Geochemical mass-balance in intensely weathered soils, Darling Range, Western Australia

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Abstract

Chemical weathering, one of the major processes that modify the earth's surface, exerts important controls on the geochemical cycling of elements. The behavior of elements in rock weathering processes, especially in intensely weathered regolith profiles, is not very well understood. In addition, rigorous calculation of the mass fluxes during intense weathering is seldom performed. This study aimed to determine geochemical mass balance for regolith profiles subject to intense chemical weathering. Two lateritic profiles in Western Australia with different weathering intensity were studied, to investigate influence of weathering intensity on element loss or gain. GE lateritic profile (CIA values 90.8~99.2), with kaolinite and gibbsite as main weathering products, is more intensely weathered than MQ profile (CIA from 63.6 to 83.9). Calculating mass balance with Zr as the immobile element, Na, Ca, Sr, Rb and Ba were almost completely depleted in the GE profile, while in MQ profile, only Ca loss as high as 95%. Aluminium, Ti and Fe accumulate at 0.6 m depth MQ profile, which also has the highest clay content; in the GE profile, Fe is significantly enriched from 3.5-7 m, forming haematite and goethite in duricrust and ferruginous matrix.

Key Word

Laterite, weathering, geochemical anomalies, modelling, major elements

Introduction

Chemical weathering of rocks is one of the major processes that modify the earth's surface and is one of the critical processes in the geochemical cycling of elements (Ji *et al.,* 2004). Weathering intensity exerts important influence on mobilization and redistribution of different elements in a regolith profile. As the result of intense weathering, deposition, and modified by later soil-forming (pedogenic) processes on near-surface rocks, laterite (lateritic soil) represents one of the most common superficial formations in the tropics and covers long periods of time, extending over tens of millions of years (Dequincey *et al.,* 2006). Although much research on the laterization process and element mobilization has been performed worldwide (e.g. Beauvais, 1999; Beyala *et al.,* 2009; Ma *et al.,* 2007), the precise sequence of events and behavior of elements in rock weathering process and laterite formation are still not unambiguously understood. In Western Australia, high rainfall and humid weathering conditions have further enhanced rock weathering and element leaching, and form notable duricust (ferricrete) due to accumulation of iron. The purpose of this paper is to investigate the element mobilization and redistribution during intense weathering in lateritic profiles. Two lateritic profiles with different weathering intensity were studied, to investigate influence of weathering intensity on element loss or gain.

Material and Methods

Description of the study areas

The first profile is located in Mountain Quarry (31°54′54″S, 116°3′44″E), on the southern slope of Greenmount Hill, Western Australia. Here, granites typical of the Darling Range are intruded by a number of dolerite dykes. The profile is developed overlying granite with stonelines preserved from quartz veins implying in-situ weathering. The profile is 2 m-deep, samples from five depths were collected on 29th, May, 2009. The potential parent rocks, including granite and intrusive dolerite dyke were also sampled. The second profile is adjacent to Great Eastern Highway, Western Australia (31°22'30.95"S, 118°41'26.74"E) with very good bedrock (granitoid/dolerite dyke) exposure and a very deep weathered profile. The profile is 12 m deep, including saprolite, mottled clay, duricrust, and topsoil. Detailed sample information is listed in Table 1.

Analytical methods

Pretreatment of the soil samples included sieving through 2-mm plastic mesh for separation of gravel and roots/rhizomes from the -2 mm soil fraction. Part of the subsamples of the -2 mm fraction was used to determine the pH and particle size distribution. Soil pH was determined potentiometrically in the supernatant

in a 1: 5 suspension of soil: 0.01 M CaCl$_2$, and particle size distribution of soil samples were determined by the pipette method. Other soil subsamples and crushed rock samples were grounded to less than 100 meshes prior to fusion to determine major and trace elements: 0.7 g of finely ground soil was mixed with 12:22 Norrish flux (lithium metaborate/ lithium tetraborate) in a muffle furnace at 1050 °C to prepare fusion beads for determination of major elements by Philips PW1404 XRF. Two standard reference materials (OREAS and stsd-2) were analyzed together with the samples to check the accuracy and precision of the analyses. Primary minerals were identified in the thin sections of the rocks by optical microscopy; secondary minerals in the weathering products and the soil were identified by means of random powder X-ray diffraction. Relevant physical and chemical properties of the samples are listed in Table 1.

