ELEMENT MOBILITY AS A RESULT OF CHEMICAL WEATHERING IN A GRANITOID NEAR VALPARAISO, CHILE

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ABSTRACT

The chemical breakdown of the geologic environment is a source of both beneficial and toxic elements in biological and water systems. A saprolite is preserved when the chemical weathering rate of bedrock exceeds its erosion rate. Rates and styles of geochemical reactions are important when evaluating the risk of toxicity in near surface ecosystems. A saprolite, developed in a Carboniferous granitoid, in the Chilean Coastal Range, was overlain by Pleistocene granitic fluvial gravels more than 2.2 Ma ago (minimum cosmogenic nuclide exposure age). An impermeable duripan (iron-cemented soil horizon) has developed in the gravels, reducing the meteoric flux and therefore the weathering rate through the saprolite below. The saprolite and overlying gravels were sampled for geochemical analyses at varying depths to 8.3 m, including a weakly weathered sample at the base of the section. The concentration of many mobile elements generally increase with depth, reflecting the greater weathering near the surface. Some elements decreased or remained constant, depending on solubility of their original host mineral or the soil forming properties of the secondary minerals they formed. The continuation of the trends through the Pleistocene nonconformity indicates that weathering continued after the sediments were deposited. Significant deviations from these trends with depth occur at 1.79 and 2.37 m below the surface—the depth corresponding to the duripan layer, just below the zone of most intense weathering.

The chemical index of weathering (CIW) and the chemical index of alteration (CIA) show maxima of 77 and 73 (unitless), respectively which is consistent with intense weathering of granodiorite. The results indicate that the third and fourth zones of saprolite alteration are preserved, indicating that there has been a significant loss by erosion of the top portion of the saprolite prior to deposition of the fluvial gravels. REE ratios, and trends in the EU anomaly are opposite for the gravels and bedrock samples, in part reflecting the transport of weathering products such as clays. Net leach rates of the most mobile elements (e.g. Na and Ca) are on the order of 10 mg/g integrated over the entire exposure section.

Key words: granite, weathering, geochemistry, element mobility, REE, Santo Domingo Complex, duripan, chemical index of weathering, chemical index of alteration.

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1.0 INTRODUCTION

The geologic environment is important for human wellbeing because it is the primary natural source of both beneficial and potentially toxic elements in soil and water systems. Exchanges of these elements in the geologic environment are facilitated by both physical weathering—that is, the break up of material by physical processes, or chemical weathering—the process by which rock is decomposed at the atomic level by exposure to water or air, with little transport of the material from the area. This study focuses on extreme chemical weathering of granitic rocks, the most common rock type in Earth's continental crust. When granitoids become deeply chemically altered, the in situ residual product is referred to as "saprolite", a partially disaggregated rock, which maintains structures that were present in the original unweathered rock (Bates and Jackson, 1987).

A saprolite is preserved when the weathering rate of bedrock greatly exceeds its surface erosion rate. Breakdown of the less resistant minerals into their constituent parts occurs in response to the presence of oxygen and moisture through chemical interactions, which depend on rock composition and mineralogy, pH, redox potential, presence and nature of overlying soils, presence and composition of fluids, temperature, permeability, and microbial activity. As well anthropogenic interference, such as road or housing development, which exposes new material to the atmosphere can result in increased weathering. Typically the intensity of weathering decreases with depth below the surface. As the saprolite develops, elements which are more soluble under typical atmospheric conditions, are more mobile (such as Na, Ca, As, U, Rb) and can be released into the environment. Some of these more mobile elements form new minerals while other incompatible or weakly bonded elements, such as Cs, Ba, U, or Rb, are evacuated from the granite and released into the water and neighbouring soils and ecosystems. Immobile elements and chemically resistant (refractory) minerals can remain in situ. New minerals generated may or may not be good adsorbers (attracting charged ions to their surfaces) or absorbers (they permit other elements into their structures) of other released elements. The migration of mass from a saprolite results in straining—a net loss of density due to inflation of the rock or leaching. This results in a short-lived positive feedback in which more intense weathering may occur because the system is more permeable and open, and can result in ground instability issues as well. The rate of saprolite development decreases with time as the availability of soluble minerals and mobile element diminishes. Therefore the rate of release of toxic elements to the environment is controlled by the rate of weathering.

A Carboniferous (290 million year old, (Ma)) granitic saprolite exposure in the Chilean Coastal Range outcrops along a recently constructed highway near Valparaiso, Chile (Fig. 1.1). In this area, overlying fluvial (stream-deposited) sediments have protected the profile from erosion over the past 2 Ma (Gosse, unpublished cosmogenic nuclide geochronology data). Additionally a duripan (an impermeable Fe-cemented soil horizon) has developed in the sediment, which has reduced water movement (and thus the weathering rate) in the saprolite below the duripan. The area is presently semi-arid with yearly temperature averages of approximately 17ºC in January (summer) and 12ºC in July (winter) at 110 m elevation (33º22'51.46"S-71º37'62.74"W). Average rainfall is approx. 400mm/yr (Paskoff and Manriquez, 1998).

The study area is located in a rapidly developing residential suburb close to Santiago, (Fig. 1.2, 1.3) meaning that proper geochemical analyses of this area will allow for the assessment of element leaching which may have health impacts on the nearby residential areas. The primary reason for studying this exact site from an environmental point of view is its deep (> 8 m) and recent exposure which provide optimal conditions to describe and characterize the geochemistry of

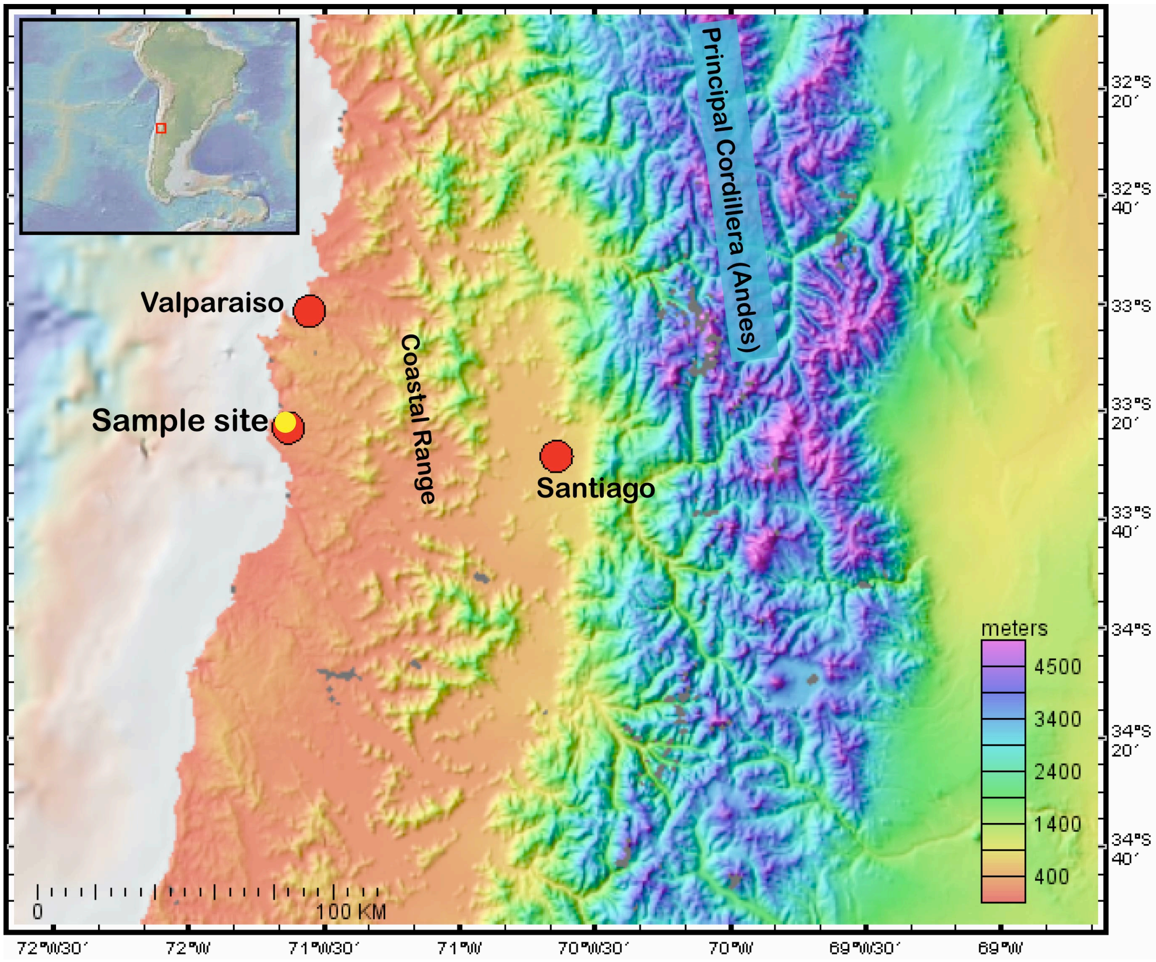

Figure 1.1. Digital elevation model of the sample area. Sample site and surrounding areas labeled. (GeoMapApp, 2004)

Figure 1.2. View of sample location from the Pacific ocean looking north east. (Google Earth, 2007)

Figure 1.3 View of road along which samples were taken. (Google Earth, 2007)

the saprolite. The alternatives, such as a 10 cm diameter core, shallower exposures, and old exposure are available elsewhere, but have obvious disadvantages of non-ideal open systems with limited visibility.

The study site is situated along the tectonically active coast of Chile where frequent and relatively high magnitude earthquakes occur. Seismic events are known to cause slope failure in rocks with low yield strength such as a well developed saprolite. This rock type therefore creates an engineering challenge to build seismically robust structures. The landscape in the area, of which the saprolite comprises a key element, contains geomorphological markers, which record the history of rock uplift and erosion in the area. An understanding of the saprolite history will contribute to our understanding of the post-Miocene (since 5.3 Ma) tectonic history of the highly populated region. The observation that saprolites require high humidity, but low surface runoff to cause the intense leaching creating saprolite, indicates that the saprolite is no longer forming in the current environment, and that a significant climate change must have occurred prior to the deposition of the fluvial gravels 2 million years ago.

The objectives of this study are to use geochemistry of the saprolite to examine the history of weathering and saprolite development by measuring major, minor and rare earth elements (REE) at the sample site. Various weathering indices (the chemical index of alteration (CIA) (Nesbitt and Young, 1983) and the chemical index of weathering (CIW) (Harnois, 1988)) and ratios of rare earth elements (REEs) also provide information regarding the flux of elements from minerals or their absorption in clays. Chemical composition of this granite is previously unknown and there is a possibility of release of potentially toxic elements from this saprolite—chemical anomalies will be sought. Additionally, the results of this study will be used to interpret the relative flux of elements due to surface processes over time using the parent rock as a reference point, and to use weathering trends and chemistry to assess fluvial gravel provenance. Overall the study will improve understanding styles of chemical weathering on granite in its natural environment elsewhere in the world. As this granite has never been studied and due to its recent exposure, any incompletely weathered material is more prone to weathering during rainfall events. Due to the unknown chemistry of the granite the potential leaching of toxic elements into the hydrosphere or biosphere is not clear. Saprolite research in Nova Scotia has led to the discovery of sources of U, Rn and Hg leaching (O`Beirne-Ryan and Zentilli, 2006) as well as studies in France showing chemical weathering as a cause for release of potentially toxic quantities of Cd, Al and As into wetlands (Olivie-Lauquet *et al.*, 2001). As all granites are of slightly different chemical composition, geochemical analyses of specific areas are needed to understand potential effects of chemical weathering at any given location. Granites in Chile probably do not have the same geochemistry and thus toxicity as those of Nova Scotia or France and this study marks the first detailed study on the chemical weathering processes of this particular Chilean granite.

This is also important to study climate change may be causing changes to weathering rates in areas of current saprolitization (where the saprolite is currently at the surface weathering). Amplified weathering rates cause minerals to breakdown more quickly into component parts and therefore there may be increased element mobility in areas previously thought to be unchanging.

2.0 PREVIOUS RESEARCH

The process of weathering has been examined by a number of studies and has been shown to contribute to element mobility within a rock profile, which could lead to the leaching of elements into water systems (Oliva *et al.*, 2002; Cramer & Nesbitt, 1983). The following review cannot be comprehensive due to space limitations. However, results of studies most relevant to the study are reviewed here.

