by groundwaters were ultimately derived from the breakdown of this tholeiitic precursor itself. Moreover, the uniform composition of the Ambenali formation offers an ideal substrate for assessing the chemical variations accompanying

Table 1

Lithology and mineralogy of the laterite samples from Bidar and Goa and the bole samples from Ambenali

Sample	Depth	Lithology	Mineralogy
<i>Bidar</i> (17°54.87'N, 77°32.39'E)			
BB9	2	Vermiform laterite	Haematite, goethite, Kaolinite
BB8	5	Nodular laterite	Haematite, goethite, kaolinite
BB7	6	Base of laterite	Haematite, goethite, kaolinite
BB6	11	Laterite base/top of saprolite	Haematite, goethite, kaolinite
BB5	13	Saprolized basalt	Haematite, goethite, kaolinite, magnetite
BB4	15	Reddened saprolite	Haematite, goethite, kaolinite, magnetite
BB3	26	Deeply weathered basalt	Haematite, goethite, kaolinite, magnetite
BB2	35	Low alteration basalt	Anorthite, augite, illite
BB1	47	Unaltered basalt	Anorthite, augite
<i>Goa</i> (15°28.44'N, 73°52.35'E)			
SQ14	0	Indurated laterite	Iron, traces of clay and quartz
SQ13	2.5	Indurated laterite	Iron, traces of clay and quartz
SQ12	3.5	Indurated laterite	Iron, traces of clay and quartz
SQ11	7.5	Massive laterite	Iron 96%, quartz 2%, clay 2%
SQ10	8.5	Semi-indurated laterite, nodules fusing together	Iron 95%, quartz 2%, clay 3%
SQ09	12	Increased nodule density and size	Iron 50%, quartz 45%, clay 5%
SQ08	13.5	Base of nodular laterite, haematite segregations present	Quartz 50%, iron 45%, clay 5%
SQ07	14	Laterite base/top of altered greywacke	Quartz 75%, iron 22%, biotite 2%, muscovite 1%
SQ06	15	Top of reddened greywacke, soft and well consolidated	Quartz 75%, biotite 12%, feldspar 6%, iron 5%, muscovite 2%
SQ05	22.5	Soft weathered greywacke, base of weathered zone	Quartz 74%, biotite 20%, feldspar 2%, muscovite 2%, chlorite 1%, opaques <1%
SQ04	25.5	Softer, white weathered greywacke	Quartz 80%, biotite 8%, feldspar 8%, chlorite/muscovite 3%, opaque 1%
SQ03	30	Lighter greywacke from start of weathered zone	Quartz 75%, biotite 12%, feldspar 8%, opaque 2%, other 3%
SQ02	34	Unaltered greywacke	Quartz 75%, biotite 15%, feldspar 5%, opaque 2%, other 3%
<i>Ambenali</i> (17°57.10'N, 73°34.58'E)			
MPr2a	10	Uniform fine grained ash	
MPr2b	70	Blocky, lithified, reworked ash	
MPr2c	90	Fine-grained ash	
MPr2d	140	Weathered flow top material	

SQ12	0.5636±0.0006	1.80	142	403	19.62	40.89	36.42	0.06	0.15	0.06	0.12	0.645	2.278	17.2	20	38	339	23.6	9.2	626	908	58	51
SQ11	0.8181±0.0012	17.8	393	116	15.20	13.58	68.33	0.57	0.13	0.05	0.07	0.511	0.664	12.1	15	36	99	11.2	7.0	60	153	119	33
Dupl. ^b	0.7803±0.0011	20.0	428	113																			
SQ10	0.5335±0.0004	2.76	175	323	17.21	30.52	49.64	0.02	0.10	0.05	0.64	0.276	1.842	12.6	7.0	19	257	21.2	4.2	780	839	59	42
SQ9	1.7807±0.0017	128	1067	48.5	67.86	18.95	10.78	0.02	0.30	0.05	0.07	1.345	0.730	7.28	26	7.2	219	21.4	5.8	157	149	41	36
SQ8	1.6051±0.0002	65.4	610	53.6	67.46	19.62	10.25	0.02	0.32	0.05	0.08	1.428	0.854	7.23	30	9.1	261	22.2	7.2	151	130	42	33
Dupl. ^b	1.6350±0.0022	69.9	642	53.6																			
SQ7	2.0880±0.0014	23.1	155	40.4	71.19	18.62	7.64	0.06	0.51	0.05	0.09	1.760	0.756	6.59	37	6.5	265	25.1	6.0	124	91	67	30
SQ6	4.1502±0.0028	104	559	39.2	75.27	13.43	3.38	0.05	1.62	0.43	3.51	2.445	0.431	1.80	73	109	134	14.2	4.4	65	66	22	37
SQ5	4.4108±0.0021	141	801	42.1	64.21	16.38	7.63	0.17	4.13	0.43	2.76	3.954	0.483	2.52	132	81	138	14.2	4.4	88	81	41	65
SQ4	2.5774±0.0021	110	519	29.6	79.50	11.41	2.43	0.07	1.29	0.56	3.54	1.632	0.320	1.29	43	100	92	6.7	2.7	44	44	15	38
SQ3	5.1968±0.0054	82.0	458	44.4	69.67	13.90	5.58	0.11	2.88	0.66	3.24	3.200	0.577	1.52	100	108	228	18.7	7.5	98	107	43	55
SQ2	4.6592±0.0067	123	708	43.4	67.77	14.65	6.08	0.13	3.07	0.95	3.31	3.684	0.562	1.34	118	114	194	15.6	5.7	92	108	38	59
Dupl. ^b	4.0495±0.0030	139	747	39.4																			
<i>Dharwar basement</i>																							
IND108	0.7426±0.0011			4.20	71.61	14.40	2.49	0.04	0.64	1.79	3.88	4.43	0.40	0.42	152	233	272	14.8	2.3	30	12	4.7	10
IND114	1.7662±0.0070			4.47	74.07	13.92	1.42	0.02	0.29	1.42	3.75	4.54	0.22	0.36	143	220	141	17.4	0.7	11	6.9	2.9	6
IND120	1.6692±0.0039			2.40	73.49	14.27	1.15	0.03	0.47	1.65	4.19	3.72	0.13	0.75	94	192	84	9.9	0.2	14	6.8	3.5	3
Bhima	0.1752±0.0008	11.5	74	31.0	16.64	2.33	1.34	0.06	0.95	42.29	0.39	0.34	0.34	34.6	17	268	28	4.6	0.1	13	6.9	7.4	8.1
Lst																							
BIF	1.3449±0.0037	786	2825	19.6	55.05	0.18	43.98	0.01	0.09	0.03	0.01	0.01	0.02	0.72	1.4	0.3	5.1	1.6	D.L.	D.L.	25	D.L.	21

^aErrors shown are 2σmean; ¹⁸⁷Os/¹⁸⁸Os ratios normalised using ¹⁹²Os/¹⁸⁸Os=3.08271 and corrected using measured ¹⁸O/¹⁶O and ¹⁷O/¹⁶O of 0.002047 and 0.0037, respectively. Given isotope ratios are blank corrected.