Table 1. Selected physical and chemical properties of samples from each profile.

Sample ID [1]	Depth (m)	soil pH [2]	clay%	silt%	sand%	CIA	C%	Description
MQ15	0.08	4.88	18.39	10.29	71.32	71.0	2.04	Horizon A topsoil
MQ14	0.25	5.16	30.47	1.75	67.79	75.7	0.28	Horizon A topsoil
MQ13	0.60	4.83	50.31	0.76	48.93	83.9	0.32	
MQ12	1.10	4.75	25.56	1.98	72.46	75.7	0.11	
MQ11	1.60	4.62	23.25	2.45	74.30	68.5	0.09	
MQ10	2.00	4.65	18.00	0.83	81.16	63.6	0.07	saprolite
GEA1	0.09	5.09	1.91	3.20	94.89	90.8	4.66	Horizon A topsoil
GEA2	0.12	5.03	1.46	2.84	95.70	94.0	1.46	Horizon A topsoil
GEA3	0.23	5.33	1.86	2.91	95.23	93.3	0.80	Horizon A topsoil
GE6	3.50	6.12	2.30	6.98	90.72	99.2	0.38	ferricrete
GE5	7.00	5.96	19.30	2.27	78.43	97.6	0.21	ferruginous matrix
GE4	8.40	5.75	18.85	9.69	71.46	94.3	0.04	mottled clay
GE3	10.00	5.52	22.56	8.12	69.31	98.9	0.03	mottled clay
GE2	11.40	5.26	22.64	7.68	69.67	97.8	0.03	saprolite
GE1	12.50	4.77	24.67	12.59	62.74	94.6	0.07	low saprolite

[1] The first two letters of sample codes identify each profile: Mountain Quarry (MQ) and Great Eastern Highway (GE).
[2] pH was determined in a 1:5 suspension of soil: 0.01 M CaCl$_2$

Results and discussion
Weathering intensity and mineral composition
To quantitatively evaluate the intensity of chemical weathering, the Chemical Index of Alteration (CIA, Nesbitt and Young 1982) was used. The CIA values of regolith samples are in Table 1. In the MQ profile, CIA decreases from MQ13 to saprolite, ranging from 63.6 to 83.9. For the GE profile, CIA varies substantially from the regolith-bedrock interface to the top of the profile, with two peaks at GE6 and GE3; the regolith is more intensely weathered than MQ profile, with CIA values 90.8~99.2. Weathering indices of topsoils in both profiles (MQ15, MQ14, GEA1, GEA2 and GEA3) are lower than the subsoils, which may be because the original weathered topsoil has been eroded.

The main minerals present in the samples collected from MQ profile are quartz, plagioclase, muscovite, microcline and clay minerals. In contrast, the main minerals in GE regolith samples (Table 1) are kaolinite and gibbsite. In GE6 (duricrust), the iron oxides haematite and goethite were identified.

Chemical composition
To quantify the net result of pedogenic weathering, a geochemical mass balance calculation was used in this study. The formula (Equation (1) assumes an immobile element behaves conservatively and corrects mobile element concentrations for volumetric strain during weathering and pedogenesis).

$$\tau_{i,j} = \left(\frac{C_{i,p}}{C_{i,w}}\right)\left(\frac{C_{j,w}}{C_{j,p}}\right) - 1 \tag{1}$$

Where C represents concentration, with subscript i for immobile element, j for element of interest, w for weathered material and p for parent rock. If $\tau_{i,j} = -1$, the element i is completely depleted during weathering.