2.1 Geographic and geologic setting

The study site is located within 20 km of Valparaiso, Chile, along a main highway. There are houses in the area, the closest of which are within a kilometer. The site is currently situated under a cultivated Eucalyptus forest and the land may have been previously used for agriculture but has been let go fallow. Water sources for the area are not well delineated at the point of the study. Possibilities include groundwater or surface waters, both of which may be affecting saprolite weathering, depending chiefly on flow rate.

The study area is in the Coastal Chilean Range, which is a narrow (10 km) low relief (300 m) semi-arid upland, which separates the Central Depression from the Pacific Ocean (Fig. 1.1). The study site lies within the Santo Domingo Complex of Carboniferous arc intrusive (Parada *et al.,* 1999) and locally exposes a granodiorite at elevations of 100 to 110 m. Extensive low gradient topographic surfaces cutting the landscape represent paleofluvial channels or marine terraces, which record the history of relative sea level changes due to tectonics and climate change (Parada *et al.*, 1988). In the Coastal Range to the south, fossiliferous Miocene marine sediments cover saprolite currently above 150 m. In contrast, the granodiorite saprolite in this study site is covered with fluvial gravels at 100 to 130 m, an indication of significantly different tectonic histories over just

200 km (Gosse, *pers. comm.*). Several granitic plutons of different ages have been identified in the Coastal Range and adjoining tectonic provinces (Parada *et al.*, 1988; 1999).

Besides its interesting tectonic setting, the recent exposure and access of this locality, the apparent extremely low rate of surface erosion, and the indication of long exposure duration based on preliminary soils data and cosmogenic nuclide geochronology, are factors that make this site ideal for examining weathering history. Preliminary soil and stratigraphic analysis by E. McDonald and J. Gosse indicate that the saprolite is covered by an average of about 1 m of fluvial gravels (which are not a part of the saprolite unit), which in turn underlies 60 cm of eolian sediment, with distinct contacts between all three units (Fig. 2.2). Very well developed soils have formed from the eolian silts and fluvial gravel parent material. One significant soil horizon is a duripan layer, within which the upper three samples were taken for this study. A duripan is a layer of material which is naturally cemented together and found near the exposed surface. Duripans have been interpreted to develop as a result of deep weathering of a low relief surface (Bland and Rolls, 1998).

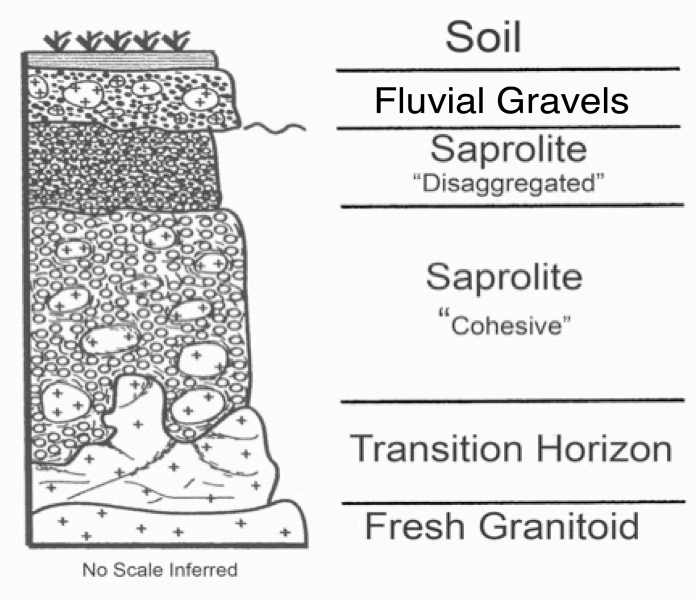

Figure 2.2 Saprolite formation in granitoid bedrock. Shown are the layers found at the sample site. Note that eolian sediments have developed into soil (adapted from O'Beirne-Ryan & Zentilli, 2006).

Surfaces in this area are generally ancient marine terraces and thus have a low relief. The duripan at this location contains rounded pebbles and cobbles (up to 25 cm diameter), and many of these clasts appear relatively unweathered in thin section, which suggests there was transport of the sediments on the weathered granitoid. The duripan is therefore a separate unit from the saprolite, though it is also made up of similar granitic parent material. The provenance of this gravel is unknown and therefore is an objective of this study. There is an increasing amount of disaggregated granite (termed grus) toward the base of the duripan. Although in nearby locations sedimentary bedding has been preserved, most of the upper metre has been mixed due to biologic, and in the case of the upper 30 cm, anthropogenic processes. The duripan shows extensive weathering of feldspars and an abundant accumulation of clay on mineral grains (MacDonald, *pers. comm.*). The mixed zones are clearly evident in the field and were avoided when sampling. Clay minerals are more likely to retain mobile elements and so are important considerations in this study.

Previous geochemical studies of igneous bodies in the area have attempted to show the origin of the magmas but have not identified element mobility or changes due to weathering (Parada *et al.*, 1999). The chronology of the exposure of the granite and the soil analysis in the sediment above the granite are being conducted concurrently by John Gosse and Eric MacDonald over a three year period.

2.2 Chemical weathering

Chemical weathering refers to the interaction between solution and rock and their weathering residues (Nesbitt and Young, 1989). In some studies this excludes any reactions between permanent or perched water tables and the interactions of groundwater with rock (Nesbitt and Young, 1989). Weathering includes rock alteration impacted by atmospheric conditions both above and below the water table. The redistribution of elements in the rock profile is strongly controlled by the interaction between water and minerals, oxidizing environments (unless aided by microbial activity), and organic acids, so weathering in the soil and unsaturated zone above the groundwater table may be faster than below the groundwater table. This interaction will be more influential on less stable and less resistant minerals, causing them to leach elements. The interaction results in a residue of the more resistant components in a rock (Fig. 2.3).

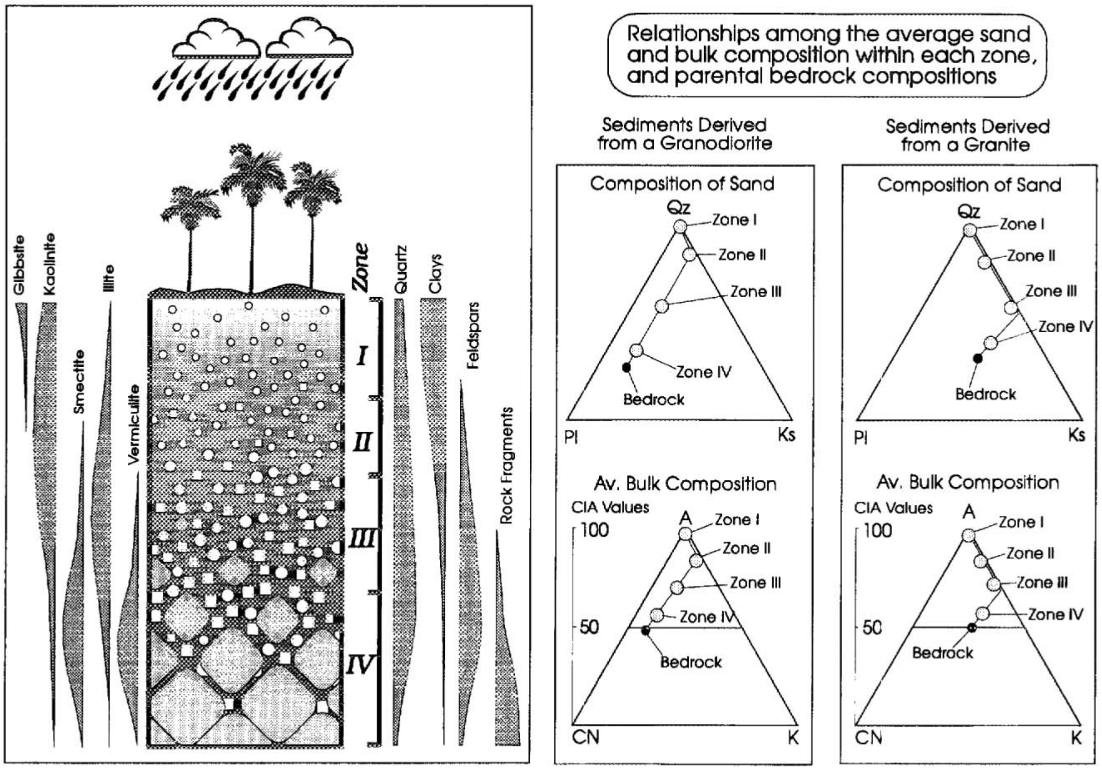

Figure 2.3 An idealized weathering profile in granitic bedrock. On the left the rock composition is plotted indicating composition in the four weathering zones, where zone IV is the least weathered and I is the most weathered. The bulk composition ternary diagrams indicate the percent composition of Al (A), Ca+Na (CN) and K. These are then referenced to the chemical index of weathering (CIA) values with 100 being a fully weathered rock and 50 being an average unweathered granite. (From Nesbitt *et al.,* 1997)

2.2.1 Principles of solution geochemistry

A mineral is a solid element or compound with a regular repeating crystal structure and a definite chemical composition (Nesse, 2000). Crystal lattices are formed through either ionic, covalent or metallic bonds between atoms, and commonly with van der Walls and hydrogen bonding. Granite is a plutonic rock type formed at high temperatures and pressures within the earth. When minerals formed under these conditions are exhumed from their crystallization depths (e.g. > 5 km) to the surface by erosion over long time periods, geochemical reactions during this ascent favour crystal forms and minerals that are more stable at cooler temperatures and lower pressures found at earths surface. The atomic structure determines the shape of the overall mineral as well as the bonding types and therefore bond strengths. The atomic structure and bond strength controls the ability of those elements to chemically weather as well as substitute for one another.

Chemical weathering typically involves numerous simultaneous reactions, but can be summarized with the following common example:

$$\text{Silicates} + H_2O \Leftrightarrow \text{clay minerals} + Si_xO_y + \text{ions in solution}$$

(Nesse, 2000). Atmospheric, biologic, or soil-derived CO_2 or HCO_3^- in solution results in carbonic acid which assists in breaking down silicates. Other organic acids may contribute as well. In the case of a granitic rock, composed mainly of quartz (SiO_2) , plagioclase feldspar ($NaAlSi_3O_8$ to $CaAl_2Si_2O_8$), K-feldspars ($(Na,K)AlSi_3O_8$) and micas (biotite and muscovite, $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$ and $KAl_3Si_3O_{10}(OH)_2$ respectively). Various weathering studies have shown that the principal breakdown of granite is first the plagioclse, followed by K-feldspar and mica (Bland and Rolls, 1998; Nesbitt and Young, 1989). Reactions governing mineral dissolution differ depending on the mineral (Table 2.1). Mineral dissolution can occur both congruently (where a mineral will go completely into solution with no precipitate remaining) or incongruently (where a mineral will go into solution and release ions will form insoluble new minerals). Aluminosilicate minerals will typically dissolve incongruently, that is they will dissolve and then re-precipitate as another mineral, resulting in numerous mineral phases throughout breakdown. These are dependent on the original chemical composition of the starting mineral, as well as other elements in the environment (Birkeland, 1999). Precipitating minerals depends chiefly upon pH, redox conditions, temperature, and concurrent reactions with other dissolving minerals and element species in solution.

Table 2.1 Minerals common in a granite which undergo weathering. Note that cong. = congruent; incong. = incongruent; diss. = dissolution; oxid.= oxidation (adapted from Berner and Berner, 1996)

Mineral	Gerneralized Composition	Rock type	Main Reaction
Plagioclase feldspar	Solid solution between $NaAlSi_3O_8$ (albite) and $CaAl_2SiO_8$ (anorthite)	Igneous Metamorphic	Incong. diss. by acids
K-feldspar	$KAlSi_3O_8$	Igneous Metamorphic Sedimentary	Incong. diss. by acids
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Igneous Metamorphic	Incong. diss. by acids Oxid. of Fe
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Metamorphic	Incong. diss. by acids
Quartz	SiO_2	Ignous	Resistant to diss.