^bDuplicate results for the same laterite powder split using the high pressure high temperature microwave digestion (HP-HT).

D.L.: samples below detection limit.

laterite formation, because any changes in chemistry are unlikely to be a result of parent-rock heterogeneity. In addition, the intracontinental location precludes any marine influence on the chemistry, through aerosols or precipitation, but does not rule out the presence of continental derived aeolian material. The profile at Goa is ~35 m thick and developed on a Proterozoic greywacke that forms part of the Dharwar supergroup. In contrast to the site at Bidar, the relatively low topography of the laterite and the heterogeneity of the Dharwar craton raises the possibility of lateral input of groundwater potentially sourced by a range of lithologies. Moreover, unlike the Ambenali formation, the parent greywacke shows some chemical variation both laterally and vertically.

2.2. Sample description

The two profiles are shown in detail in Fig. 2 and sample depths and descriptions of their lithology and mineralogy given in Table 1 (previously reported in Mason, 1999; Berger and Widdowson, 2001; Kisakurek et al., 2004). Both show progression from unaltered rock at the base to increasingly altered rock towards the surface, and both have a hard indurated iron cap at the surface (“cuirasse”) together with a distinct paleowater-table horizon a few meters below the cap. The laterite profiles can be divided into zones based on the level of alteration reflected in their physical properties, mineralogy and elemental behaviour (Fig. 2). Zone I is unaltered or slightly altered bedrock. Zone II is altered bedrock increasingly so up the profile. At Bidar the crystalline groundmass of the basalt is initially replaced by illite and kaolinite clay, similarly at Goa primary quartz, biotite and feldspar are also replaced by clays in this zone. Moving up, the primary mineralogy is lost, and the groundmass becomes mottled due to the development of Fe and Al oxides and oxyhydroxides. Zone III is the paleowater-table horizon, and Zone IV is the Fe-rich indurated laterite crust. Within Zone IV no remnant of the protolith texture or primary mineralogy remains. The high haematite content of the Zone IV samples indicates that well drained oxidising conditions prevailed.

There is no petrographic evidence for significant input of aeolian material to either profile, supporting the view that the laterite profiles across the Deccan region were predominantly formed by in situ alteration of the underlying bedrock. However, for the profile at Bidar, Sr, Nd and Li isotope data have been taken to indicate aeolian input of weathered continental material to the top of the profile (Mason et al., 2000; Kisakurek et al., 2004). Consequently, a number of potential sources of local aeolian material have been examined here including

basement granite, banded iron formation (BIF) and a limestone all from the Dharwar craton.

Finally, a sequence of Deccan ‘bole’ samples have also been analysed. These are highly weathered basaltic material or basaltic ash that developed between successive lava flows (i.e. during a hiatus in eruption). The bole samples studied are from a locality close to the village of Ambenali, and comprise a ~1.4 m profile sandwiched between two massive lava flows. The base of the profile is marked by weathered flow top material that is overlain by fine-grained ash which is increasingly weathered towards the top of the bole horizon. These bole samples serve to illustrate the behaviour of Re and Os in weathered basalt/ash that has not had sufficient time to develop into a laterite.

3. Methods

3.1. Sampling and sample preparation

Samples were taken from each of the profiles (sample locations shown in Fig. 2) chosen as representative of each key horizon, or else taken immediately above or below (i.e. bracketing) levels where distinct textural changes are observed. Because the weathering profiles are highly heterogeneous large samples (between 1 and 3 kg) were taken, and these large samples were then homogenised by milling in agate.

3.2. Major and trace element analysis

Bulk materials from the weathering profiles and surrounding basement rocks were analysed by XRF for major elements and ICP-MS for trace elements. Full details of the analytical procedures are given elsewhere (Kisakurek et al., 2004; Kisakurek et al., 2005).

3.3. Re–Os isotopic analysis

Rhenium and Os were separated from laterite and rock samples using techniques previously described (Birck et al., 1997) and analysed using negative thermal ionisation mass spectrometry (N-TIMS). Sample powders were spiked with a mixed ^{185}Re – ^{190}Os spike solution and dissolved using a mixture of HF and teflon distilled HBr at 140 °C for 72 h. Osmium samples were oxidised by CrO_3 (in HNO_3) and extracted into liquid Br_2 . The Br_2 solution was then dried down and the residue purified by microdistillation. An aliquot for Re analysis was dissolved in 2M HNO_3 and extracted using *iso*-amylol. All samples were loaded onto high purity Pt ribbon for analysis. Re and Os samples were analysed as OsO_3^- and ReO_4^- oxides by

negative TIMS. The average total procedural blank for the Bidar samples was 0.41 pg for Os and 4.75 pg for Re; the Os isotopic composition of the blank ($^{187}\text{Os}/^{188}\text{Os}$) was 0.179 ± 0.005 . Corresponding blanks for Goa were 0.22 pg for Os and 4.42 pg for Re; the Os isotopic composition of the blank was 0.186 ± 0.007 . There is a possibility that low temperature acid digestion may not recover all the Re and Os present in the samples, particularly when PGE-rich phases are present (Meisel et al., 2003). Thus, in order to ensure that both Re and Os are fully recovered from the samples studied here, high pressure and high temperature microwave sample decomposition (Multiwave 3000, Anton Paar®) was also used. The duplicated samples were chosen so as to be representative of the entire range observed for both profiles. Approximately 0.2 g of sample material was spiked and digested using HF+HCl (3:3 ml) acid mixture in a fluoropolymer vessel at 240 °C and 60 bar for 2 h. The solutions were then transferred into a PFA pressure vial, evaporated to dryness and redissolved with HF-HBr (2:2 ml) at 150 °C for 48 h. The subsequent step of sample oxidation and Os extraction was similar to

that described above. The average total procedural blank was 0.083 pg for Os with $^{187}\text{Os}/^{188}\text{Os}$ of 0.250 ± 0.021 and 3.6 pg for Re.

4. Results

4.1. Major and trace element data

Major and trace element data for both profiles are given in Table 2. Above the zone of unaltered bedrock (Zone I) both profiles show a decrease in the concentration of the more mobile elements (e.g. Ca, Na, K and Mg) relative to the parent rock, towards the surface (Zones II, III and IV). The decrease in mobile elements is accompanied by a decrease in SiO_2 , and relative enrichments in Fe and Al contents (Fig. 2). This pattern of chemical change is interrupted at the level of the paleowater table (~11–14 m depth at Bidar, ~7–8.5 m depth at Goa) where there is considerable relative enrichment of Fe, and a relative depletion of both Si and Al.

