Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks

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CHEMICAL PROCESSES AFFECTING THE MOBILITY OF MAJOR, MINOR AND TRACE ELEMENTS DURING WEATHERING OF GRANITIC ROCKS

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Abstract

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The behaviour of 38 major and trace elements as well as changes in the mineralogy have been examined in 10 weathering profiles developing on some Portuguese granitic rocks.

Element mobilities are calculated from geochemical data normalized with respect to Ti in the fresh parent rock. Chemical elements are divided into two groups, immobile and mobile, on the basis of their geochemical distribution during weathering. Elements that are immobile during weathering are Zr, Hf, Fe, Al, Th, Nb, Sc and the REE. Very mobile are Ca, Na, P, K, Sr, Ba, Rb, Mg and Si. Mobile elements are derived mainly from leachable minerals such as feldspars, micas and apatites, whereas immobile elements are either concentrated in resistate phases or strongly adsorbed by secondary minerals.

The geochemical behaviour of Mn, Cr, V, Fe and Ce is very dependent on redox conditions. Redox transformations of these elements can be used to set limits on the oxidation state of a weathering suite.

The REE are mobilized or fractionated during late stages of weathering, but not during moderate stages of weathering. This fractionation is caused by selective leaching of rocks composed of both stable and unstable minerals containing REE.

1. Introduction

Chemical weathering of rocks is one of the major processes which modify the Earth's surface and is one of the vital processes in the geochemical cycling of elements (Berg, 1932). The rate and nature of chemical weathering vary widely and are controlled by many variables such as parent-rock type, topography, climate and biological activity. The mobilization and redistribution of trace elements during weath-ering is particularly complicated because these elements are affected by various processes such as dissolution of primary minerals, formation of secondary phases, redox processes, transport of material, coprecipitation and ion exchange on various minerals (Harris and Adams, 1966; Nesbitt, 1979; Chesworth et al., 1981; Fritz and Ragland, 1980; Nesbitt et al., 1980; Cramer and Nesbitt, 1983; Fritz and Mohr, 1984). Nevertheless some general statements apply.

In a thermodynamic sense, weathering sys-

tems are open, irreversible and incongruent. Weathering reactions are irreversible because they take place primarily as a result of disequilibria between the rocks and their current physico-chemical conditions. Garrels and Mackenzie (1967) and Helgeson et al. (1969) viewed the weathering process as an acid–base reaction where an acid, i.e. H_2CO_3, is neutralized by a solid base (e.g., feldspar) to produce secondary minerals (e.g., clays) and dissolved salts. This heterogeneous chemical system is open and incongruent, because the dissolved salts are carried away by flowing groundwater. The composition of the remaining solid phase differs markedly from the initial solid phase (e.g., fresh rock).

Major-element mobility (Polynov, 1937) and mineral stability (Goldlich, 1938) sequences are strictly applicable only on a global scale. On smaller scales, the relative importance of parent-rock type and groundwater is highly variable and different sequences are found. These sequences are interrelated because mineralogy is the predominant factor controlling the mobility of major elements (Harris and Adams, 1966).

Granular rocks are not homogeneously altered (Cleaves, 1983; Velde, 1984; Brimhall and Dietrich, 1987), because most of these rocks are fractured. In the fractured zones and fissures the fluid content is variable and intermittent; the main chemical process is dissolution since undersaturated water flows through at a high rate. Kaolinite, gibbsite and other oxides are found in these bleached or oxidized zones, because all dissolved salts are removed (Velde, 1984). Because the mass of the rock is frequently below the water table the water often has a relatively long residence time and the water–rock system is closer to a state of equilibrium. It will be clear that the "classical" horizon concept, as applied to soil classifications, is not valid during incipient and moderate stages of rock weathering.

Another important aspect of weathering is oxidation (Holland, 1984; Velde, 1984). The mobility of multivalent ions such as Fe and Mn depends to a large degree on the redox potential; both of these ions are moderately soluble under reducing conditions and very insoluble under oxidizing conditions. Clay minerals may be transformed upon oxidation (Velde, 1984), for example, a transition from trioctahedral to dioctahedral minerals.

The purpose of this study is to investigate the chemical weathering of a single rock group, namely granitic rocks, in one environmental setting. Emphasis is given particularly to processes affecting the mobilization and redistribution of selected elements. For the granites in the drainage basin of the Rio Vouga (northern Portugal) abundant data are available from various studies on geomorphology (Schermerhorn, 1959), hydrogeochemistry (Van der Weijden et al., 1984; Dekkers et al., 1986; Comans et al., 1987), water–rock interaction (Ten Haven et al., 1985), petrology and geochemistry (Oen, 1958; Schermerhorn, 1959; Pinto, 1983). We therefore decided to use the granitic rocks from this area for our investigation.

2. Background information

2.1. Geomorphology

The present climatic regime in the Rio Vouga basin is temperate, with dry summers and rainy winters (Comans et al., 1987).

Most of the sample area can be classed as hilly upland (Schermerhorn, 1959), but some steep valleys, reflecting a large fault system, are present. Fairly recent block faulting is inferred from the differences in denudation on the sides of these fault-related steep valleys. The uplifted blocks are characterized by the dominance of residual boulders (e.g., core-stones or wool-sacks) and a limited thickness of weathered rock. As Johann Wolfgang von Goethe has already indicated, these wool-sacks were produced by spheroidal sub-soil weathering and the subsequent removal of the mantle of decayed rocks. The presence of wool-sacks, due to en-

hanced denudation, points to rejuvenation of block faulting (Schermerhorn, 1959). The granites of the opposite block are deeply weathered; it is not uncommon to find a saprolitic layer 10 m thick. The altered granites preserve their original texture, but become friable. This indicates an in situ alteration.

2.2. Petrology

The two major rock types in northern Portugal are metasediments and Hercynian granites (Fig. 1). The latter can be subdivided into older (330–320 Ma) and younger (320–280 Ma) granites on the basis of both structural and field relations and geochronological data (Schermerhorn, 1987). Both an older (Abas) and a younger granite (São Pedro do Sul) have been chosen for the present investigation. The average chemical composition of these granites will be shown in Table II on p. 263.