2.2.2 Element mobility and substitution during chemical weathering

An early study of weathering showed that during chemical weathering of minerals, elements will leach in a non-stoichiometric manner (Beyer, 1871) i.e. they will not leach to the exact proportions of the constituents specified by the chemical formula of a mineral. This adds more difficulty in predicting which elements of the mineral will move and when (Boeglin and Probst, 1998). Element mobility is controlled by a number of physical and chemical factors but is primarily a function of charge and ionic radius of the element, as well as other elements in the solution and minerals. Other conditions of the solution, such as pH, Eh, and dissolved anionic species can also influence mobility. Goldschmidt (1945) proposed guidelines regarding the fate of released ions with the calculation of an ionic potential, that is, the ratio of the charge to the ionic radius.

Other studies have indicated the ease with which ions can leach from rocks during chemical weathering and have established the following ranking based on Polynov's ion mobility series, in which phase I is very mobile and phase V is relatively immobile (Hudson, 1995):

Cl > SO_4 > Na > Ca > Mg > K > Si > Fe > Al
— phase I→←II→←—— III→← IV→← V ——

Some minerals contain REEs, which belong to the actinide series of the periodic table. These are further subdivided into heavy and light rare earth elements (HREE and LREE respectively) based on molecular mass. Cramer and Nesbitt (1983) showed that heavy REEs have greater mobility during chemical weathering of minerals due to their ionic strength and low bonding capacities. As well, as minerals fractionate, the HREE can be adsorbed by these minerals and move. Fractionation refers to the separation of elements during some physical, chemical, or biological process. In the case of chemical weathering, not all elements will participate in the same reactions or to the same degree (ionic potential), so elements favouring participation will become mobile and leave the nonparticipating elements to for the residuum. Weathering rate studies by Afifi (1985) show that despite non-stoichiometric leaching, some element mobilities vary predictably with pH. These studies showed, for example, that Al^{3+} will leach out of a mineral at a pH of 5, and will, rapidly and readily, will form a metastable precipitate. The study also showed that as pH lowers to about 3, Al^{3+} will become mobile again and will precipitate for a second and then a third time.

Additional factors relating to the mobility and substitution of elements is their compatibility. Compatibility, the capacity of an element to fit into an atomic structure or substitute for another, is governed principally by charge as well as the size of the atom. Some proposed rules of substitution are that elements will substitute if (Goldshmidt, 1945)

1. Atomic radii is less than 15% different
2. The is a difference of charge of 1 or less, assuming electric neutrality is maintained
3. Two atoms can occupy the same position in the lattice, where the one with higher ionic potential will form a stronger bond and remain

2.2.3 Previous studies and measuring chemical weathering

Important preliminary studies into chemical weathering used a mass balance equation to compare the alteration product with the parent rock (Cramer and Nesbitt, 1983). To accomplish this a reference element, such as immobile zirconium (Zr) or titanium (Ti), is chosen from the most immobile elements in the section. The ratio of this reference element to all other elements measured is a means of determining the variation in the elemental chemistry with depth while avoiding differences in concentration due to mineralogical composition of the specific sample. Without this normalization, small samples with different mineralogy from others collected from the same rock will yield different concentrations (e.g. if a quartz rich sample was selected, it may not contain much Na or Ca, relative to a more average granite sample from the same outcrop) . The ratio of the elements to an immobile reference element also provides a means to measure the decrease in the volume of the rock during weathering. Nesbitt (1979) describes the following equation where I is the immobile element as compared to any element X in the sample (s), compared with the concentration in the parent rock (p)

$$\% \text{ Change} = ((X_s / I_s) / (X_p / I_p) - 1) \times 100$$

Most saprolites can be considered open systems (to vegetation, rainfall, soil processes and oxygen), and are therefore subject to the acquisition or removal of elements by outside sources of elements, making interpretation complex. It is for this reason that many studies have favoured controlled experiments in laboratories over natural systems.

Several useful indices have been developed in attempt to quantify the magnitude of weathering that has occurred in a saprolite (Nesbitt, 1979; Nesbitt and Young, 1982; Harnois, 1988). These are mostly based on the idea that Al_2O_3 is a relatively immobile element and therefore the indices measure the relative percent change of more mobile oxides such as Na_2O, CaO and K_2O. Some indices use Zr or Ti as the immobile element (Nesbitt, 1979). Ruxton (1968) measured a weathering potential index, involving all major oxides, which was then modified by Vogel (1973) to remove Fe_2O_3 and TiO_2 due to their relative immobility. The chemical index of alteration (Nesbitt and Young, 1982) and chemical index of weathering (Harnois, 1988) are used in this study and further described in the methods section.

2.2.4 Factors affecting chemical weathering

Weathering rates are determined by a combination of rock type, mineralogy, chemistry, climate, soil depth, vegetative cover, microbial action and topography, and lithology (rock type) is an important control on many of these factors (eg. Kram *et al.*, 1997) (Table 2.2).

Table 2.2 The physical properties of rock relevant to weathering (Bland & Rolls, 1998).

Inherent	**Mechanical**
1 Texture: including grain size and its relation to porosity, surface area, permeability and capillarity 2 Discontinuities at various scales 3 Water content, measured by natural moisture content; water absorbtion capacity; saturation coefficient	1 Compressive strength 2 Shear strength 3 Tensile strength 4 Elasticity

Climate is important as temperature controls the kinetics of chemical reactions and precipitation will affect the amount of erosion, porewater, and humidity in an area (Oliva *et al.*, 2002). Despite its coastal proximity, the study area presently has a semi-arid climate, so erosion and weathering are likely slow. What little weathering is occurring due to limited rainfall and moisture in the air is probably limited to the uppermost metre of the section above the impermeable duripan. To form the saprolite that is preserved today, past climates were most likely tropical, providing the intense leaching needed for such extensive weathering. Topsoil depth affects weathering rates as it influences water residence time in the region, thus playing a large role in chemical weathering (Oliva *et al.*, 2002). The uppermost horizons in the eolian sediments extend to approximately 30 cm depth and are in sharp contact with fluvial gravels, under which the saprolite is preserved (Fig. 2.2). Bacteria hosted by the soil may influence the dissolution of minerals. A study by Ullman *et al.* (1995) found that bacteria can both enhance and inhibit the dissolution of minerals in nature due to the production of organic acids during biological functions. These will affect the pH of the environment, which will affect element mobility as described in the following section. As well as organic acids, cell walls and extracellular polymers produced by the bacteria are sometimes able to bind with metals. This could both enhance solubility by forming complexes with these metals in solution, or decrease solubility by reacting with the surface of minerals and aiding in the formation of secondary stable phases out of elements in solution (Ullman *et al.,* 1995).

Vegetative cover is another factor in mineral dissolution as root systems cause a decrease in pH within soil due to nitrification and acidic (carbonic and other organic) gases and solutions. Vegetation also protects the area from physical erosion. The surface of the study area has a broad (several km^2) shallow dipping (<10 °) well drained slope. Root systems are evident in the uppermost soils units and ancient root casts and evidence of plant induced bioturbation has been interpreted from preliminary field examination by E. McDonald. .

2.2.5 Seawater interaction and weathering

Marine erosional terraces cutting saprolites to the south of the study area indicate that the saprolite has once been inundated by seawater. No physical evidence of sea water interaction is apparent at the study locality, but if sea water did influence the rock, the site will have an important bearing on paleo-sea level and rock uplift rates in the Coastal Cordillera. The effects of seawater on granite weathering have not been widely studied. There are, however, some reports of the chemical effects of chlorides from sea salt on granite systems (Rivas et al., 2003). Salt crystallization will induce physical weathering by the associated volume change when saline solutions evaporate between crystal boundaries and in small fractures. In granites exposed to salt water, chlorides were found in increased concentrations from the parent rock, and decreased in concentration with depth (Rivas et al., 2003). The halides can cause lower pH and the dominant constituents of sea water (alkalis) and halides are generally mobile and therefore can catalyse or accelerate weathering reactions or induce reactions that would not have occurred. Sea water interactions have been proposed as an important chemical weathering agent for saprolites in Nova Scotia (O'Beirne-Ryan and Zentilli, 2003). In the proposed study, Cl^-, F^- and B concentrations are being analysed in an attempt to understand the depth of influence of seawater infiltration into the granite. Using two isotopes of boron, previous studies have determined marine versus non-marine origin of the element in a rock profile, thus potentially helping to determine the geologic history of the rock (Barth, 1998). Unfortunately, due to time and money constraints, isotopic analyses are beyond the scope of this thesis research.

3.0 METHODOLOGY

3.1 Sample Collection

Twelve samples of the saprolite and covering sediments were collected by J.-L. Antinao, J. Gosse, and E. McDonald in January 20, 2007 (Fig. 3.1). Although the exposure was recently excavated (within two years of sampling), they were careful to begin sampling only after the outermost 2 cm of saprolite and 25 cm of sediment were removed. Samples spanned the entire 9 m section and were positioned to optimize all analyses (geochemical, geochronological, tracer) and to ensure at least one sample was collected per soil horizon. Though 12 samples were taken, only eight were used in this study in order to ensure sufficient sample mass for the cosmogenic nuclide experiments. Eight samples were deemed sufficient to show the trends that are required to meet the objectives of this thesis. Samples ranged in size from 2100 g (lowermost sample CHI-07-702, 8.29 m from surface) to 825 g (uppermost sample, CHI-07-721, 1.52 m from surface) (Table 3.1). Sampling methods involved scrapping away the outermost layer of accumulated dusts and particles, then chipping out a rock sample of adequate size. These were then transported to Dalhousie University for further processing

3.2 Sample site description

The sample site is an unvegetated, 55º slope of exposed “bedrock” at 33º22’51.456”S; 71º37’59.627”W. It is approximately 15 meters off the road. Soil thickness in the area reaches a measured depth of 107 cm and the uppermost surface is vegetated with eucalyptus. Trees now grow in some areas around the sample site on the terrace.

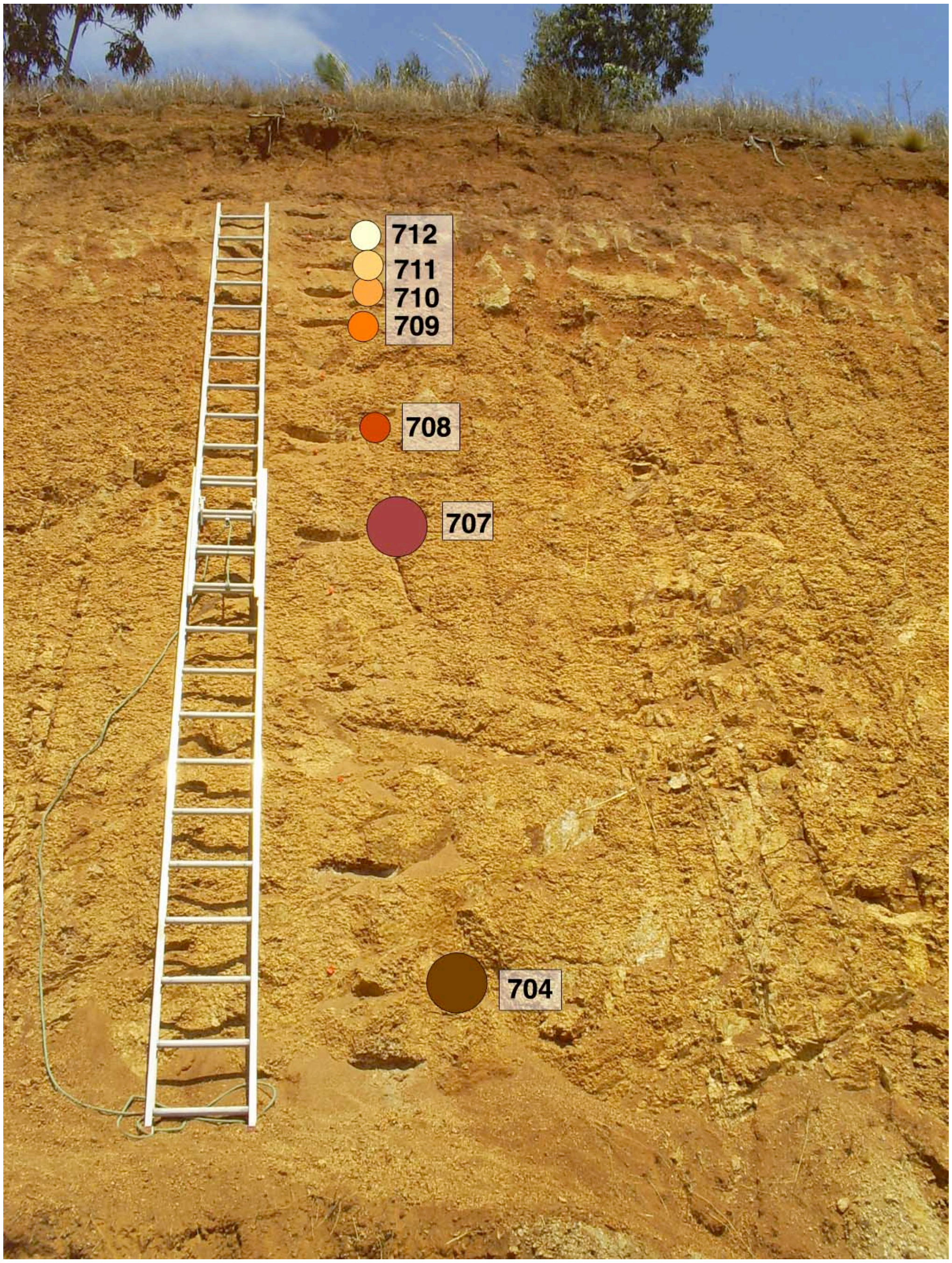

Figure 3.1. Sample site with specific sample locations indicated by coloured circles. Note that this colour scheme will follow throughout this thesis with black representing the lowermost, least weathered sample, and light yellow representing the top and most weathered sample. (photo by J. Gosse, 2007)