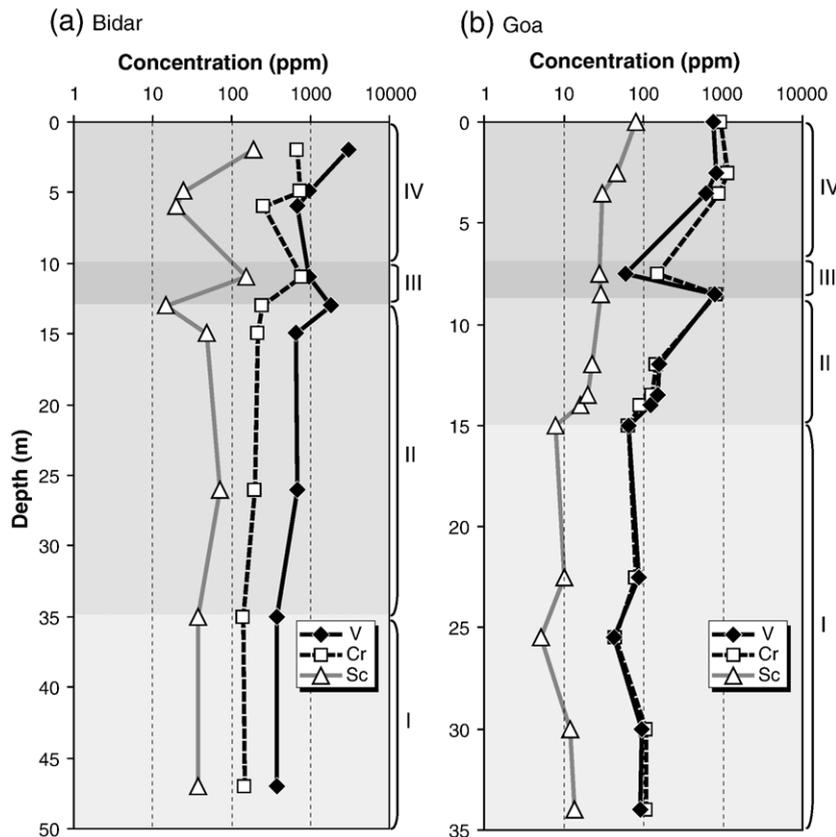


Fig. 3. Trace element profiles for (a) Bidar and (b) Goa, showing that the immobile transition elements such as V, Cr and Sc are enriched in the laterite compared to the parent rock.

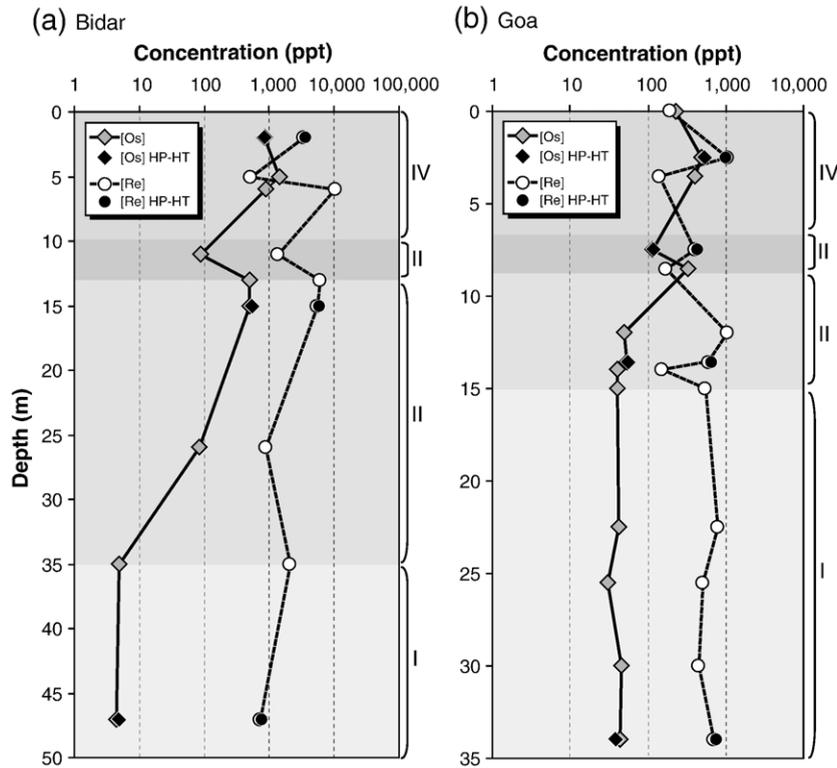


Fig. 4. Re and Os concentration profiles for (a) Bidar and (b) Goa. The parent rocks have relatively low Re and Os concentrations. However, both profiles show a significant increase in Re and Os concentration with increasing alteration, with the highest values being seen in the Fe-rich laterite cap. For both profiles enrichment of Os is always greater than Re, consistent with previous work. In addition, both profiles show a decrease in the concentration of Re and Os at the level of the paleowatertable.

The variation of trace elements with depth is also similar for both profiles. The concentration of mobile trace elements, such as Sr and Rb, is highest in the unaltered bedrock and decreases as the rock becomes more altered (and permeability increases) (Table 2). At Goa there is a sharp change in permeability at 15 m depth that is marked by a line of seepage and loss of the mobile elements. Relatively immobile transition elements such as Cu, V, Sc and Cr are enriched in the upper half of the laterite profile, and have lowest concentrations in the unaltered bedrock (Fig. 3).

4.2. Re–Os elemental data

The concentrations of Os and Re at Bidar show significant variation with depth (Fig. 4). Osmium concentrations increase from 4 ppt at 47 m depth to 1410 ppt at 5 m depth, a 300-fold increase. While Re concentrations are higher than those of Os, increasing from 0.7 ppb at 47 m depth to 10 ppb at 6 m depth, the level of enrichment is much lower (some 14-fold). Similar Re and Os variations are observed at Goa. Osmium

concentrations increase from 43 ppt at 34 m depth to 492 ppt at 2.5 m depth, an enrichment factor of >11. Rhenium has higher concentrations than Os, increasing from 0.7 ppb at 34 m depth to 1 ppb at 2.5 m depth, an enrichment factor of 1.4. The pattern of increasing Re and Os concentration towards the top of the profile is interrupted by a sharp decrease in the concentration of both elements at the level of the paleowatertable. Duplicate measurements made using microwave digestion, indicate little difference in Re and Os concentration (10% or less) from those obtained by HF-HBr dissolution (Table 2; Fig. 4). In summary, both profiles show an enrichment in Re and Os, and both show a depletion of these elements at the level of the watertable. However, the level of enrichment (relative to the parent rock) is an order of magnitude greater in the profile at Bidar compared to that at Goa.