2.2.1. Abas granite.
The Abas granite has a medium- to coarse-grained, equi-granular to porphyritic texture (Oen, 1958; Ten Haven et al., 1985). Postmagmatic processes such as albitization, muscovitization, greisenization and retrogradation, are omnipresent and more pronounced in certain areas (R. Konings, pers. commun., 1986). The major mineralogical constituents are quartz, K-feldspar, plagioclase, the latter being often replaced by albite; minor components are biotite and white mica. The biotites enclose many accessory minerals: zircon, apatite, rutile and ilmenite. During the muscovitization and greisenization stages biotites are changed into muscovite and tourmaline, and the number of inclusions decrease gradually. Chloritization of biotite is frequently observed during the retrogradation and muscovite is mainly of secondary origin (Oen, 1958). Sericitization and postmagmatic corrosion of feldspars is omnipresent.

2.2.2. São Pedro do Sul granite.
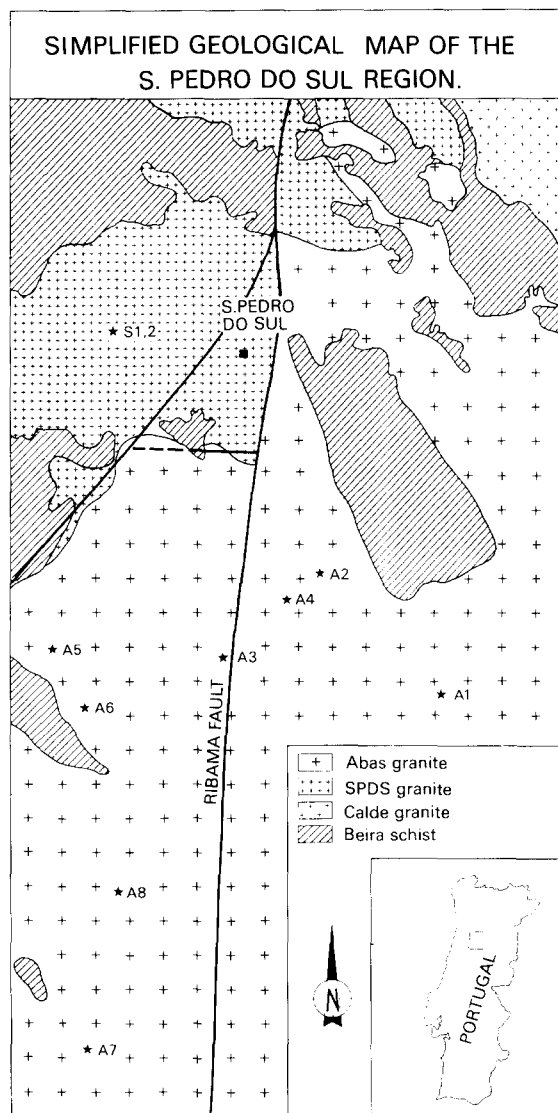The São Pedro do Sul (henceforward SPDS) granite is me-

Fig. 1. Simplified geologiccal map of the São Pedro do Sul region showing the sample locations. (*A1* to *A8* are the ABAS *1* to ABAS *8* suites and *S1,2* indicates the location where the SPDS profiles have been sampled).

dium-grained and porphyritic (Oen, 1958; Schermerhorn, 1959; Peinador Fernandes, 1970; Basham et al., 1984; Ten Haven et al., 1985; Dekkers et al., 1986). Quartz, plagioclase and K-feldspar are the major constituents, minor constituents being biotite and white mica. Chloritization of the biotites is usually incipient only. The accessory minerals zircon, apatite, monazite, ilmenite, leucoxene, rutile and

sillimanite are found enclosed in the micas. The unaltered granite has a blue appearance.

3. Field and laboratory methods

3.1. Sampling

One of the main difficulties in weathering studies is the selection of suitable residual soils. Therefore sampling sites had to meet the following stringent criteria: they should have a textural similarity to parent-rock and a favourable geomorphic setting.

The presence of boulders with or without weathering rinds encased in a matrix of friable rock, which has a texture very similar to the unaltered rock, is an indication of in situ alteration. The most favourable geomorphic setting is a relatively flat topographically high area, where physical transport of material by means of processes such as soil creep and solifluction is minimized. Special care was taken to exclude sites which showed evidence of recent denudation.

During the summer of 1985, 10 weathering profiles were collected on the two granites (Fig. 1). In contrast to other studies (e.g., Nesbitt, 1979; Nesbitt et al., 1980; Minarik et al., 1983) we did not sample in a vertical profile, but gathered about 15 chips having a similar degree of alteration, selecting according to a relative field alteration scale. The final field sample weight averaged ~1.5–2 kg. The generalized relative field alteration scale is as follows:

(1) Unaltered rock
(2) Compact rock with some cracks and cleavage; some oxidation or colour change is evident
(3) Slightly friable rock with altered plagioclase crystals
(4) Friable rock with both feldspars altered; texture still is rather similar to that of unaltered rocks, but the sample can be crumbled between one's fingers
(5) Texture lost; no separate grains are recognizable
(6) Soil; generally contains organic matter, plant roots and allochthonous meterials

The reasoning behind this approach is that the granitic rocks under investigation are not homogeneously altered (i.e. fractured). This approach also reduces inter-sample error, which may especially influence trace-element distributions. In order to make a comparison of the two sampling methods (i.e. in a vertical profile or according to the generalized field alteration scale), we sampled the SPDS granite using both methods in the same quarry.

3.2. Analytical techniques

After appropriate crushing, splitting, pulverization and homogenization procedures, each sample was analyzed in duplicate for Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, Si, P, S, Cu, Zn, Y, Ti, V, Mn and Fe by inductively coupled plasma emission spectrometry (ICPES) (ARL® 34.000). The element concentrations of Nb and Zr were determined by X-ray fluorescence (XRF) (Philips® PW 1400) on pressed powder briquettes. The samples were further analyzed in duplicate by instrumental neutron activation analysis (INAA) for Rb, Cs, Sc, Hf, Th, U, Ta, Cr, As and the rare-earth elements (REE) (La, Ce, Nd, Sm, Eu, Tb, Yb). Structural H_2O content was determined by the Penfield method. Details of the analytical procedures for ICPES and XRF are described by De Lange et al. (1987) and for INAA by Van der Sloot and Zonderhuis (1979).