Although this equation provides a tool for estimating elemental loss or gain of a profile, the mass balance

equations have several critical assumptions. First, there should be a genetic relationship between regolith and its parent material. Second, since the calculations are highly dependent on immobile elemental concentrations, the reference element should be conservative in its real sense. The chosen immobile element for this analysis is Zr, because Zr primarily resides in zircon, which is resistant to chemical weathering and inter-sample variations in Zr are less than for Ti.

Alkalis and alkaline earths – In the GE profile, the weathering is complete and extreme, while in the MQ profile, the weathering and leaching process is still in progress. The alkali and alkaline earth elements in both profile are highly depleted, especially in the GE profile; calcium (Ca), sodium (Na), strontium (Sr), barium (Ba) and rubidium (Rb) were almost completely depleted; 83%~97% potassium (K) and 66%~85% magnesium (Mg) were also leached from the profile relative to its assumed parent rock (Figure 1).

In the MQ samples, Ca is the element with highest loss (80%~95%), reflecting minimal anorthite feldspar remaining in the profile; followed by Na (25%~80%), Mg (40%~60%) and K (30%~50%). Rb, Sr and Ba losses were 40%~53%, 60%~75%, 25%~55% respectively (Figure 1). Hence, with continued weathering of MQ profile, anorthitic plagioclase will progressively be replaced by clay minerals (kaolinite in this study). Alkali- and alkaline-earth elements may also be fixed by exchange and adsorption onto secondary clay minerals, or incorporation into structural sites of clays (Nesbitt *et al.,* 1980).
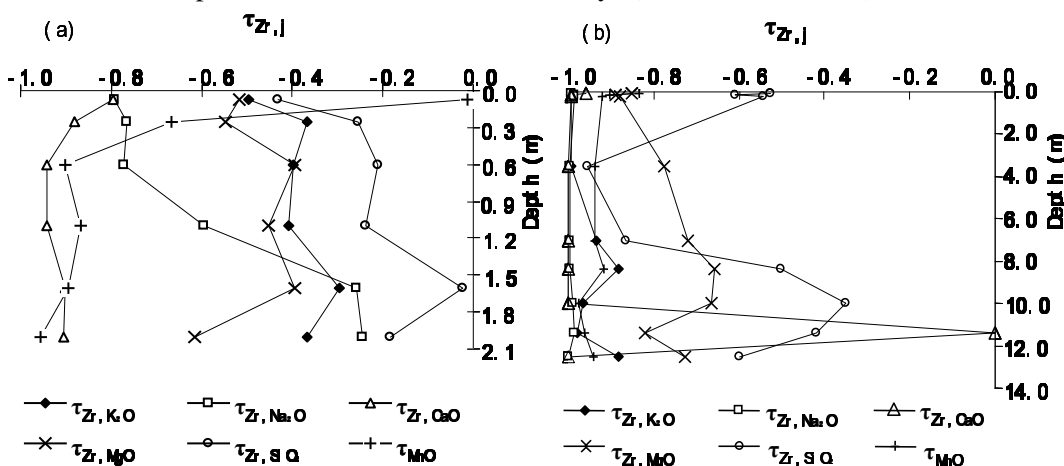

Figure 1. Depth profiles for geochemical mass-balance (τ = solute gain or loss) of Ca, Na, K, Mn, Mg and Si for (a) the Mountain Quarry (MQ) profile and (b) the Great Eastern Highway (GE) profile.