4.3. Re–Os isotope data

For both profiles parent-rock $^{187}\text{Re}/^{188}\text{Os}$ ratios are greater than those of the overlying laterite and

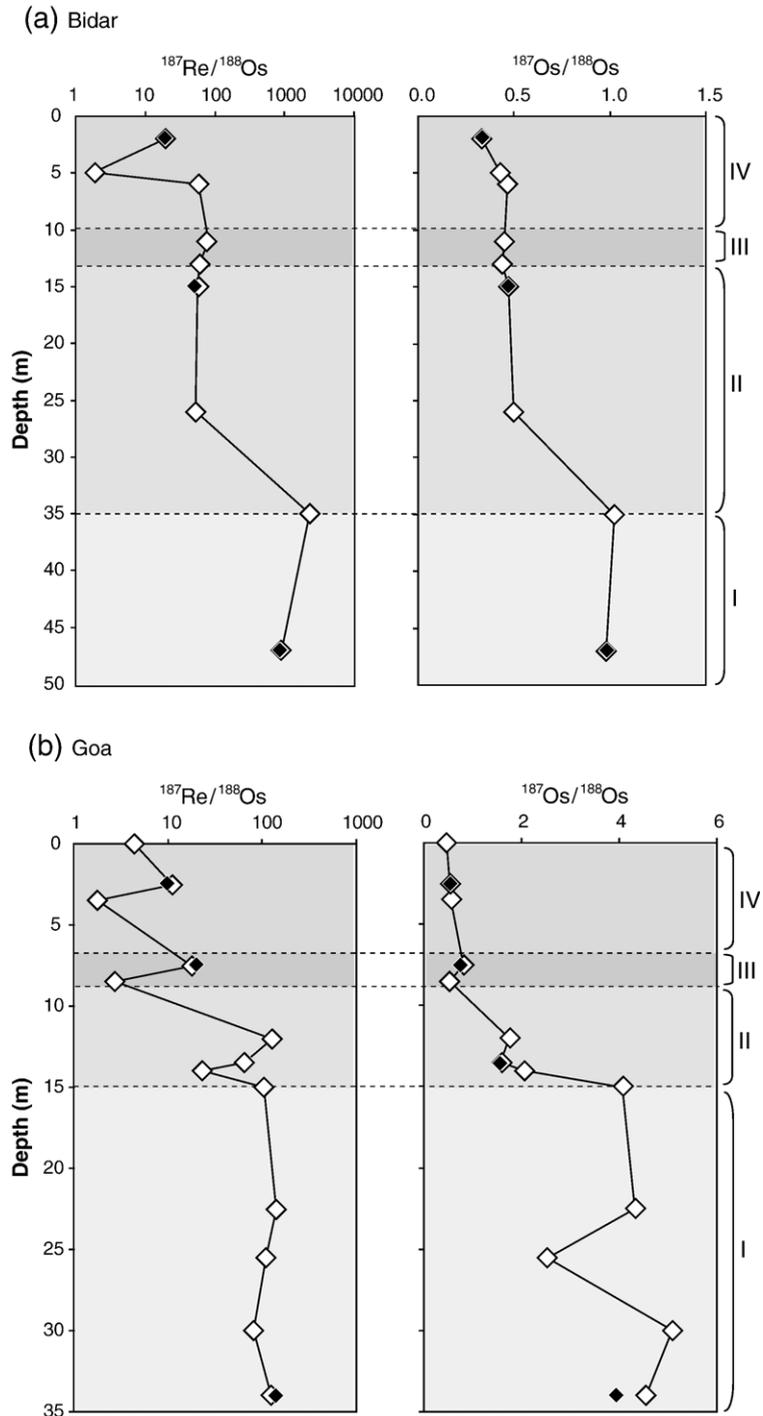


Fig. 5. $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios shown against depth at (a) Bidar and (b) Goa. The $^{187}\text{Re}/^{188}\text{Os}$ and ratios of the laterite are, with one exception, always lower than the those of the parent rock. The measured $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios are also always less radiogenic than the parent rock (see text).

$^{187}\text{Os}/^{188}\text{Os}$ ratios are also in general more radiogenic; the least radiogenic ratios being found at the surface. At Bidar, $^{187}\text{Re}/^{188}\text{Os}$ drops from 2286 at 35 m depth to 2 at

5 m depth. $^{187}\text{Os}/^{188}\text{Os}$ ratios show a similar pattern, falling from 0.98 at 45 m depth to 0.33 at 2 m. Both isotope ratios shift to lower values where the Os

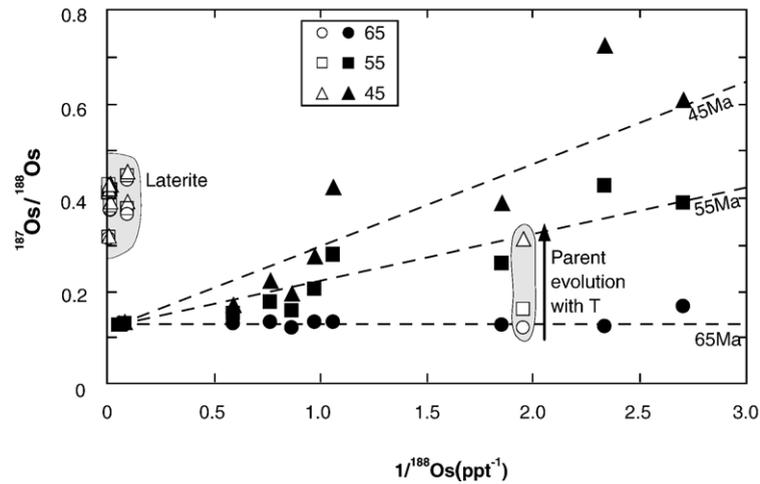


Fig. 6. Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios against Os concentration (shown as $1/[^{188}\text{Os}]$) for the laterite and parent rock at Bidar (open symbols) and previously published data for the Deccan basalts (filled symbols). For the laterite samples there is no significant change in $^{187}\text{Os}/^{188}\text{Os}$ composition over the 20 Ma between basalt eruption and the end of laterite formation. However the parent basalt (and other Deccan basalts) rapidly evolve to radiogenic Os isotope values and may have possessed an appropriate composition at 45 Ma to source the laterite, albeit that the laterite is significantly enriched in Os. Initial ratios calculated using: $(^{187}\text{Os}/^{188}\text{Os})_i = (^{187}\text{Os}/^{188}\text{Os})_a - [(^{187}\text{Re}/^{188}\text{Os})_a \times e^{(\lambda t - 1)}]$ where λ is the decay constant of Os (taken as $1.66 \times 10^{-11} \text{ yr}^{-1}$).

concentration starts to increase (between 35 and 26 m depth). A similar pattern is observed in the Goa profile; both $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios shift to lower values towards the surface. The parent rock has a $^{187}\text{Re}/^{188}\text{Os}$ ratio of ~ 100 , and a $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~ 4.5 ; these values are far more radiogenic than those of Deccan basalt. Both ratios fall as the Os concentration starts to rise at 12 m depth. The $^{187}\text{Re}/^{188}\text{Os}$ ratio at the surface is 4.4 and the $^{187}\text{Os}/^{188}\text{Os}$ ratio is 0.48, similar to

the values recorded at Bidar. Duplicate measurements, given in Table 2 and also shown in Fig. 5, show a consistent reproducibility to within 5% for $^{187}\text{Os}/^{188}\text{Os}$ ratio from both dissolution techniques.