The quality of the analysis was monitored by the simultaneous analysis of some in-house and international standards. On the basis of replicate analyses ($N=11$) of an appropriate in-house granitic standard (GRAN-1), precision is better than ±2% for Sc, Cr, Nd, Sr, Be, Ba, Mn, Fe, P, Al, Ca, Ti, Y and K; ±5% for Rb, La, Ce, Th, Hf, Si, S, Mg, Na and Li; ±10% for Cs, Tb, Sm, Yb, Zn, Cu, Nb and Zr; and better than ±15% for Ta, Eu and U. Accuracy for most elements is satisfactory and values obtained by different methods were coincident within their analytical errors.

The mineralogy of the fraction <2 μm of the residual soils was determined by X-ray diffraction (XRD). We made duplicate oriented XRD glass slides for each sample, one sample being

saturated with K and the other with Mg. The samples were analyzed from 2° to 70° (2θ) on a Philips X-ray diffractometer using Cu-K_α radiation. After this measurement, another analysis was performed after the Mg-saturated mount for each sample had been treated with glycol, and the K-saturated mount was heated to 500°C. Clay minerals present in the soils were identified according to the method of Thorez (1975). Mean intensities of the strongest reflection are tabulated. These are not quantitative estimates of mineral abundance but do allow one to assess variation between samples.

3.3. Evaluation of data

The choice of a reference frame is the most important assumption for any mass-balance calculation of an open system.

The isovolumetric approach using density measurement (Millot and Bonifas, 1955; Gardner et al., 1978) can be very useful to assess element mobility, provided no deposition has occurred from outside the weathering profile and provided neither expansion nor contraction has taken place. The assumption of constant volume is difficult to prove unequivocally. In addition, sampling according to the isovolumetric approach is very cumbersome when dealing with rocks having varying degrees of hardness, coherence or porosity, i.e. specimen incoherence may prevent a density measurement.

Therefore, we have chosen the immobile-element approach (Goldlich, 1938; Nesbitt, 1979; Nesbitt et al., 1980; Chesworth et al., 1981; Cramer and Nesbitt, 1983; Gascoyne and Cramer, 1987; Kronberg et al., 1987). Because all elements are soluble to some degree, the basic assumption of the immobile behaviour of some elements is invalid. However, in a geological context weathering profiles generally exist for a short period only and components with extremely low aqueous solubilities will not be significantly mobilized. Ratios of elements are not influenced by changes in the amount (i.e. removal) of other constituents; consequently changes in ratios are particularly useful when applied to related samples of a weathering profile. Ti may be selected as the element for normalization on the basis of its low solubility and its presence in several stable primary minerals such as rutile, ilmenite and titanite. When these minerals are decomposed, Ti readily forms insoluble Ti-oxides and Fe-Ti-oxyhydroxides (Nesbitt, 1979). Furthermore, we have verified the immobility of Ti compared with the other components by the intercomponental ratio method (see Chesworth et al., 1981).

The percentage increase or decrease of any element X in a sample, relative to fresh parent rock can be calculated according to (Nesbitt, 1979):

PERC.CHANGE =

$$[(X/Ti)_{sample}/(X/Ti)_{parent} - 1] * 100 \qquad (1)$$

In order to compare various weathering profiles, we must have an independent measure for the degree of alteration of each sample and the maturity of each residual soil. We therefore introduce the parameter DEGREE defined as:

$$DEGREE = (1 - R_{sample}/R_{parent}) \qquad (2)$$

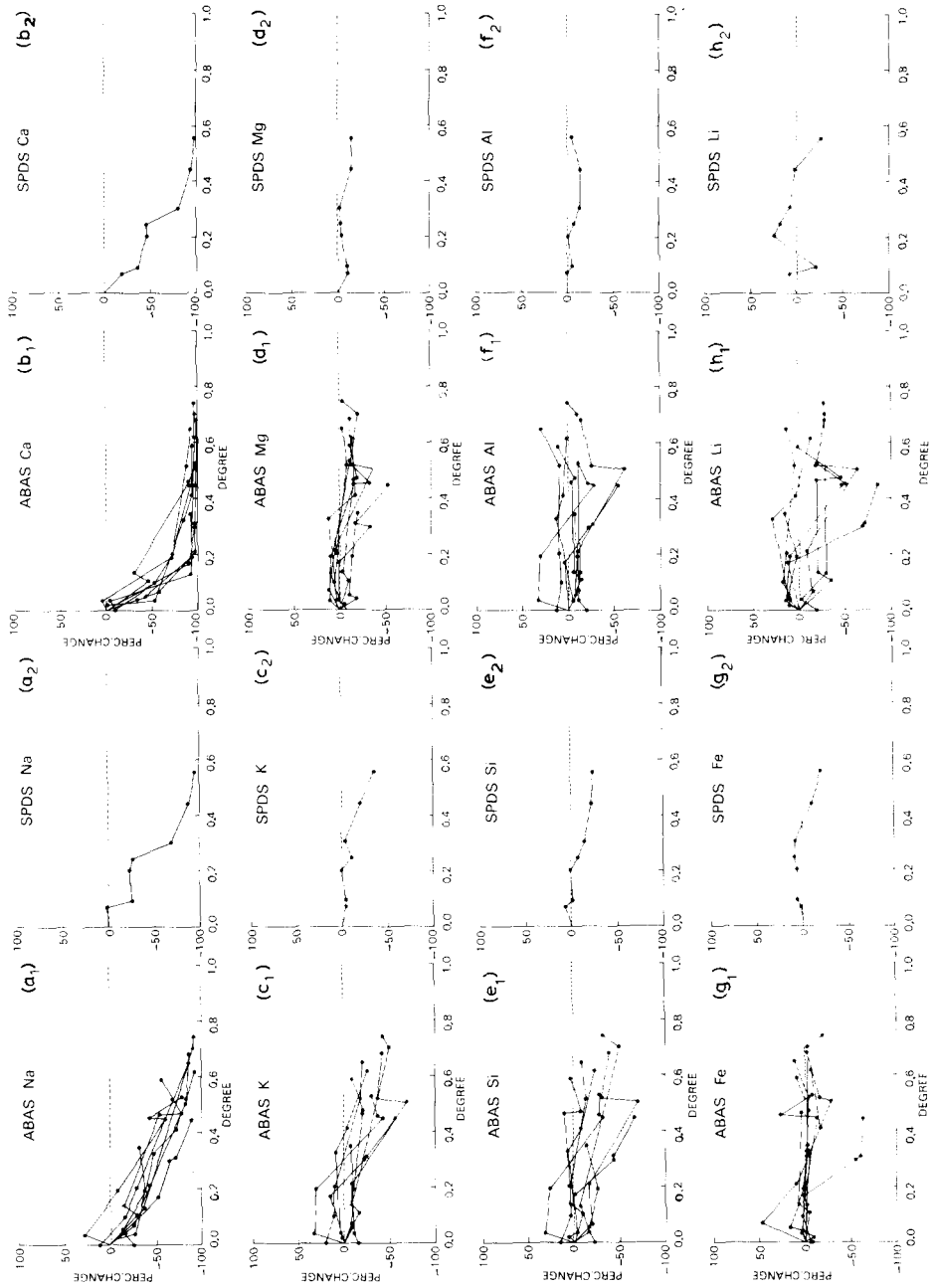where the ratio R is calculated according to:

$$R = (CaO + Na_2O + K_2O)/(Al_2O_3 + H_2O) \qquad (3)$$

This ratio R is a measure for the degree of feldspar breakdown and the accumulation and formation of clay minerals. The parameter DEGREE approaches 1 whenever minerals such as gibbsite and kaolin prevail and is equal to 0 for unaltered rocks.

The introduction of this, at first sight, rather complex parameter has some clear advantages.

It can be considered as a linearized progress variable of field data and it is comparable with the theoretical progress variables such as those introduced by Helgeson et al. (1969). The parameter DEGREE provides a more reliable estimate of chemical weathering intensity than profile depth (horizon approach) or distance
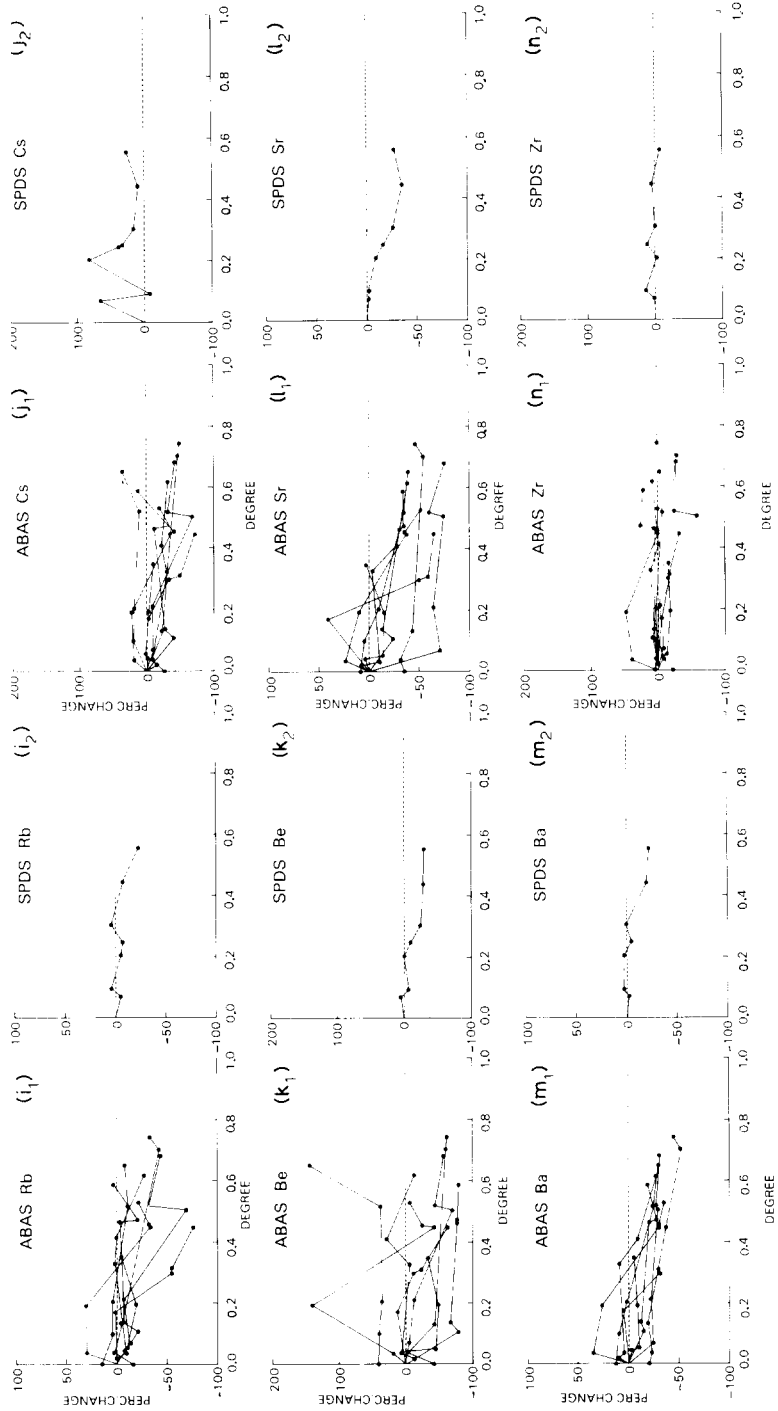
(b₂) SPDS Ca