Translocation of aluminum and iron –in the MQ profile, mass balance calculations suggest that iron, aluminum and titanium accumulate in regolith samples, all peaking in sample MQ13 (Figure 2(a)). Sample MQ13 also had highest clay proportion, which accounted for enrichment of aluminum. It is likely that, with intense weathering, mafic silicates (e.g. biotite) broke down, and Fe(II) is released and transferred downwards, rapidly oxidized and precipitated as hydrous oxides in the subsoil, or adsorbed by clay minerals.
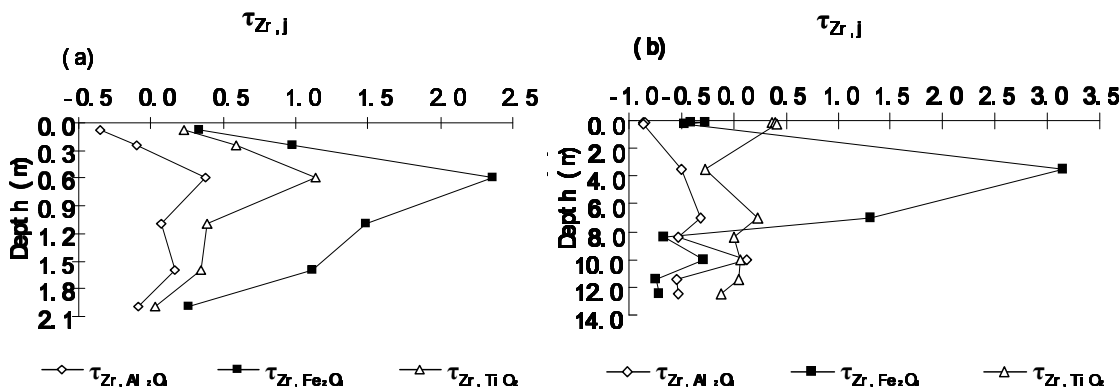

Figure 2. Depth profiles for geochemical mass-balance (τ = absolute gain or loss) of Al, Fe, and Ti for (a) the Mountain Quarry (MQ) profile and (b) the Great Eastern Highway (GE) profile.

For GE samples, iron showed enrichment mid-profile with depletion in the topsoil and at depth (Figure 2(b)). Aluminum was leached from the GE profile, and titanium behaves approximately conservatively (Figure

2(b)). Except for the GE3 mottled clay sample, aluminum was depleted by approximately 50%. Haematite and goethite were identified in samples GE5 and GE6 (ferricrete) which showed addition of iron. This depth (GE6) may be the original groundwater table; iron leached from the topsoil, transferred downwards by rainfall, with the groundwater slowly decreasing, iron was oxidized and precipitated as Fe(III) oxyhydroxides. The Ti: Zr ratio was relatively constant (0.1~0.4) in most of samples in GE profile, except possible depletion in GE6 (duricrust) and GE1 (saprolite). While it is generally considered that Ti is a conserved element, Ti is mobile in extreme weathering conditions. Further work using scanning electron microscopy will examine physical evidence for weathering of Ti-bearing minerals (e.g. biotite, or even refractory minerals such as titanite and anatase), which may have resulted in Ti translocation.
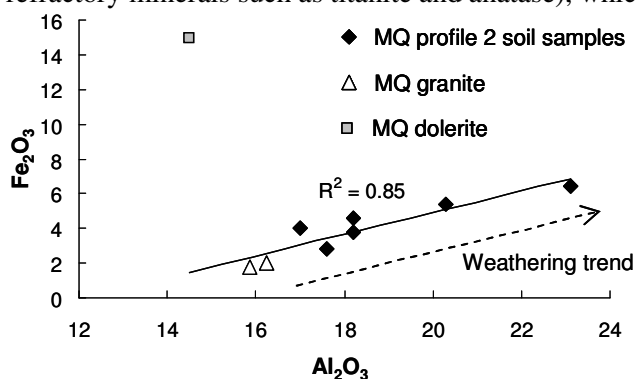

Figure 3. Plot of Fe_2O_3 vs. Al_2O_3 for regolith and parent rocks from Mountain Quarry (MQ), showing evidence confirming the assumed parent material of the profile.

Conclusion

Some trends are apparent in the mobilization and redistribution of elements in intensely to extremely weathered profiles developed on granite in Western Australia. Losses of elements based on mass balance calculations are consistent with the degree of weathering calculated by weathering indices, and mineralogy of the weathered regolith. Fe, Al, and Ti show variable behaviour, with the most intensely weathered profile only showing evidence of Fe accumulation in ferruginous duricrust. The less weathered profile has accumulations of Fe, Al and Ti; the contents of these elements (e.g., Al: Fe ratio) provide geochemical confirmation of the parent material.

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