Figure 3.2 Rock samples laid out on the ground where the upper right corner represents the base of the profile (8.29 m from surface) and the bottom left represents an upper sample. (photo by J. Gosse, 2007)

Figure 3.3 Sample collection bags for the two lowermost samples. (photo by J. Gosse, 2007)

3.3 Sample preparation

Samples were crushed at Dalhousie Geochronology Centre by Guang Yang to less than 500 μm using a Braun jaw crusher and BICO Disc Pulverizer which were cleaned thoroughly between samples. Samples were then homogenized through shaking and mixing by hand and allowed to settle for at least 10 minutes. Samples were then split using a sand splitter to give 800g or 600g parts. This amount was then powdered by myself using a circular puck grinder. Samples were then split again into 50 g parts, one of which was sent to SGS Laboratories in Lakefield, ON for analysis. A blind duplicate of sample CHI-07-708 was sent as sample CHI-07-713 for quality assurance.

3.4 Sample analyses

Samples were analysed at SGS Minerals (185 Concession St., Lakefield, ON, K0L 2H0, contact: Debbie Waldon) for 8 major, 28 selected minor, and 17 rare earth elements data. Samples were prepared and analysed by qualified lab technicians at SGS Minerals. Procedures varied depending on the element being sought (Table 3.2). Sample mass for all procedures was near or less than 1 g. Due to difficulties obtaining details regarding procedures from the lab not all information regarding equipment and personnel is available at this time.

3.5 Data analysis

Microsoft Excell 2004 for Mac (version 11.4.1), licensed to Jessica Drysdale was used for the majority of the data analysis. This program was used due to it's relative simplicity and availability at Dalhousie University. The program was used to perform calculations as well as construct figures, graphs and tables.

Table 3.2 Procedures for specific elements during geochemical analysis.

Procedure	Elements or oxides
Borate Fusion XRF:	SiO_2; Al_2O_3; Fe_2O_3; P_2O_5; Na_2O; TiO_2; Cr_2O_3; V_2O_5; CaO; MgO; K_2O; MnO, LOI
Leco Analyzer:	C, S
XRF Pressed Pellet:	Cl
Ion Specific Electrode Probe:	F
ICP-MS Scan:	Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo,
Strong acid digestion	Na, Ni, P, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Y, Yb, Zn
ICP-MS Rare Earth Scan:	Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U,
ICP (KOH) Fusion:	B
Dionex:	Br

The program Petrograph 2beta, developed by Maurizio Petrelli (2005) was used for REE diagrams and some REE ratio calculations. This program was used as it is free and available on the internet with no licensing requirements. The program has normalizing factors provided from other published works and allows for the calculation and graphing of large amounts of data with relative ease. The program SYSTAT (version 12.0.1) was used by Remi Daigle to correlate raw data to obtain a Pearsons correlation coefficient matrix. This program is licensed to the Bedford Institute of Oceanography (Dartmouth, Nova Scotia) and we used due to the ease with which the program can compute a matrix correlating 59 variables.

Calculations were made to determine the leach potential of certain elements from the profile. These calculations were based on a method determined by J. Drysdale and J. Gosse and are outlined in Appendix III. These calculations make a number of assumptions regarding the saprolite profile:

1. The profile has weathered in a consistent way from the base of the section (8.29 m) to surface through various soil and lithologic horizons.

2. Atoms have leached consistently in a logarithmic manner from surface to the base of the section.
3. Sample CHI-07-702 is unweathered and forms the basis for comparison of all other samples.
4. Titanium is a relatively immobile element during weathering.

Calculations normalize Ca, Na and K to Ti. The difference between a sample and CHI-07-702 was then calculated, followed by a conversion of this difference to a number of atoms. A graph of sample depth vs. leached atoms was constructed. A logarithmic trend line equation was then integrated to determine the area under the curve. This was then used to determine the number of leached atoms of Na, Ca and K respectively per gram of rock.

3.6 Sources of error

Samples were taken to represent the weathered profile at a certain depth, however due to the textured nature of the profile, the rock is not perfectly homogenous in mineralogy and despite attempts to minimize the risk, a sample may not be representative of a larger volume of the rock. As well, there may be error related to the use of fertilizers on farmland directly above the sample site. This would introduce K, and depending on the fertilizer may contain other elements. Due to the proximity of this site to a road, there is also potential contamination from car exhaust as well as dust from the road. This is despite the diligence with which samples were taken to get deep enough into the rock that this is not an issue.

Some lighter fractions of the rock may have become airborne and lost during both crushing and powdering. Precautions were taken not to open the machines for 2-5 minutes after each sample to allow for dust to settle. As well, though machines were cleaned prior to use, some contamination from the interior of the circular puck grinder may have resulted (<1% Cr and Pb contamination).

Laboratory machinery error is unavailable at this time, however duplicates or triplicates were made of all samples. Samples with error greater than 1% are MgO (16%), P_2O_5 (29%), MnO (18%), C (50%), Cl (15%), Co (6%). Due to the volatile nature of most of these elements this is not uncommon. As well boron concentrations were reanalyzed due to a large (50%) deviation from the duplicate. The reanalysis found B to be below detection limits All calculated percent errors are shown in Appendix 1. Raw geochemical data is in Table 4.1 (Results section).

Computer programs used may have introduced negligible error to calculations. It is more likely however that errors occurred due to human error during calculations and creation of equations. Assumptions made during leached atom calculations are identified in section 3.5.

4.0 RESULTS

Raw geochemical data as well as ratio and weathering indices calculations are shown in Table 4.1 at the end of this section.

4.1 Oxides, minor and trace elements

Sample results were plotted as element concentrations with depth for major oxides (Fig. 4.1), minor and trace (Fig. 4.2) and REE (Fig. 4.3). Notably these figures all indicate peak enrichment or depletions of elements at depths between 1.79 m and 2.37 m from surface. This coincides with the duripan layer identified in the field and previously described in the geological setting section.

Overall Al_2O_3 and SiO_2 remain fairly consistent in concentration throughout the profile. MnO, Na_2O, K_2O and CaO all show general depletion toward the surface, whereas TiO_2, MgO, LOI and Fe_2O_3 show general increases toward the surface. Peaks in the duripan generally coincide with the overall trend of the oxide through the whole vertical section, with the exception of P_2O_5, which shows increases but no overall chance in concentration over the whole section.

Minor and trace elements show similar patterns to the oxides in that there is positive or negative anomaly in concentration in the duripan. Tl, Sr and Be remain constant with decreased concentration at 1.79 m. Y and Mo show overall increases with depth, with lowest concentrations in the duripan. Cl, Zn, V, F, Co and Ni show increased concentrations in the duripan, with Zn, Ni and V decreasing in concentration with depth and Cl, Co and somewhat F increase in concentration with depth.

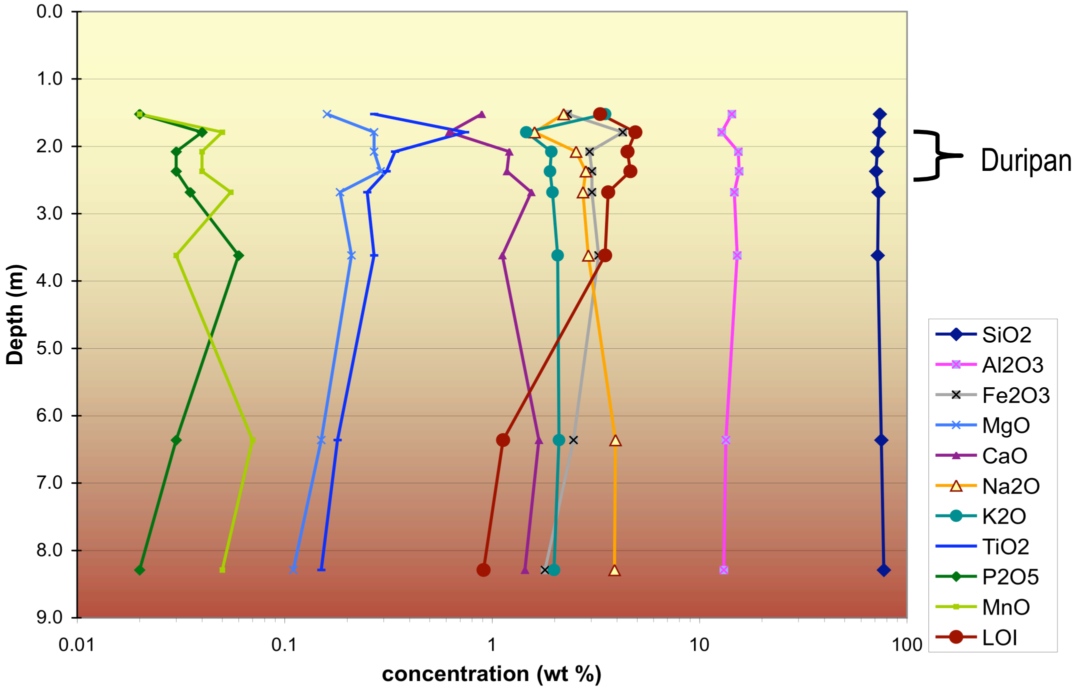

Figure 4.1 Oxide concentrations with depth. Peak concentrations or depletions occur primarily in the duripan.

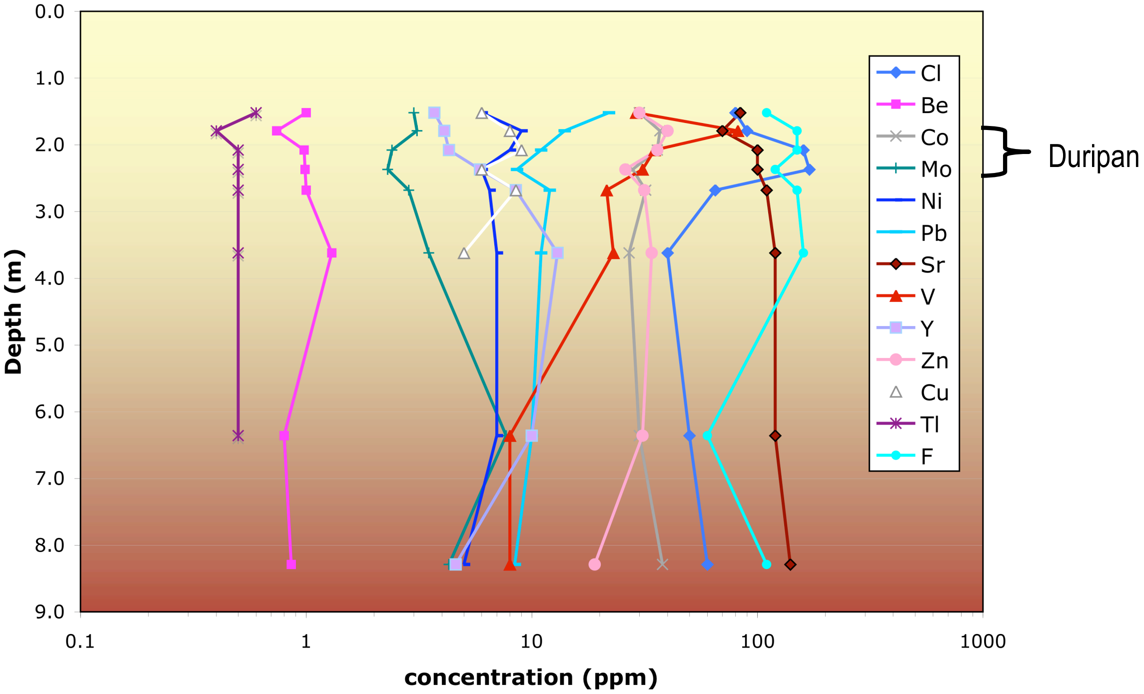

Figure 4.2 Minor and trace element concentrations with depth.