(b₁) ABAS Ca

(a₂) SPDS Na

(a₁) ABAS Na

(d₂) SPDS Mg

(d₁) ABAS Mg

(c₂) SPDS K

(c₁) ABAS K

(f₂) SPDS Al

(f₁) ABAS Al

(e₂) SPDS Si

(e₁) ABAS Si

(h₂) SPDS Li

(h₁) ABAS Li
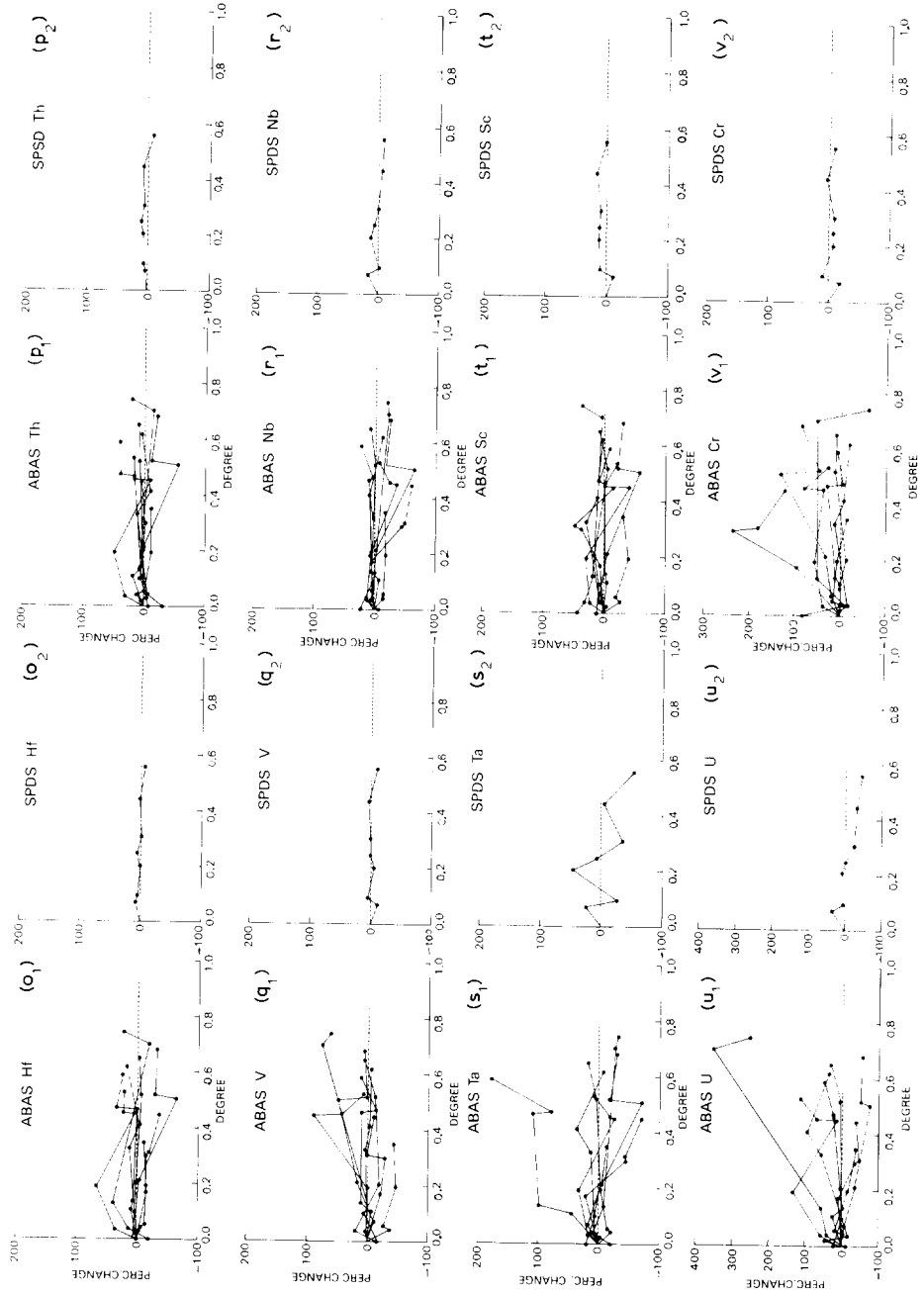
(g₂) SPDS Fe

(g₁) ABAS Fe

Fig. 2a-n. For caption see p. 261.

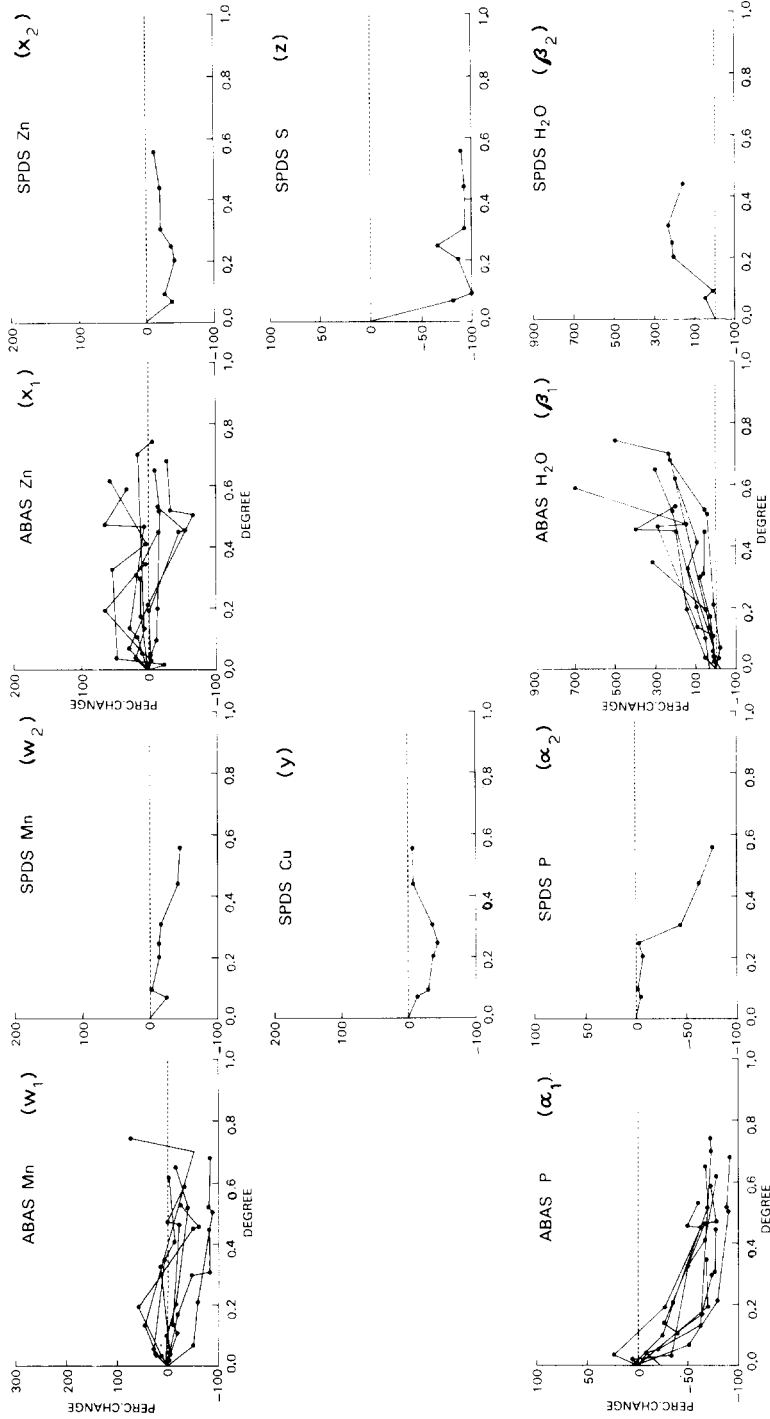Fig. 2. Percentage change. normalized with respect to Ti, of individual elements/component (PERC. CHANGE) vs. the degree of chemical alteration (DEGREE). (For the SPDS granite, samples with DEGREE > 0.8 are not shown.)

from a core-stone centre since rocks are not homogeneously altered. Differences in the initial composition of the parent rocks are reduced but not eliminated since weathering processes are dependent on the composition of the parent rock (e.g., Holland, 1984).