4.4. Basement lithologies and bole samples

The three granite samples analysed have Os concentrations of ~ 4 ppt; similar to the unaltered basalt at Bidar

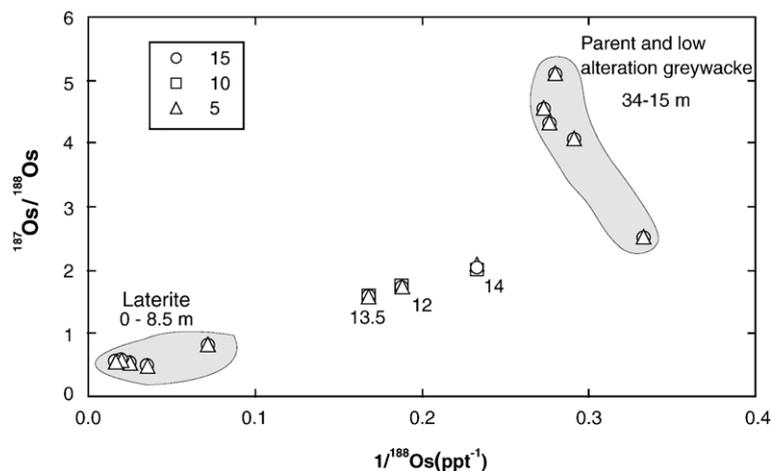


Fig. 7. Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios against Os concentration (shown as $1/[^{188}\text{Os}]$) for the laterite and parent rock at Goa. The have initial Os isotope compositions have been calculated for 5, 10 and 15 Ma of radiogenic growth of ^{187}Os . In contrast, to Bidar there is no significant change in $^{187}\text{Os}/^{188}\text{Os}$ ratios of the parent greywacke over these time intervals, and its composition is too radiogenic to exclusively source the laterite material, indicating that there must have been some external source of Os.

but far lower than the laterites at both Bidar and Goa. The $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions of the granites range from 0.74 to 1.77, and are far more radiogenic than the surface compositions of either laterite profile. The BIF and limestone samples from the Dharwar craton have Os concentrations of between 20 and 31 ppt, an order of magnitude lower than the highest concentrations recorded at Goa and two orders of magnitude lower than recorded at Bidar. The $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio of the Bhima limestone is relatively unradiogenic (0.175) while the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the BIF is relatively radiogenic (1.345). The basalt bole samples have Os concentrations between 20 and 44 ppt, and $^{187}\text{Os}/^{188}\text{Os}$ ratios of between 0.157 and 0.171. The concentration of Re is variable ranging from 97 to 1080 ppt, and consequently the $^{187}\text{Re}/^{188}\text{Os}$ ratio also shows wide variation from 23 to 119.

5. Discussion

5.1. Elemental variations

The variation in the chemical composition of both profiles is very similar, and consistent with previous studies of laterite formation on comparable protoliths (e.g. Brimhall et al., 1991; Widdowson and Cox, 1996; Tardy, 1997). The data indicate loss of the more mobile elements (e.g. Ca, Na, Mg, K, Rb and Sr) in the earlier stages of weathering, followed by a decrease in silica content, facilitated initially by the breakdown of the primary mineralogy, and subsequently by the breakdown of neo-formed clay minerals. The depletion in mobile elements is accompanied by a concomitant increase in the concentration of less mobile elements within the developing laterite profile, in particular Fe, Al and Ti, typically considered as residual. Superimposed on this pattern of enrichment and depletion is element behaviour at the watertable, since many elements are controlled by the change in redox conditions at this level. For example, iron can exist as reduced Fe^{2+} that is mobile or oxidised Fe^{3+} that is immobile. The paleowatertable marks a change in the redox conditions from sub-oxic to oxic so that Fe^{2+} is oxidised to immobile Fe^{3+} that is then deposited as oxides or oxyhydroxides.

At both Bidar and Goa high Re and Os concentrations occur in the upper parts of the profile, coinciding with significant Fe_2O_3 enrichment and SiO_2 depletion. Enrichment of trace metals, in particular the rare earth elements (REE) in heavily weathered and lateritized soils has been widely recognised (Walter et al., 1995; Koppil et al., 1996; Nesbitt and Markovics, 1997; Braun et al., 1998). The REE's form mobile complexes with phos-

phates, fluorides and carbonates (Walter et al., 1995), can be mobilised by organic matter (Braun et al., 1998) and can be trapped by Fe- and Mn-oxides (Walter et al., 1995; Koppil et al., 1996). Significant PGE enrichment in lateritic soils has also been documented (Mann, 1984; Bowles, 1986; Roquin et al., 1990; Bowles et al., 1994; Eliopoulos and Economou-Eliopoulos, 2000; Brown et al., 2003) and attributed to supergene enrichment and co-precipitation of PGE-rich alloys with iron and manganese oxides. Lateritic soils are considered to develop in a high Eh (+200–+800 mV) and low pH (2–5) environment (Mann, 1984; Bowles, 1986), and these conditions are thought to arise because cations such as Fe^{2+} are removed from solution under increasingly oxidising conditions (Mann, 1984). The release of protons into solution causes pH to decrease; and where Fe^{2+} concentrations are high, such as just below the water table, pH can be as low as 2 (Bowles, 1986). Under these conditions the PGEs become mobile by forming complexes with species such as chlorides, oxides and hydroxides as well as with organic matter such as oxalates and humic acid (Bowles, 1986; Mountain and Wood, 1988; Bowles et al., 1994; Oberthur et al., 2003). However, not all of the PGEs have the same mobility: for example Pd is considered to be more mobile than Pt (Mountain and Wood, 1988; Traore et al., 2006) and more readily enters the aqueous phase in solution (Bowles et al., 1994), whilst available data suggests that Os is amongst the most soluble (Bowles, 1986). The PGEs are then progressively removed from solution as conditions become increasingly oxidising and pH increases towards the surface. Here there are high concentrations of poorly crystalline secondary phases such as Mn- and Fe-oxyhydroxides that act as scavengers of metal ions in solution (Kuhnel, 1987). This secondary mineral crystallisation accounts for the high PGE, Au and Ag concentrations in a number of weathering profiles (Bowles, 1986; Mann, 1984; Roquin et al., 1990; Bowles et al., 1994; Brown et al., 2003) and the same processes can also account for the high Re and Os concentrations seen in the laterites studied here. That is, high Eh and low pH conditions cause Re and Os dissolution, and redistribution occurs via groundwaters. Subsequently with increasing pH in the upper part of the laterite profile, both elements are scavenged out of solution and precipitate either as PGE-rich alloys or are strongly partitioned into oxides or oxyhydroxides.