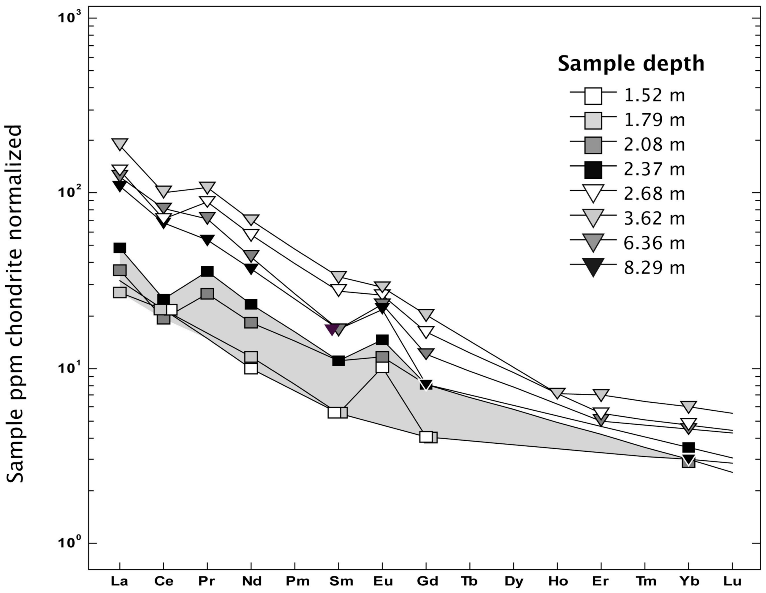

Figure 4.3. Rare earth element plot for the saprolite and fluvial gravels. Squares show element abundances in the gravels, whereas triangles show abundance in the granite. Data is normalized to chondrite (Haskin *et al.*, 1968)

4.2 Rare earth elements

Abundances of the LREE and HREE vary systematically with depth, but differently for the saprolite than the cover sediments. The lowest depth (saprolite) sample has a REE signature that is intermediate relative to all other samples, but is the lowest concentration of the saprolite samples (black triangle). The increase in REE concentration toward the surface has been identified in other weathered profiles and will be discussed in section 5. The deepest sample in the sediments above the saprolite actually has a REE concentration that is lower than the bottommost (freshest) saprolite sample. Shallower sediment samples record a general decrease in REE concentration. A distinct positive Eu anomaly in the deepest saprolite sample is mimicked by a similar magnitude positive anomaly in the overlying sediments. This is consistent with the observation that the feldspars in the gravels appear in thin section to be only slightly weathered. Above the deepest saprolite sample the Eu anomaly becomes less positive and essentially neutral toward the top of the section in the granite.

4.3 Statistical correlation and leaching calculations

Statistical correlations were calculated from the raw data in order to facilitate interpretation. The program SYSTAT 12 was used to complete Pearson's correlation coefficients between all pairs of data of the 59 elements. Appendix 2 shows correlation data. Some element pairs or groups showing significantly high correlation values are included in the discussion. An absolute value of 7 was chosen initially as a high correlation value, the rare earth elements all show the highest correlation and are a focus of the discussion.

Using geochemical analysis results calculations were done to determine the leach rate of Na, Ca and K from the profile. These elements were chosen as they are among the most mobile elements (see Discussion, Fig. 5.5). Final calculations show leach potential of 36.2 mg Na/g rock, 12.1 mg Ca/g rock, and 17.6 mg K/g rock.

4.4 Mineralogy thin sections

Thin sections were made for two samples, 702 (8.29 m) and 710 (2.08 m), analysis is shown in the images below. Plagioclase minerals were assessed for Ca content using the Michèl-Levy method. The anorthite content of the plagioclase in sample CHI-07-702 at the base of the saprolite is An30 +/- 5. Similarly, for the upper portion of the sediments the Anorthite content is An30+/5 (sample CHI-07-710).

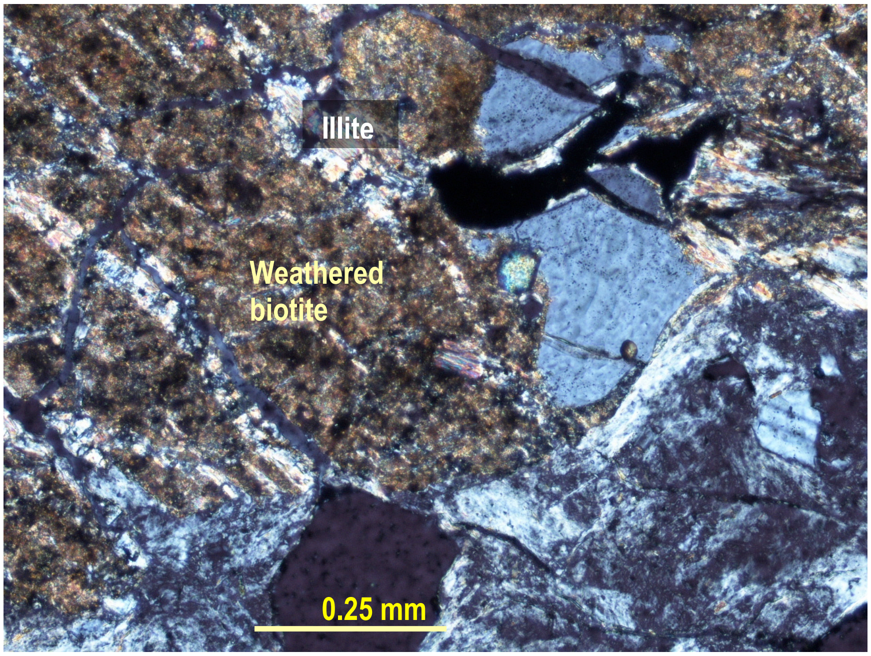

Figure 4.4 Thin section of sample CHI-07-710 showing largely weathered biotites and accompanied by relatively unweathered plagioclase.

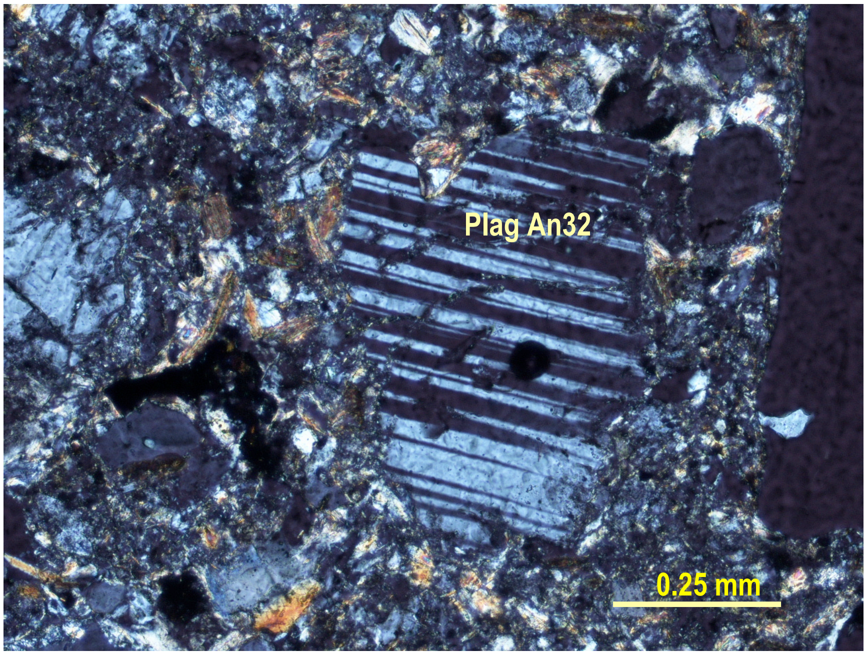

Figure 4.5 Thin section of sample CHI-07-710 showing highly weathered biotite, accompanied by ilite.

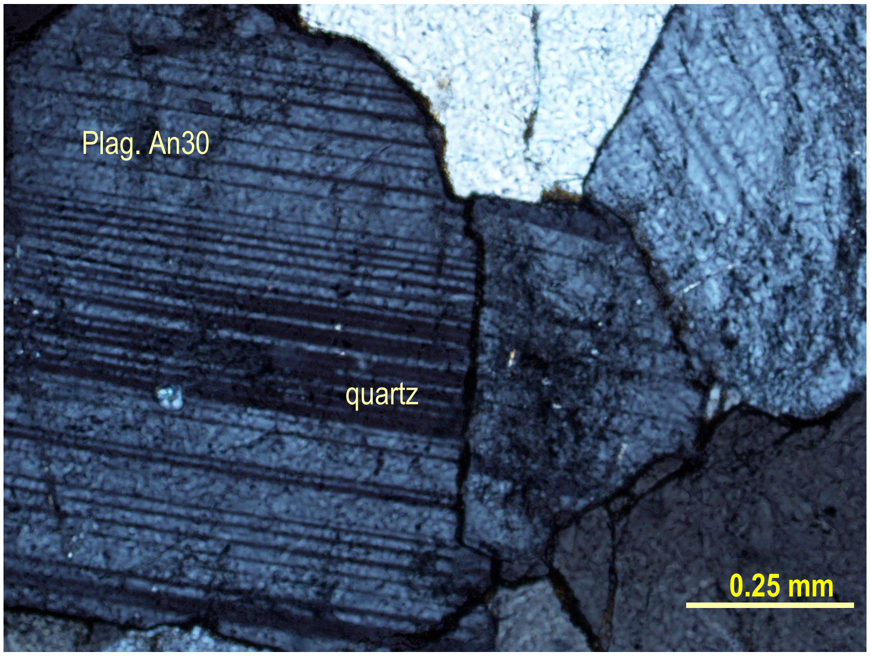

Figure 4.6 Thin section of sample CHI-07-702, relatively unweathered granite. Mineral grains are much larger than in the weathered sample.

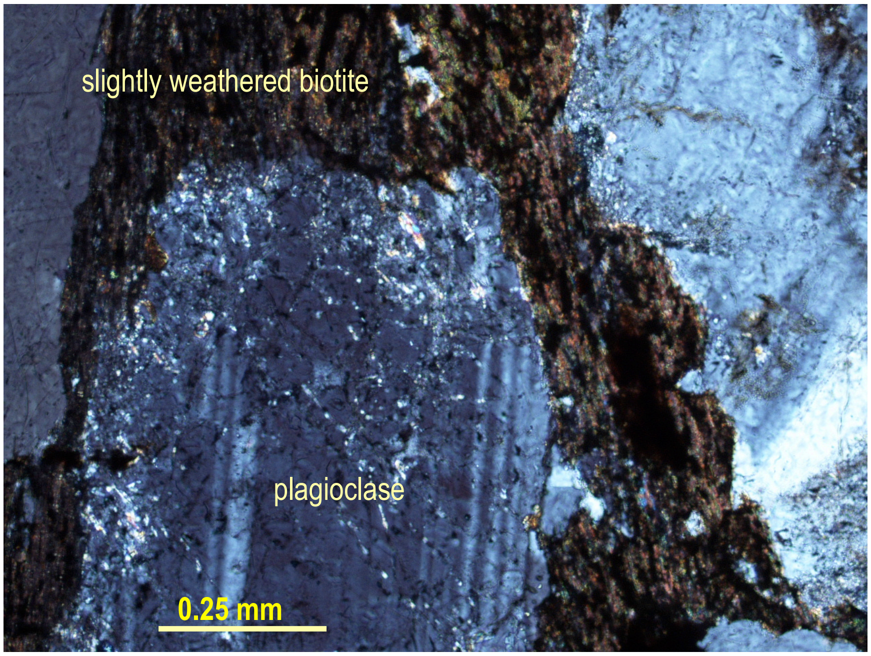

Figure 4.7 Thin section of lowermost sample CHI-07-702 showing indications that there has been some alteration of biotite at the base of the profile.