Diagrams in which the DEGREE and PERC.CHANGE are plotted on the abscissa and ordinate, respectively, allow the simultaneous presentation of various weathering sequences. It is easy to trace progress of weathering from the abscissa and to make a quantitative comparison of element losses. Although some scatter is caused by differences in the composition of the parent rock, in the depth at which weathering occurred, and in the accumulation of analytical error during the calculation, general trends can be extracted from such diagrams.

Before the DEGREE vs. PERC.CHANGE diagrams are presented, we have to compare our generalized field alteration scale with our parameter DEGREE. Both alteration profiles on the SPDS granite, i.e. one sampled according to our generalized field alteration scale and the other according to the vertical sampling method (i.e. according to the horizon concept), are from the same quarry. Data from those profiles have therefore been merged in Fig. 2 (to be discussed in the next section) and from the consistent trends it follows that sampling according to the generalized field alteration scale will not bias our results. (Perhaps it should be mentioned that the SPDS granite is relatively unfractured and that the requirements for the validity of the horizon concept are almost satisfied.)

In addition, the maturity of the alteration suites as calculated (eq. 2) correlates well with the relative amount of illite present in the <2 μm fraction of the residual soils (Table I).

4. Results

4.1. Soil mineralogy

The residual soils developing on the Abas granite are a complex mixture of kaolinite,

TABLE I

Soil mineralogy (<2-μm fraction)

	K	G	Q	I	V	Kfeld	DEGREE
ABAS 1	100	—	57	80	—	+	0.45
ABAS 2	84	72	100	54	29	—	0.51
ABAS 3	100	—	61	89	—	+	0.35
ABAS 4	55	85	100	40	19	—	0.46
ABAS 5	100	33	45	40	—	—	0.54
ABAS 6	23	100	35	12	2	+	0.52
ABAS 7	32	100	32	16	—	+	0.45
ABAS 8	24	24	100	18	13	+	0.70

K = kaolinite; G = gibbsite; Q = quartz; I = illite; V = vermiculite; Kfeld = K-feldspar; DEGREE = measure for chemical alteration calculated according to eq. 2.

gibbsite, illite, quartz, vermiculite, feldspar and amorphous material; however, several distinct mineralogical differences can be observed (Table I).

The suites ABAS 1 and 3 are distinct because gibbsite is absent, whereas kaolinite and illite are dominant, accompanied by lesser amounts of quartz and feldspar. In contrast, in the remaining profiles on the Abas granites, gibbsite, kaolinite and quartz predominate and illite and feldspar are less abundant. In addition, the residual soils of the suites ABAS 2, 4, 6 and 8, are characterized by the presence of vermiculite. This authigenic mineral is known to be formed in the lower part of the soil sequence (Velde, 1984).

The residual soils on the SPDS granite are composed almost entirely of an X-ray-amorphous phase with only minor amounts of poorly crystallized (very broad XRD peaks) kaolinite or metahalloysite. Fe minerals, while clearly ubiquitous in all profiles, are poorly represented by diffractograms; the majority of Fe-oxyhydroxides therefore must be associated with X-ray-amorphous phases such as surface coatings.

4.2. Chemical changes during incipient and moderate stages of alteration

The percentage change of elements, relative to TiO_2, as a function of the degree of altera-

TABLE II

Average composition of the SPDS granite and the Abas granite [all in ppm, except major elements (%)]

Element	SPDS (N=2)	Abas (N=8)
Si (%)	31.9	33.7
Al	8.06	7.95
K	4.74	3.84
Na	2.09	2.31
Ca	0.73	0.25
Mg	0.53	0.16
Fe	2.06	0.91
H_2O	1.21	1.70
Mn (ppm)	180	201
P	2,085	1,739
Ti	3,519	868
Li	101	309
Rb	316	407
Cs	5	35
Be	4	12
Sr	102	41
Ba	447	126
Th	112	9
U	11	14
V	34	6
Nb	6	14
Ta	0.8	3.2
Zn	140	75
Cu	7.6	4.6
S	370	23
As	2.0	6.1
Sc	3.9	2.9
Y	14	7
La	87	12
Ce	228	28
Nd	112	24
Sm	20	4
Eu	0.88	0.34
Tb	0.57	0.17
Yb	2.6	0.86
Hf	8.4	2.1
Zr	286	94
Cr	19.2	4.6

tion, are presented graphically in Fig. 2. The profiles on the Abas (8) and SPDS (2) granite are given separately because of the widely different parent-rock petrology (see Section 2.2.), chemical composition (Table II) and residual soil mineralogy (Table I).

The intensively altered residual soils on the SPDS granite (DEGREE > 0.8) are not discussed in the present section, because these environments differ so much that main trends will be obscured. These samples are discussed in a separate section (Section 4.3).

4.2.1. Major elements. In general, Na, Ca and K are concentrated mainly in feldspars. The significant decreasing trends for Na, Ca and K in the SPDS granite (Fig. 2a, b and c, respec.) therefore reflect the alteration of feldspars. Both Ca and Na decrease more rapidly than K and both are depleted more than K. These trends result primarily from the greater alteration rate of plagioclase compared to that of K-feldspar. A rough estimate of the relative weathering rates can be obtained from the slopes in Fig. 2a–c; plagioclase alters $\sim$3 ($\pm$1) times faster than K-feldspar. Note also that K-feldspar was the only feldspar found in the residual soils (Table I). The behaviour of Na and K during the weathering of the Abas granite is similar to that found during the alteration of the SPDS granite, but Ca is depleted more rapidly. This reflects either the presence of a Ca-rich feldspar (i.e. those feldspars with a high alteration rate) or rapid weathering of apatite. The very low Ca content of the Abas granite does not totally compensate for the P content of the rock (as apatite), and points to a pure albitic composition of the plagioclase (see Table II). Both the whole-rock composition (Table II) and petrographic observations support the latter possibility; no Ca-rich feldspar is expected to be found. In addition, the P alteration diagram for the Abas granite (Fig. 2α) also reflects a rapid decrease of apatite during the incipient stages of weathering. The significant decreasing trend for Ca therefore reflects the instability of apatites in the Abas granite, but the alteration of plagioclase in the SPDS granite.