The variation in Re and Os, in particular those seen at the level of the paleowatertable (Fig. 4, Zone III) indicates that they are mobile. The extent of this mobility can be assessed by comparison with an 'immobile' index element. Elements such as Ti, Th and Zr are considered

to be relatively immobile in surface weathering environments because of their relatively high field strength and low solubility in water, for this reason they are often used in the study of weathering processes (Brimhall and Dietrich, 1987; Brown et al., 2003). Nevertheless it should be remembered that they are not totally immobile and can be mobilised in extreme weathering conditions, or in the presence of high levels of organic matter (Oliva et al., 1999; Hodson, 2002). In this study Zr has been used as the index element because its concentration shows the least variation over the two profiles, when compared to the concentration in the parent rock. Re and Os concentrations normalised to Zr and Ti show little difference in patterns of enrichment or depletion (Supplementary Fig. 1), where enrichment or depletion can be defined by:

$$\% \text{ enrichment / depletion} = 100 \times \frac{R_n - R_i}{R_i}$$

In this equation R is the ratio of the element concentration to the Zr concentration and the subscripts i and n indicate the bedrock and weathered horizon respectively. At Bidar there are substantial enrichments of both Os and Re. The highest Os enrichment occurs at 5 m depth where the laterite is $\sim 19,000\%$ enriched relative to the parent rock, and Re is enriched by 920%. At Goa most samples are enriched in Os relative to the bedrock, the sample at 2–5 m depth being enriched by 630%. Concentrations of Re are very variable; some horizons contain higher Re and some lower Re than the parent rock. It is important to note that the Zr content at the level of the watertable is $\sim 40\%$ lower than the parent basalt, suggesting that this element may also have been mobilised. The net effect of this relative mobilisation of Zr will be to enhance the relative depletion of Re and Os. However, throughout the remainder of the profile the trends revealed by Zr normalisation remain unaffected.

The pattern of increasing enrichment in Os towards the laterite surface has also been observed in a laterite with a granodiorite parent rock from Burkina Faso, west Africa (Sharma et al., 1998) but these authors report low levels of Re at the surface (lower even than the parent rock) which is in contrast to the profiles at Bidar and Goa.

5.2. Re–Os isotope variations

Elemental enrichment of Os relative to Re in both profiles has an impact on the measured parent/daughter $^{187}\text{Re}/^{188}\text{Os}$ ratios. Both profiles show a decrease in $^{187}\text{Re}/^{188}\text{Os}$ with increasing alteration. Because ^{187}Os is produced from the β -decay of ^{187}Re it can be anticipated that with time the altered laterite samples will develop a

less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope composition than the parent rock. Accordingly both profiles show $^{187}\text{Os}/^{188}\text{Os}$ values that are significantly less radiogenic than the parent rock with increasing alteration (i.e. up the profile). As will be seen for the profile at Goa this is not simply due to in situ decay of ^{187}Re but reflects the sources and distribution of Re and Os. Therefore, for the profiles studied here and elsewhere (Sharma et al., 1998) the data indicate that laterites possess a less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope composition than the parent rock from which they were formed, and this relationship appears to hold irrespective of rock type or age, or the timing of laterite formation.

Figs. 4 and 5 show that any differences between results gained from the two dissolution methods used in this study are very small. Microwave dissolution gave slightly higher Re concentrations for samples from both laterite profiles and higher Os concentrations at Bidar which may indicate the efficiency of this method. However these differences have little consequence for the pattern of element distribution through the profiles, and do not affect the isotope ratios.

5.3. Basalt bole samples

The basaltic red ‘boles’ are relatively short lived weathering profiles that developed between successive lava flows in the uppermost lava sequences of the Deccan. These boles have been subject to intense tropical weathering (hence their red colour), but laterite formation *sensu stricto* did not occur (Schellmann, 1981), and thus they serve to distinguish the effects of element transport in a low pH, high Eh environment from straightforward basalt weathering at higher pH conditions. The Os concentrations in the boles are higher than the parent basalt at Bidar, but within the range observed for other Deccan basalts. However, the Os concentrations remain much lower than those observed in the laterite at Bidar. Rhenium concentrations are high at the base of the bole profile, similar to concentrations in unaltered basalt, but Re contents decline at higher levels where they are lower (in most cases) than the laterite at Bidar. The low Re and relatively low Os concentration results in generally low $^{187}\text{Re}/^{188}\text{Os}$ ratios and relatively unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions, but all are within the range observed for unaltered Deccan basalt (Allegre et al., 1999).

Thus, overall the bole samples appear to have experienced Re loss, with little or no Os enrichment, relative to the unweathered parent basalt. However, they do not show the either the extreme or differential enrichment of $\text{Os} > \text{Re}$ seen in the laterite samples. This is presumably because there has been little external input of

Re or Os to the profile, and pH and Eh conditions have not resulted in significant mobility of these elements.

5.4. Origin of elemental and isotope variations

5.4.1. In situ parent-rock weathering

There are a number of different processes that may have been responsible for the high levels of Re and Os found in the laterites studied here. It is possible that this enrichment is simply due to in situ weathering of the parent rock where Re and Os are located in weathering resistant minerals retained in the residue.

In order to estimate the amount of parent rock needed to supply the Re and Os found in the laterite, the Os (and Re) content of each horizon (Os_n) is weighted by the horizon thickness (h_n) and its absolute density (ρ_n).

$$Os = \sum_{n=1}^{n=x} [Os]_n h_n \rho_n.$$

Using this equation the total Os content of the Bidar profile is 3×10^{-5} kg/m² and at Goa it is 7.6×10^{-6} kg/m². The total mass of Os that can be supplied from parent basalt to the Bidar profile is 5.8×10^{-7} kg/m², which is 1.9% of the estimated Os. Using the same method for Re the precursor basalt can contribute 35% of the total Re, emphasising the greater level of Os enrichment in the profile. At Goa, the parent greywacke can supply 45% of the Os and all of the Re measured in the profile.

The same approach can be used to calculate the mass of Re or Os in 1 m of bedrock to give an estimate of the number of metres of parent rock that would have to be weathered and removed in order to concentrate the estimated masses of Re and Os. The high Os enrichment in the laterite at Bidar demands the weathering and erosion of some 2600 m of parent basalt to account for the laterite Os content; while 42 m of vertical loss is required at Goa. It has been suggested that some two thirds of the initial volume of the Deccan basalt may have been removed by weathering and erosion over the past 65 Ma (Courtilot et al., 1988). However, the Ambenali formation at Bidar represents the uppermost flow units of the Deccan eruptions (Widdowson et al., 2000) and such volumes of basalt loss seem unlikely at this locality. Therefore, the elemental data appears to suggest that a direct, vertical, contribution by weathering and removal of the parent rock, concentrating Re and Os in the residue, is unlikely to supply the Re and Os at Bidar. However, such a process could potentially provide much of the Re and Os in the laterite at Goa.