Table 4.1 . Chemical composition of weathered granitoid. Samples are listed from least to most weathered from left to right. Major elements are shown in wt% oxides. All other elements are shown in ppm.CIA = [Al2O3/(Al2O3 + CaO + Na2O + K2O)] x100 and CIW = [Al2O3/(Al2O3 + CaO + Na2O)] in molecular proportions. Eu/Eu* = EuN/(SmN x GdN)0.5 ; Ce/Ce* = CeN/(SmN x NdN)0.5 where N is normalized to chondrite (Haskin et al., 1968)

Sample	**CHI-07-701**	**CHI-07-704**	**CHI-07-707**	**CHI-07-708**	**CHI-07-709**	**CHI-07-710**	**CHI-07-711**	**CHI-07-712**
Depth	**8.29**	**6.36**	**3.62**	**2.68**	**2.37**	**2.08**	**1.79**	**1.52**
SiO2	77.4	75.2	72.3	72.8	70.9	72	73.3	73.9
Al2O3	13.1	13.4	15.2	14.7	15.5	15.4	12.8	14.3
Fe2O3	1.8	2.47	3.26	3.03	3.03	2.95	4.26	2.31
MgO	0.11	0.15	0.21	0.17	0.29	0.27	0.27	0.16
CaO	1.44	1.68	1.12	1.54	1.18	1.21	0.62	0.89
Na2O	3.89	3.93	2.91	2.75	2.83	2.54	1.6	2.21
K2O	1.99	2.1	2.07	1.96	1.9	1.93	1.46	3.51
TiO2	0.15	0.18	0.27	0.25	0.31	0.34	0.74	0.27
P2O5	0.02	0.03	0.06	0.04	0.03	0.03	0.04	0.02
MnO	0.05	0.07	0.03	0.05	0.04	0.04	0.05	0.02
Cr2O3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
V2O5	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01
LOI	0.91	1.13	3.51	3.65	4.64	4.5	4.9	3.32
Sum	100.9	100.3	100.9	101	100.6	101.3	100.1	100.9
S	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
C(t)	0.01	0.02	0.02	0.03	0.04	0.04	0.1	0.04
F	0.011	0.006	0.016	0.015	0.012	0.015	0.015	0.011
Cl	60	50	40	70	170	160	90	80
Ag	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.5	0.3	0.4
As	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Ba	2100	2000	2000	1900	1400	1200	710	1500
Be	0.86	0.8	1.3	1	0.99	0.98	0.74	1
Bi	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Cd	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Co	38	30	27	31	28	36	37	30
Cr	< 4	< 4	< 4	< 4	< 4	< 4	8	< 4
Cu	< 3	< 3	5	5	6	9	8	6
Li	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Mo	4.3	7.7	3.5	2.4	2.3	2.4	3.1	3
Ni	5	7	7	6	6	8	9	6
Pb	8.4	10	11	11	8.6	11	14	22
Sb	< 10	< 10	< 10	< 10	< 10	< 10	75	< 10
Se	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sn	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Sr	140	120	120	110	100	100	70	84
Tl	< 0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.6
V	8	8	23	21	31	35	82	29
Y	4.6	10	13	9.6	5.9	4.3	4.1	3.7
Zn	19	31	34	30	26	36	40	30
Ce	59	72	89	63	22	17	19	19
Dy	1	2	3	3	1	1	< 1	< 1
Er	< 0.8	1	1.4	1.1	< 0.8	< 0.8	< 0.8	< 0.8
Eu	1.5	1.6	2	1.8	1	0.8	< 0.6	0.7
Gd	2	3	5	4	2	2	1	1
Ho	< 0.4	< 0.4	0.5	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
La	36	41	62	46	16	12	9	< 8
Lu	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Nd	22	26	42	35	14	11	7	6
Pr	6	8	12	10	4	3	< 2	< 2
Sc	4	3	5	5	6	6	6	5
Sm	3	3	6	5	2	2	1	1
Tb	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Th	6	4	8	7	4	4	5	9
Tm	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8
U	0.8	0.4	0.9	0.8	0.9	0.9	1	1.5
Yb	0.6	0.9	1.2	0.9	0.7	0.6	0.6	0.6
B	< 40	< 40	< 40	< 40	< 40	< 40	< 40	< 40
Br	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Zr	220	390	260	200	<200	200	270	<200
CIA	54.0	53.2	62.6	57.9	63.6	64.5	70.6	61.2
CIW	59.2	58.5	69.0	63.7	69.5	70.7	77.3	73.1
Eu/Eu*	2.13	-	1.219	1.52	1.191	1.09	1.62	1.77
Ce/Ce*	-	-	0.62	0.60	0.64	0.71	0.87	0.88

5.0 INTERPRETATION and DISCUSSION

The chemical results are used to (i) establish the intensity and history of weathering of the field site, (ii) quantify element mobility and flux through the profile, and (iii) constrain the provenance of the fluvial gravel unit that caps the saprolite.

5.1 Weathering indices

Chemical weathering can be quantified through spatial comparisons of relative concentrations of the most mobile elements Na, Ca and K. Studies have shown that a common final weathering product of alumino-silicate minerals is kaolinite ($Al_2Si_2O_5(OH)_4$) (Nesbitt and Young, 1982; Harnois, 1988) and gibbsite (Al(OH)3. Weathering trends were calculated using the chemical index of weathering (CIA) using the following formula (Nesbitt and Young 1982)

$$CIA = \frac{Al_2O_3}{Al_2O_3 + Na_2O + K_2O + CaO} \times 100$$

Additionally the chemical index of weathering was calculated using the following formula (Harnois, 1988):

$$CIW = \frac{Al_2O_3}{Al_2O_3 + Na_2O + CaO} \times 100$$

Potassium can be mobilized through dissolution or it can be retained by clay minerals depending on the environment. It is therefore not included in the CIW equation as it may not display trends relevant to weathering.

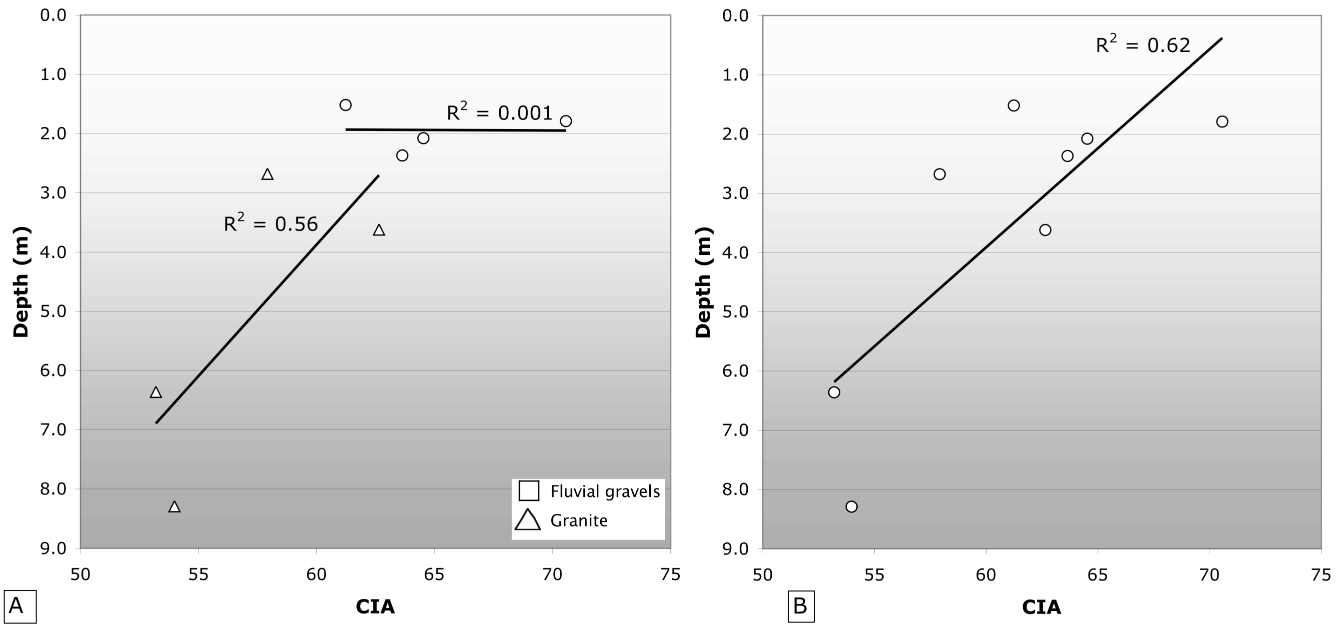

Figure 5.1 CIA values for each sample depth. Figure A separates in-situ weathering of the granite from overlying fluvial gravels and sediments. Figure B plots the same points with a single linear trend line.

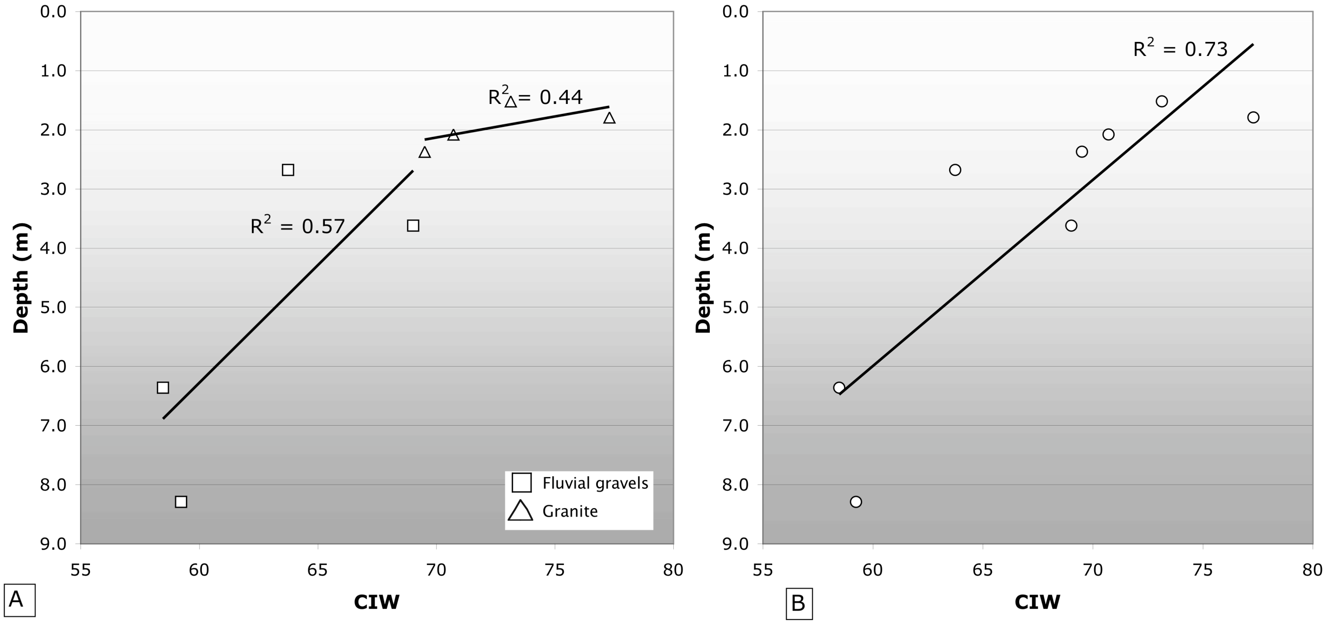

Figure 5.2 CIW value for each sample with depth. As indicated in figure 5.1, A shows trend lines for the in-situ weathered granite as well as the upper fluvial gravels and sediments. B shows a linear trend for the whole section.