The decrease of Mg is significant but not large (Fig. 2d). In the unaltered granite the bulk of this element is located in biotite, which alters rapidly during progressive alteration. In the al-

tered rock the majority of Mg is probably incorporated in vermiculite (Table II) or in octahedral sites of illites (Stevens et al., 1979) and only a minor amount is lost.

The geochemical distribution of Si (Fig. 2e) is similar in all profiles on both granites; Si decreases with an increasing degree of alteration.

Both Al and Fe are often considered to be essentially immobile during weathering; the observed profiles (Fig. 2f and g) show that these elements are not mobilized. However, some inhomogeneity may be caused by grain-size fluctuations (Rice, 1973; Koons et al., 1980) and redox fluctuations.

4.2.2. Minor and trace elements. No significant trend is apparent for Li although a tendency to depletion can be seen (Fig. 2h). Li is known to be concentrated in micas (Wedepohl, 1969; Neiva et al., 1987) or Li-phosphate minerals, and upon weathering Li can be incorporated in kaolinite (Ashrey, 1973) or mica-type clay minerals.

The distribution of Rb and Cs is closely linked with that of K, but the decrease of these elements is somewhat less than that of K (Fig. 2i and j). K-feldspars are known to contain more Rb and Cs than biotite and because the latter mineral weathers more readily than K-feldspar, Rb and Cs are expected to be less depleted than K. In addition, cation exchange predicts (Garrels and Christ, 1965; Stumm and Morgan, 1981; Morel, 1983) that on clay minerals large cations such as Rb and Cs are preferentially retained over K.

The distribution of Be in the SPDS granite is rather regular and shows a significant depletion. The behaviour of Be (Fig. 2k) resembles most the behaviour of Mg (Fig. 2d); both are concentrated in micas. However, the distribution of Be in weathering suites on the Abas granite is irregular and may reflect the varying abundance of the mineral beryl, which according to field and petrographic observations is a minor component of this granite. In all profiles investigated the geochemical distribution of Sr

is similar to that of Ca; strontium always decreases with increasing alteration of the rock (Fig. 21). Because of its size Sr is more readily exchanged onto clays than Ca.

Ba is concentrated mainly in K-feldspar. Its geochemical distribution is most similar to that of K (Fig. 2m).

The diagrams for Zr, Hf and Th (Fig. 2n, o and p, respec.) show that these elements were, at least with respect to Ti, essentially immobile in all profiles. These observations agree very well with the predicted mobilities of these elements (Cramer and Nesbitt, 1983).

Similarly, the geochemical distribution of V, Nb, Sc and Ta shows that these elements are rather immobile during weathering (Fig. 2q, r, s and t, respec.). A similar observation for various rock-types was made by Cramer and Nesbitt (1983). Some irregularity in the distribution of V may be caused by its redox chemistry (see Section 4.4.), but the scatter for Ta must be due to analytical error.

Depletions as well as enrichments are observed for U (Fig. 2u). The geochemical distribution of U during weathering has been studied extensively (e.g., Pliler and Adams, 1962; Harris and Adams, 1966; Barbier and Ranchin, 1969; Zielinski, 1982; Cramer and Nesbitt, 1983; Michel, 1984; Guthrie and Kleeman, 1986; Kamineni et al., 1986), but no general trend can be deduced. The geochemistry of U is particularly complicated because redox processes, phosphate, organic and carbonate complexing, sorption equilibria, the abundance of V and P, and the initial site of U, may all control its distribution. U occurs principally in three modes: background, as a resistate, and in an interstitial position (Guthrie and Kleeman, 1986). The limited mobility of U in the weathering suites on the SPDS granite is probably related to its initial distribution over these three modes; Basham et al. (1984) suggested that a considerable part of U in the SPDS granite is found in refractory and non-leachable minerals. Therefore, the geochemistry of U is too complex for general conclusions to be extracted

concerning its distribution during weathering.

The geochemical distribution of Cr and Mn is rather irregular (Fig. 2v and w, respec.); this can probably be attributed to redox processes (see Section 4.4.). Cr either remains immobile or is added to the profile, whereas Mn is depleted or remains immobile.

A major portion of the Zn and Cu in the parent rocks is contained in biotite and sulphides, which rapidly alter upon weathering. However, no significant trend is evident for either Zn or Cu (Fig. 2x and y, respec.). Both Harris and Adams (1966) and Rice (1973) found an enrichment of Zn and Cu in the fine fraction, which mainly comprises secondary minerals. The majority of Zn and Cu is incorporated in or adsorbed on authigenic clay minerals. No data for Cu and S are shown for the weathering profiles on the Abas granite, because the values were generally too close to the detection limit to be reliable. Sulphur is rapidly oxidized during incipient weathering and is therefore lost from the weathering profile (Fig. 2z), because sulphate is very soluble.

The distribution of P is similar in all profiles investigated; P always decreases with an increasing degree of alteration (Fig. 2α). The main source of this element is apatite, which is unstable during weathering (Rice, 1973). Note that the P decrease in the incipient stages of weathering of the SPDS granite is negligible, whereas it is significant for the Abas granite. However, the final depletion is comparable. This is probably related to the presence of post-magmatic secondary apatite in the Abas granite (see also Ca in Section 4.2.1.).

Finally, the amount of bound water increases in all profiles (Fig. 2β). The significant increasing trend reflects the formation of clay minerals with structural OH$^-$ groups.