The Os isotope data can also be used to evaluate whether the relatively unradiogenic Os at both sites could

be derived from the parent rock. Laterite formation at Bidar is thought to have commenced at or soon after the final Deccan eruptions at ~65 Ma, and ceased sometime between 55 and 45 Ma, when the profile was elevated above the level of the watertable (Widdowson, 1997). At first sight it would appear that laterite and parent rock at this locality possess very different ¹⁸⁷Os/¹⁸⁸Os isotope compositions. However, the laterite has a much lower parent/daughter ¹⁸⁷Re/¹⁸⁸Os ratio and thus growth of radiogenic ¹⁸⁷Os from the decay of ¹⁸⁷Re may have been very different both over the 10–20 Ma of laterite formation, and up to the present-day. Assuming that there has been no recent mobility of Re or Os calculations indicate that the Os isotope compositions of the laterites have not changed significantly over the past 65 Ma. Initial ¹⁸⁷Os/¹⁸⁸Os isotope ratios have also been calculated for the parent basalt to take into account the amount of ¹⁸⁷Os growth since between 65 and 45 Ma, and are shown against Os concentration in Fig. 6. The ¹⁸⁷Os/¹⁸⁸Os of the parent basalt was relatively unradiogenic at the time of eruption at 65 Ma (¹⁸⁷Os/¹⁸⁸Os ≈ 0.128; this study and Allegre et al. (1999)). However, over the timescale of laterite formation the basalts will have evolved to much more radiogenic values such that the Os isotope composition of the parent basalt at 55 to 45 Ma could have sourced the laterite at that time (Fig. 6).

At Goa the parent greywacke again possesses much more radiogenic ¹⁸⁷Os/¹⁸⁸Os isotope compositions than the overlying laterite and higher ¹⁸⁷Re/¹⁸⁸Os ratios. Laterite formation at Goa occurred during the late Tertiary (between 20 and 30 Ma) and is ongoing today, providing a 30 Ma maximum timescale for the radiogenic growth of ¹⁸⁷Os. However, calculations indicate that even if laterite formation started at 30 Ma the greywacke will have been only slightly less radiogenic than at the present-day, and there will have been little resolvable change in the composition of the laterite (Fig. 7). Therefore these calculations indicate that the unradiogenic Os isotope compositions of the laterite at Goa cannot have been simply acquired from the parent greywacke.

Overall, these data indicate that there must have been some form of external input of Re and Os to both profiles. While the Os isotope composition of the laterites at Bidar can be explained by ageing of the parent rock, the level of Os enrichment cannot be attributed to concentration (in residual minerals) through massive vertical weathering and erosion. Whereas at Goa, the level of Os enrichment is less, and could conceivably be supplied by the parent greywacke. However, the parent greywacke at Goa possesses Os that is too radiogenic to account for the unradiogenic Os isotope compositions seen in the overlying laterites.

5.4.2. Aeolian input

Previous isotope studies of the laterite at Bidar have concluded that some degree of aeolian input to the top of the soil profile must have occurred. With increasing laterite alteration the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope composition becomes more radiogenic, shifting from 0.704249 to 0.710099 while $^{143}\text{Nd}/^{144}\text{Nd}$ becomes less radiogenic, shifting from 0.512818 to 0.512437. This variation far exceeds the natural variation of the Ambenali basalt, and is too extreme to be explained by fractionation induced by weathering over the given timescales. Instead these isotope shifts can be explained by aeolian input of ancient continental material such as the neighbouring Dravidian Shield (Mason et al., 2000). In addition, Li isotope data suggests that this continental material must have been weathered prior to aeolian transport and deposition (Kisakurek et al., 2004). Redistribution of aeolian material input to the top of the profile could occur via dissolution and transport in groundwater and the subsequent precipitation of secondary minerals.

The Archean to Proterozoic Dharwar craton is one possible source of aeolian material. For the locality at Bidar, during the main period of laterite formation India was located to the south of the equator, and so southeast trade winds could have carried dust from this terrain (Klootwijk and Peirce, 1979). A number of potential source rocks have been studied from the Dharwar craton including granites, banded iron formation and limestone. However, while some rock types (or mixture of rock types) possess the appropriate Os isotope compositions, none have a sufficiently high Os concentration to account for those measured in the laterite. Further afield another potential source is loess, and samples from China, Europe and S. America give an average $^{187}\text{Os}/^{188}\text{Os}$ composition of 1.05 ± 0.23 , and Os and Re concentrations of 31 pg/g and 198 pg/g respectively (Peucker-Ehrenbrink and Jahn, 2001). If it is assumed that the present day dust flux of $1\text{--}10 \text{ g/m}^2/\text{yr}$ (Duce et al., 1991) is similar to that during the $\sim 15\text{--}20 \text{ Ma}$ period over which both profiles developed then it is possible to estimate the potential mass of aeolian derived Os. If it is further assumed that all this Os dissolved and entered the laterite then such aeolian sources can account for a maximum of 20% of the total Os at Bidar and 81% of the total Os at Goa. This suggests that aeolian material with an average continental crustal Os composition and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio cannot by itself account for all of the Os in these laterites, although it could account for much of the Os seen in the profile at Goa. Cosmic (interplanetary) dust is also known to have a high Os concentration and very unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope composition. The average flux of cosmic dust to Earth is $40\text{--}80 \text{ g/km}^2/\text{yr}$ (Peucker-

Ehrenbrink and Ravizza, 2000b) with an Os concentration of $\sim 50 \text{ ng/g}$ and $^{187}\text{Os}/^{188}\text{Os}$ composition of ~ 0.127 (Anders and Grevesse, 1989). Over 20 Ma a maximum of $8 \times 10^{-5} \text{ g}$ of Os could be input to the laterite profiles, accounting for 0.26% and 1% of the total Os at Bidar and Goa, respectively. This suggests that despite the high Os concentrations of cosmic dust it is unlikely to be solely responsible for the enrichment seen in the laterite profiles.

These results highlight the fundamental difficulty of sourcing the Os isotope and elemental signature seen in the laterites directly from crustal rocks. This is because first, average continental crust has a much lower Os concentration ($\sim 50 \text{ ppt}$) (Wedepohl, 1995; Peucker-Ehrenbrink and Ravizza, 2000a; Peucker-Ehrenbrink and Jahn, 2001) than that seen in the laterites (80 to 1400 ppt). Second, average continental crust also has a relatively high $^{187}\text{Re}/^{188}\text{Os}$ ratio (Esser and Turekian, 1993; Peucker-Ehrenbrink and Ravizza, 2000a, 2001) and thus ancient continental crust would be expected to develop a radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope composition, consistent with the measurements for some of the Dharwar lithologies. Therefore, in contrast to Sr and Nd, it is difficult to explain the $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of the laterites in terms of straightforward input of aeolian input of ancient continental material. It is possible to invoke the input of specific rock types, for example, the weathering and erosion of ultramafic peridotites which possess high Os concentrations and radiogenic Os compositions (e.g. Snow and Reisberg, 1995; Reisberg and Lorand, 1995). However, such peridotites do not normally possess unradiogenic Sr and radiogenic Nd compositions and so are unlikely to account for the variations seen in those systems. Alternatively it is possible that if the aeolian material was weathered prior to deposition then the Os concentration and isotope composition in this residual material may be very different from that of the bulk rock from which it was sourced.