Average CIA values for unweathered granite fall between 45 and 50, whereas a completely weathered sample would have values close to 100 (Nesbitt and Young, 1982). The lowest sample in the suite has a CIA value of 53, and the uppermost samples of this suite have values of approximately 70. CIW values of unweathered granite range from 55 to 60 (Harnois, 1988). CIW values for this sample suite range from 58 to 77. According to Harnois, the lowest sample can therefore be classified as unweathered. The uppermost samples are not fully weathered, which may indicate that material has been lost from the top part of the section. Figure 5.3 shows that potassium follows the weathering trend until the uppermost sample, which is highly enriched in potassium. As there has been farming with potential fertilizer use in the area, the influx of K has been attributed to this and thus this sample has been excluded from the trendline of Figure 5.3.

I propose the following hypothesis regarding the sequence of events leading to the modern weathering section: The weathering occurred for a long period of time creating the saprolite, which was subsequently eroded away at surface approx. 2.2 Ma, followed immediately by the deposition of fluvial gravels and subsequent weathering and soil formation. Cosmogenic nuclide dating of the granitoid below the duripan indicates that the surface was exposed for at least 2.2 Ma (Gosse, pers. com. 2008). However, as pointed out in Section 2, the saprolitization probably occurred over many millions of years since the mid-Miocene. The hypothesis would predict that the weathering trend lines would follow two different paths and thus figures 5.1 A and 5.2 A would correlate better. However, I believe the reason for better correlation in figures 5.1B and 5.2B is that the fluvial gravels have been weathered for more than 2.2 Ma so that the upper section becomes weathered to a similar degree as the top of the existing granite saprolite.

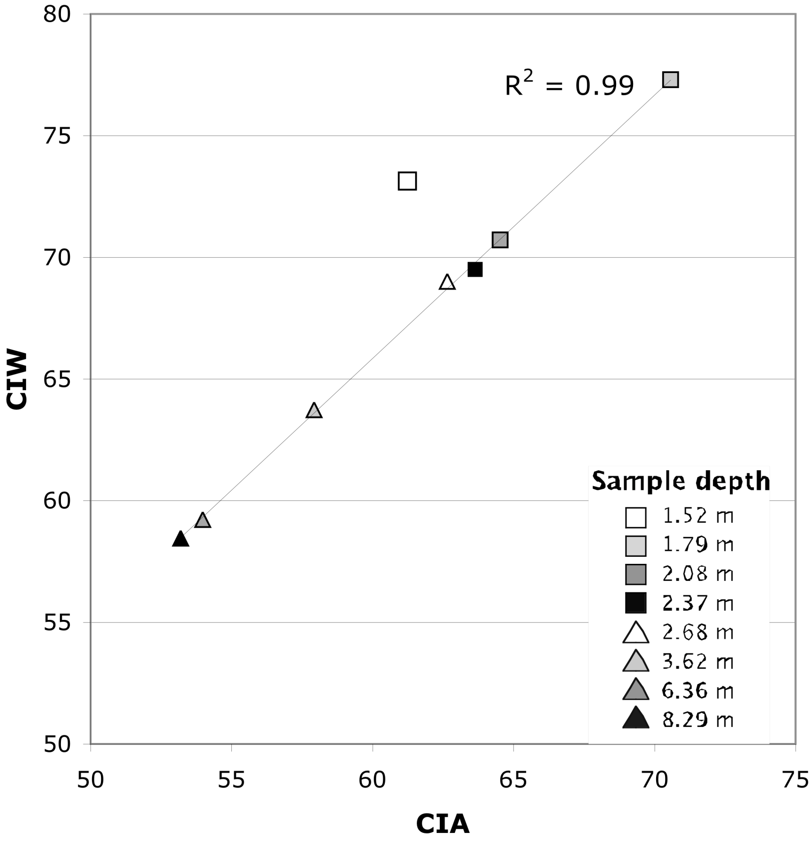

Figure 5.3 CIA versus CIW plot with data points indicating depth. Note that the uppermost sample (white square) has been excluded from the trendline as it has been enriched in K which may be due to farming in the area.

Saprolites can be divided into four zones of differential weathering with gradational boundaries (Nesbitt et al., 1997), although the volumes and elemental fluxes will vary greatly depending on the environmental factors that control weathering. When plotted on a tertiary diagram, the CIA elemental concentrations of Na+Ca, Al, and K can be used to infer weathering zone and sequential weathering history. The A-CN-K diagram for the study site shows that weathering zone III and IV are preserved, another indication of the possible truncation of the upper weathering zones and further support of the hypothesis.

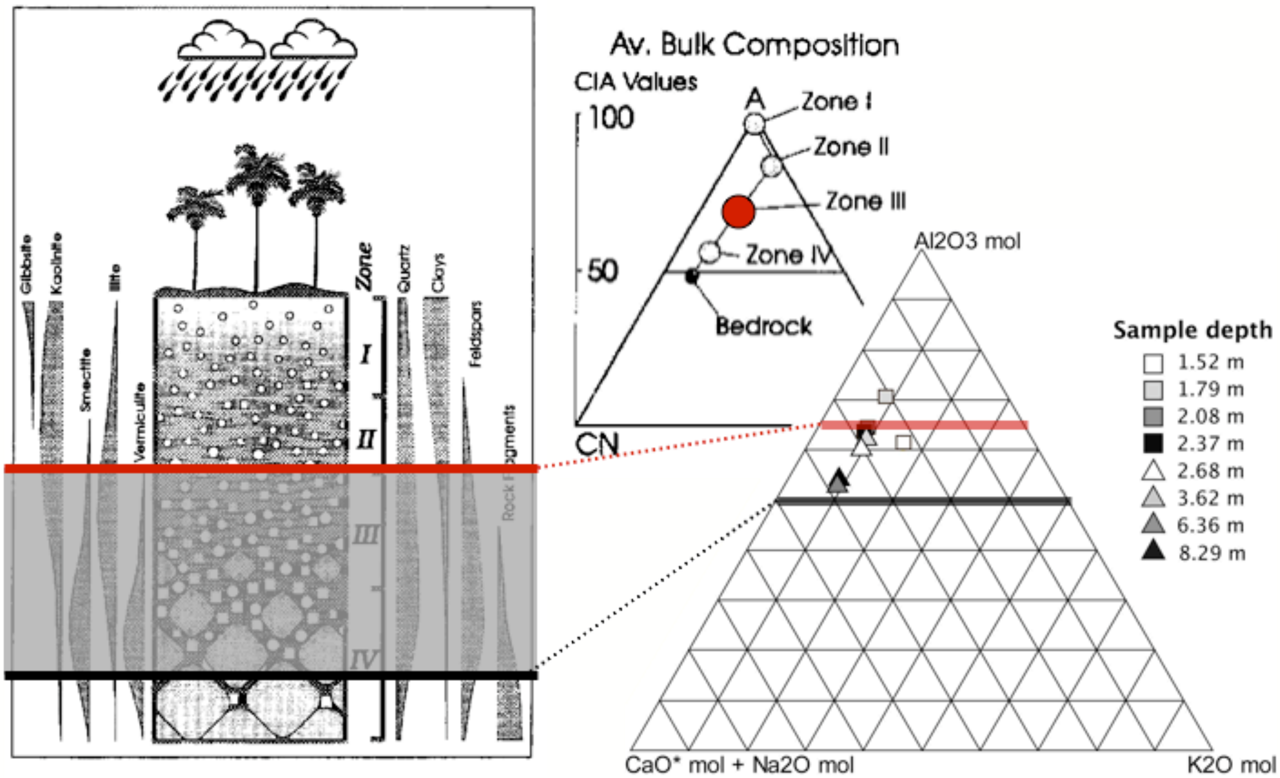

Figure 5.4 Weathering zones in a granitic saprolite. Based on average bulk composition of CaO, Na_2O, Al_2O_3 and K_2O the profile (left) has been broken into four weathering zones with the base of zone IV being parent bedrock and zone I being fully weathered. The lower right triangle shows the sample suite which implies preservation of zone III and IV weathering. The preserved section is highlighted in grey on the profile with the red line indicating the uppermost in situ weathering of granite. (adapted from Nesbitt *et al.*, 1997)

5.2 Element mobility and flux

Determining which elements are leached during chemical weathering and their relative mobility's is important to this study. Na, Ca, and K have been determined to be the most mobile elements in the weathering of granite(Fig. 5.5) (Nesbitt and Young, 1983; Harnois, 1988; Clarke *et al.*, 2004). These elements tend to leach due to in situ weathering at the same ratios as they occur in the parent material (Nesbitt and Young, 1984). Na, Ca and K are used to quantify the leachate flux due to weathering (Fig. 5.7). By integrating the area under the curve plotting the atoms per gram of sample versus depth between the current surface and the lowest sample at 8.29 m, an approximate flux was calculated. This was found to be approx. 42 mg of Na/g of rock.

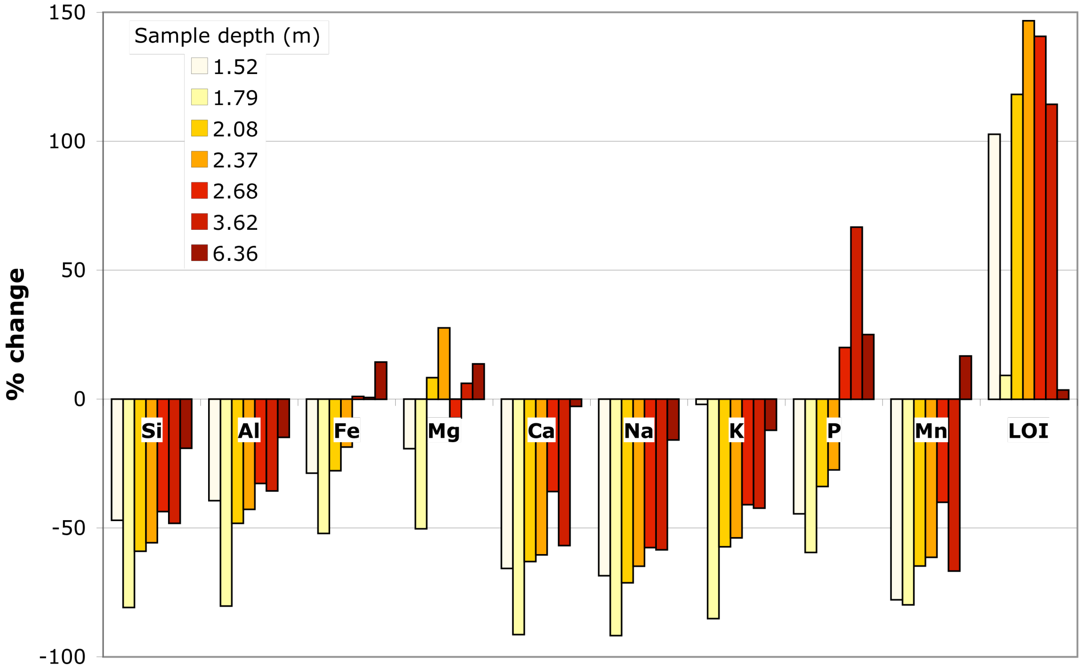

Figure 5.5 Major element percent change from the bottom most sample (702). Data is normalized to Ti.

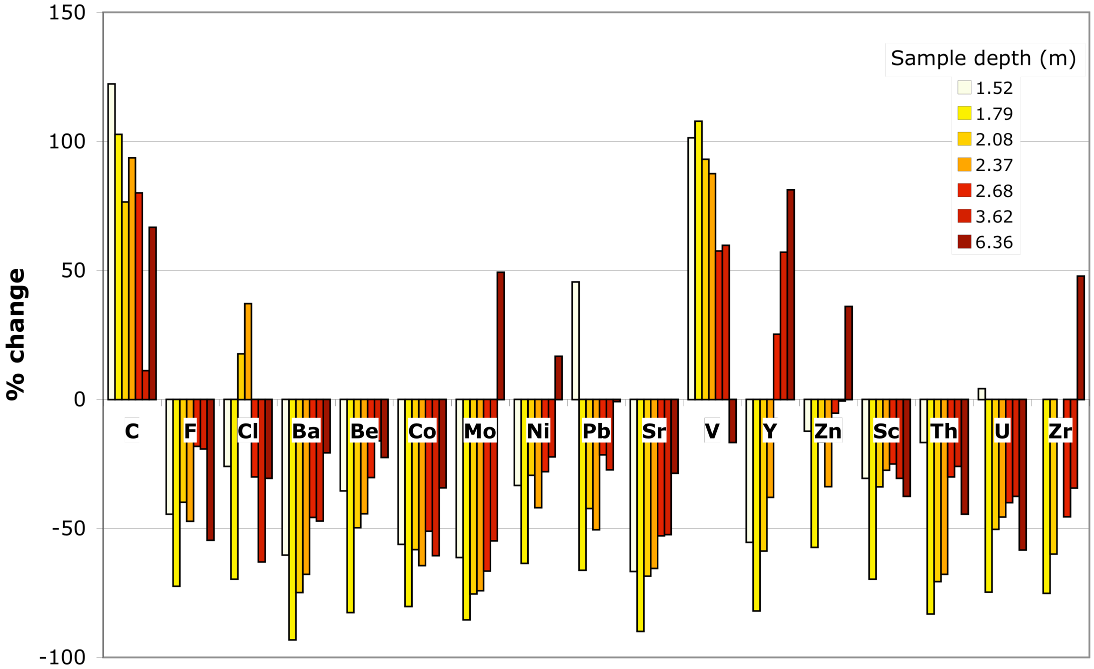

Figure 5.6 Minor and trace element percent change from sample 702 normalized to Ti.

5.3 Fluvial gravels and REE

A further support of the truncation hypothesis is the presence of fluvial gravels overlying zone III in situ weathering of the granite. The fluvial gravels have been interpreted to be of local origin and possibly from the same granite parent material as the saprolite. This interpretation is based on the similarity of trends in the REE (Fig. 5.8) throughout the entire profile (weathered granite and soils). The positive Eu anomaly, attributed to the high plagioclase ($[Na,Ca]Al_2Si_2O_8$) content of the granite, in which Ca^{2+} in the plagioclase has likely been replaced with Eu^{2+}. Calculated anomalies ($Eu/Eu^* = Eu_N / \sqrt{Sm_N/Gd_N}$ where N is the concentration normalized to chondrite (Haskin *et al*, 1968)) indicate that the uppermost sample shows the largest anomaly (2.13) and values decrease with depth in the duripan to a low of 1.22 at 2.08m. Eu/Eu* in the granite show general increasing anomalies with depth (1.09 at 3.62m, 1.62 at 6.36m and 1.77 at 8.29m). Negative Ce anomalies were also calculated and show a general increase with depth, where lowest values are found in the fluvial gravels at 0.62 (at 2.08m) and 0.60 (at 2.37m). Values then increase from 0.64 at the top of the granite to 0.88 at the base of the section. This differs from other studies showing overall retention of Ce throughout weathering profiles (Nesbitt, 1979; Condie *et al.*, 1995) and may be a reflection of minimal concentrations of cerianite though further microprobe work would be needed to assess this further.

Plagioclase and sphene ($CaTiSiO_5$) will also accommodate light REE (LREE, greater in atomic radius than Eu) accounting for the higher LREE concentrations relative to the heavy REE (HREE). It is also likely that the larger changes of the light REE concentrations is due to the incompatibility of the LREE, relative to the HREE once in solution during weathering (Compton, 2003). This however differs from other studies which suggest that the ratio of LREE to HREE,

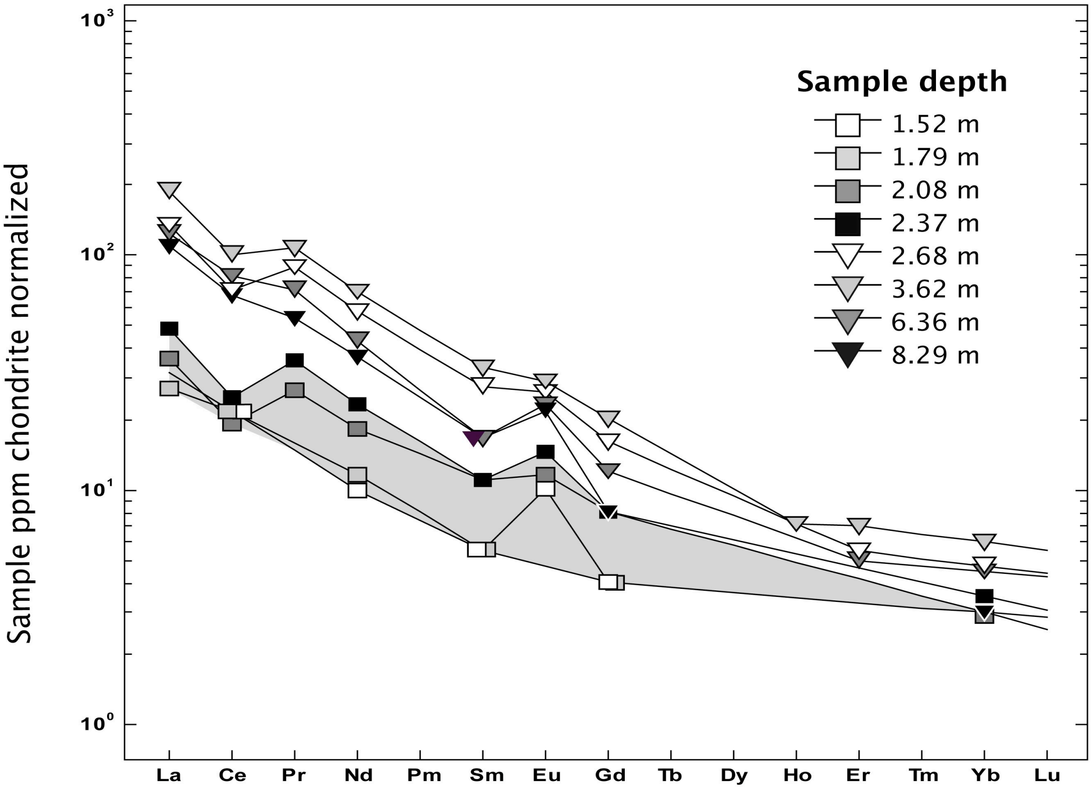

Figure 5.8 Chondrite normalized REE distribution in granite (triangles) and overlying fluvial gravels (squares). Darkened grey area indicates fluvial gravel REE distribution spacing. (Chondrite values from Haskin *et al.*, 1968)

calculated using La/Yb ratios, will show increased La/Yb ratios in weathered rock due to the preferential adsorption of LREE onto clay minerals (Nesbitt, 1979; Duddy, 1980). This study however has found that La/Yb ratios show a slight general upward decrease (from 36.4 to 28.4) followed by a large change into the fluvial gravels in which the ratio also decreases from 13.9 to 9.1. While these findings appear consistent with Condie *et al.* (1995), who found decreasing ratios upward through weathering sequences and suggest that LREE are not retained by clay minerals in a weathering profile, the decreased ratio in fluvial gravels of this study may suggest that LREE were contained in clay minerals. These were transported as suspended sediments in rivers, while the gravels were deposited in the area. Gravels have subsequently broken down into clays, containing few LREE due to the depleted nature of the parent material.

There have been numerous studies to quantify the movement of REE during weathering of granite, however the unique nature of this study site shows interesting trends in that there is an increase in the REE from the lowermost sample toward surface in the in situ weathered granite. The duripan however shows lower REE concentrations than the lowest sample, and concentrations continue to drop moving toward surface. This further confirms that the fluvial gravels are not the same material as the initial granite. Nesbitt (1979) indicated that concentrations will increase with depth due to leaching near surface due to lower pH, followed by the subsequent precipitation of the elements at depth where pH is increased. Studies have also indicated that HREE are more mobile than LREE with weathering in a temperate climate (Aubert *et al*., 2001) however the environment of formation of this saprolite was most likely a tropical setting. It has also been indicated that LREE are less mobile than HREE due to their possible sorption onto Fe oxides. This again counters findings at this sample site as the LREE show more change than HREE. Studies of granitic rocks have also shown that there is generally an increase in LREE content with greater clay content of a soil due to the adsorption of the LREE onto clays (Compton *et al*., 2003). This however is in opposition to what was found in this section as the upper samples showing high degrees of weathering and clay minerals contain the lowest REE concentrations. Again this is most likely related to climate conditions as well as the fluvial transport of the upper material at this site. With heavy rainfall REE will be removed from the system, and it is most likely that this would have occurred to overlying sediments during transport followed by increased leaching and the absorption of the elements in the duripan, explaining the increase in concentration with depth. The lower section (below 2.37 m) however decreases in REE concentration with depth. This may be due to influx from overlying sediments. Nesbitt (1979) suggested that total REE distribution in the parent granitoid is equal to the REE distribution in the weathered section. Total REE concentrations however show increased concentrations upward in the granite, with overall values close to three times the concentrations found in the fluvial gravels (42.8ppm, 42.1ppm, 50.7ppm, 64.1ppm in fluvial gravels at 1.52m, 1.79m, 2.08m and 2.37 m respectively vs. 168.8ppm, 225.1ppm, 159.6ppm and 132.4ppm at 2.68m, 3.62m, 6.36m and 8.29m respectively). This further supports that the profile has been truncated and residual weathered material from the profile is missing. Ratios sensitive to sediment provenance also indicate that the gravels may be from a different parent granite as La/Sm, Eu/Eu* and $[La/Yb]_N$ ratios are generally higher in the granite section. This could however be due to the transport of the gravels and possible association of REE with clays. As well the duripan gravel layer is somewhat cemented and may have halted the influx of fluids and further chemical weathering of the granite upon deposition, resulting in the maintenance of REE in situ.

6.0 CONCLUSIONS

The results of this study have been used to examine element mobility due to weathering, the history of weathering and saprolite development of the Santo Domingo complex saprolite at 33º22’51.46”S-71º37’62.74”W. There are no toxic elements above standards established by Health Canada guidelines for drinking water (for example Pb, U, Cd, Sb, Ba) (note organic compounds were not analysed). Chilean guidelines are likely similar but were not consulted. Element abundances have shown that in general there is a decreased abundance with increased weathering, this is particularly true for Na, Ca and K, which are used as indicators of weathering intensity. Weathering indices (CIA and CIW) for this saprolite have values of 73 and 77 respectively, indicating that the preserved section of the profile has not been fully weathered as would be expected at the top of a section. This is explained by the truncation of the most weathered part of the saprolite prior to 2.2 Ma (Gosse, unpublished). Further soils analysis, clay mineralogy, and geochronology in this saprolite will confirm the timing of the gravel deposition as well as the rate and style of soil development. Elements showing increased weight percents with increased weathering (Al_2O_3, TiO_2, SiO_2, Zr) are those which have been recognized as immobile during weathering (Faurne, 1991; Blaser *et al.*, 2000). The increased concentrations of Be are attributed to atmospheric input, as Be is an important aerosol that attaches strongly to clays in the upper soil horizons.

The REE show increasing concentrations with increased weathering of the saprolite, and an overall depleted concentration in the gravels, which, contrary to the saprolite, become depleted with weathering. From this it can be concluded that the gravels are of different parent granitic material than the saprolite below, although the exact source cannot be determined from available data. As the REE may be associated with clay minerals, and there is an increase in clay abundance upward in the sequence with weathering, this explains the REE enrichment of the upper portion of the saprolite. The gravels, which are depleted in REE relative to the saprolite, also supports this conclusion as the clay fraction of this unit would have been removed during transport, leaving REE depleted granitic material from which the duripan developed. Further analysis and clay mineralogy of samples as well as electron microprobe analysis would allow for confirmation of these conclusions.

Total flux of the most mobile elements has been calculated to 36.2 mg Na/g rock, 12.1 mg Ca/g rock, and 17.6 mg K/g rock. Methods employed for calculating flux of this mobile element could be used to interpret flux of other elements at this location.

Overall this study has shown that the saprolite shows regular weathering trends, no toxic elements or elements of risk for nearby residents, and a history of weathering prior to 2.2 Ma, followed by deposition of fluvial gravels and subsequently eolian silts.

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