Therefore, while aeolian input is likely to have had some influence on the Re–Os isotope system in the laterites, the nature and extent of this input is difficult to assess. In any event, if aeolian deposition is responsible for the external input to the laterites then this must have occurred while the groundwaters were still actively redistributing elements within the profile or else the patterns of change, including that at the watertable would be obscured.

5.4.3. Groundwater input

The chemical variations observed in both profiles provide clear evidence of the role of groundwater in the

redistribution of elements. In particular, the oxic–suboxic stratification provides a means for dissolution, transport and precipitation of both Re and Os. This raises the possibility that material may be gained or lost from the profile, not only by vertical movement from in situ weathering or aeolian input, but also by lateral movement of solute-laden groundwaters. The laterite at Bidar is remote from basement lithologies and developed upon the highest elevations. Consequently, there is no topography or adjacent rock types to drive a flow of externally sourced groundwater towards the profile. However, this does not preclude the input of groundwaters from the breakdown of the Ambenali formation itself. As was shown in Section 5.4.1 the Os isotope composition of the laterite at Bidar can be accounted for by derivation from the parent basalt, but does demand Os enrichment which could have been facilitated by Os-laden groundwaters.

Groundwaters carrying externally derived Os are much more likely to be present in the laterite at Goa, not only because of the low lying topographic position but also the presence of diverse surrounding rock types. Many of the surrounding rocks are from Archean and Proterozoic lithologies of the Dharwar craton, and therefore be expected to possess radiogenic Os isotope compositions. However, some lithologies do possess less radiogenic compositions and it is possible that Os could be input via groundwater derived from a mixture of these sources. Alternatively, the chemical signature of the groundwaters may have been derived from the nearby Deccan basalts.

6. Laterites and the surficial Os cycle

The results presented here, together with those of reported previously (Mann, 1984) suggest that laterites commonly possess much less radiogenic Os isotope compositions than their parent rock, and may also have much higher Os concentrations. Significantly, the laterites are also much less radiogenic and have much higher Os concentrations than average upper continental crust. Given the extensive geographical coverage of laterites (~30% of the exposed continental crust; Tardy, 1997), and their influence on the surface water cycle (nearly 50% of continental drainage flows through laterite terrain (Tardy, 1997)) it seems likely that they will exert a significant influence on the movement of Re and Os between the continents, oceans and atmosphere.

During their formation laterite soils may initially act to sequester both Re and Os mobilised by weathering (either from groundwaters or aeolian input). However, over time the relatively unradiogenic Os isotope composition from the weathering and erosion of laterite topsoils is likely to

influence the composition of rivers and dust that they source. There is little detailed data for rivers draining laterite terrains, however, in general global river data suggests if anything that the riverine $^{187}\text{Os}/^{188}\text{Os}$ isotope composition is actually more radiogenic than the average continental crust (Levasseur et al., 1999), possibly due to the effects of incongruent weathering. An upper limit of the Os contribution to the oceans from mineral aerosols can be calculated, from estimates of the global aerosol flux (e.g. Duce et al., 1991) and the Os content of average continental crust (Esser and Turekian, 1993; Peucker-Ehrenbrink and Ravizza, 2000a, 2001), which suggests about a 10% contribution from aerosols (e.g. Peucker-Ehrenbrink and Ravizza, 2000a). However, if 30% of that aeolian flux is derived from laterite topsoils (reflecting the continental coverage) then, at least some, aerosols may contain a much higher Os content than has previously been considered.

Changes in the balance of Os sequestered or released by laterites might be expected to accompany tectonic or climatic change. For example, uplift or cooling may lead to their enhanced physical weathering, and in particular, periods of global aridity will result in an enhanced dust flux from the continents. Conversely, during periods of global warming laterite formation may be enhanced (Dequincey et al., 2002).

7. Summary

Laterite weathering profiles at Bidar and Goa developed on different rock types, with different ages and a time interval of ~40 Ma between periods of laterisation. Nevertheless, the profiles are very similar, progressing from unaltered bedrock upwards to increasingly altered saprolite and an uppermost Fe-rich iron crust. Both profiles also preserve a watertable that is coincident with significant major and trace element variation.

Platinum group element enrichment in laterites is well documented, and the data from this study confirms that both Re and Os are highly enriched in the laterite relative to the parent rock. The pattern of Re and Os enrichment and depletion, particularly at the level of the watertable indicates that both elements are mobile. The level of Os enrichment is far greater than that of Re, which is reflected in the decreasing $^{187}\text{Re}/^{188}\text{Os}$ ratio and corresponding decrease in $^{187}\text{Os}/^{188}\text{Os}$ up profile. Laterite $^{187}\text{Os}/^{188}\text{Os}$ ratios are always less radiogenic than the parent bedrock that they developed from, consistent with previous work (Sharma et al., 1998).

The origin of the high Re and Os concentrations in the laterites remains unclear. Previous isotope studies of the laterite at Bidar have concluded that aeolian input to

the profile must have occurred. Nd and Sr isotope data suggests that the source of this material was ancient continental crust (Mason et al., 2000), while Li isotopes indicate that this material has experienced significant weathering prior to deposition (Kisakurek et al., 2004). However, for Os most potential crustal sources have low Os concentrations demanding significant aeolian deposition or the pre-concentration of Os in aerosols (perhaps as residues from weathering). Similarly average crustal sources are too radiogenic to account for the unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions observed in both laterites. Alternatively, the Re and Os may have been transported into the profile by the lateral movement of solute-laden groundwaters.

The Os concentration in laterites is similar to that found in Os-rich rock types, such as organic-rich sediments (Singh et al., 1999; Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002) and ultramafic peridotites (Jacobsen et al., 1984; Rampone et al., 1996), but in contrast to those lithologies laterites comprise a significant part of the continental land surface, and play an active role in the surface water cycle. Under those circumstances laterite formation or weathering is likely to exert a significant influence on Os behaviour in the surface environment, and that influence is itself likely to be highly sensitive to climatic or tectonic change (cf. Dequincey et al., 2002).

Acknowledgements

This work was supported by the Natural Environment Research Council (under contract NE/B502701/1).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2007.06.028. We would like to thank R. Carlson for the editorial handling and two anonymous reviewers for the constructive comments.

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