4.3. Intensively altered residual soils

Although the geochemistry of the intensively altered residual soils on the SPDS granite was not included in the previous discussion on ele-
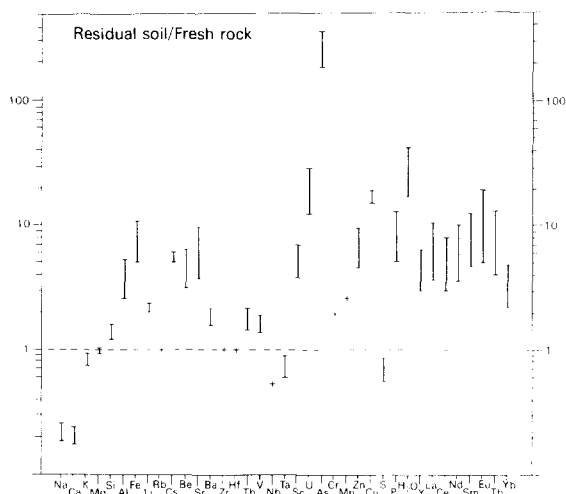

Fig. 3. Ratio of residual soils with fresh rock corrected for dilation or compaction, i.e. assuming immobility of Ti.

ment mobility during weathering, it does merit attention. The two samples to be discussed in this section (having a DEGREE of 0.81 and 0.93, respec.) were sampled from a fracture zone where transport and leaching are the dominant processes. In this late stage of weathering even the most resistant minerals are attacked (e.g. see Michel, 1984). For the sake of clarity we divide the behaviour of chemical elements into three categories: supergene, mobile and immobile elements. The latter are those which are enriched, depleted and not deviant, respectively, with respect to Ti. Fig. 3 demonstrates that large supergene enrichments with respect to Ti are found for As, H$_2$O, U, Cu, P, Fe, Zn, Sc, Si, Be, Cs, Al, Y, Sr and the REE; minor enrichments are found for V, Th, Ba, Li, Mn, Cr and Si, but Zr, Hf, Nb, Ta, Mg, K and Rb are not significantly enriched or depleted. Ca and Na are the only elements that are significantly depleted. Absolute concentrations of immobile elements during weathering will either increase as other species are removed in solution (i.e. pure physical accumulation by collapse) or will be residually diluted as supergene elements become enriched through precipitation. Note that supergene elements are only enriched with respect to physical accumulation, but the abso-

lute concentrations of these elements may be either lower or higher than in the parent rock. Mobile elements always have lower concentrations in the residual product than they have in the parent rock.

A comparison that includes only residual soils and parent rock might point to the immobility of Zr, Hf, Nb, Ta, Mg, K and Rb. However, limited mobility has been shown for Mg, K and Rb during moderate stages of weathering (Fig. 2c, d and i, respec.). That these elements are not deviant relative to the unaltered rock is explained by ion-exchange, sorption and precipitation processes in the residual soils; these processes compensate for losses during earlier stages. Therefore, one needs to exercise caution in drawing conclusions based on a simple comparison of the final weathering product and the fresh parent rock.

The strong supergene enrichment for As, U, P, Cu, Zn and Sc is most striking; maximum concentrations of 250 (As), 114 (U), 9712 (P), 62.5 (Cu), 480 (Zn) ppm are found. These elements are probably associated with Fe-oxyhydroxides. In an oxic environment, As is strongly associated with Fe, presumably in the form of arsenate adsorbed on ferric oxyhydroxides or in the form of precipitated $FeAsO_4$ (Pierce and Moore, 1982; Farmer and Lovell, 1986). Phosphorus, the Group Vb neighbour of As, is known to be adsorbed and coprecipitated with Fe-oxyhydroxides (Berner, 1973; Salomons and Foerstner, 1984). The adsorption of U on to and the association of U with amorphous ferric oxyhydroxides have been shown to occur (Barton, 1956; Van der Weijden et al., 1976, 1985; Hsi and Langmuir, 1985; Kamineni et al., 1986). Koons et al. (1980) assessed the degree of association of trace metals with Fe-oxides during rock weathering and concluded that Sc, Zn, Cr, and possibly As, Th and U are retained by Fe-oxyhydroxides. Therefore, the presence or absence of Fe-oxyhydroxides in alteration suites is of major importance for the behaviour of trace elements.

It should also be noted that the two most en-

TABLE III

Redox equilibria (pH = 6)

Equation	log K	pE
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	83.1	14.8
$HCrO_4^- + 4H^+ + 3e^- \rightleftharpoons Cr(OH)_3 + H_2O$	55.6	10.5
$MnO_{2\,(s)} + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	41.3	8.65
$2H_2VO_4^- + 4H^+ + 2e^- \rightleftharpoons V_2O_{4\,(s)} + 4H_2O$	40.4	8.20
$Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$	16.3	7.33
$UO_2(CO_3) + H^+ + 2e^- \rightleftharpoons UO_2 + HCO_3^-$	14.0	4.3
$HAsO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons HAsO_3^{2-} + H_2O$	8.1	1.07
$SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons H_2S + 4H_2O$	41.0	-2.38

Data from Langmuir (1978) and Stumm and Morgan (1981).

riched elements, As and U, may undergo a redox transformation at the same time as they precipitate and adsorb on Fe-oxyhydroxides. Of the As species, the oxidized form, arsenate, is adsorbed more readily on amorphous Fe-oxyhydroxides than the reduced form, arsenite (Pierce and Moore, 1982). The adsorption of As will consequently be enhanced by the chemical oxidation of As(III), which is possibly catalyzed by Fe- and Mn-oxyhydroxides.

More information about redox transformations will be given in the next section.

4.4. Redox transformations

Several elements can undergo transformations to different oxidation states. These oxidation–reduction reactions can be identified by a characteristic pE at which the activity of the oxidizing and the reducing agent are equal. Some relevant reduction couples are listed in Table III. Redox transformations in which the reduced or oxidized form is insoluble and the other form is relatively soluble are particularly useful for geochemists and can be used to set limits on the oxidation state of a weathering profile. It will be clear that these redox transformations can influence the removal, addition and distribution of these elements. However, little information is available concerning redox
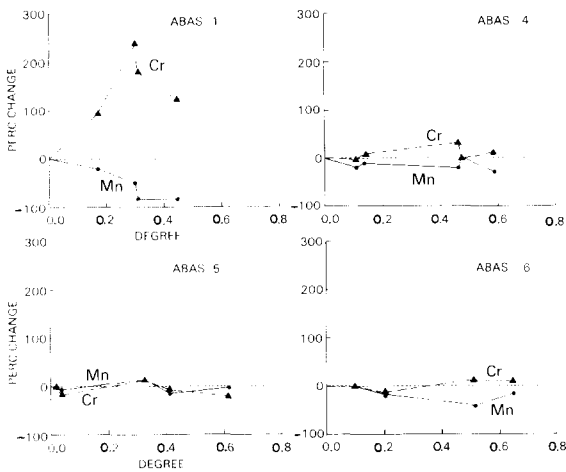
Fig. 4. Percentage change, normalized with respect to Ti, of Mn and Cr (PERC.CHANGE) vs. the degree of chemical alteration (DEGREE).
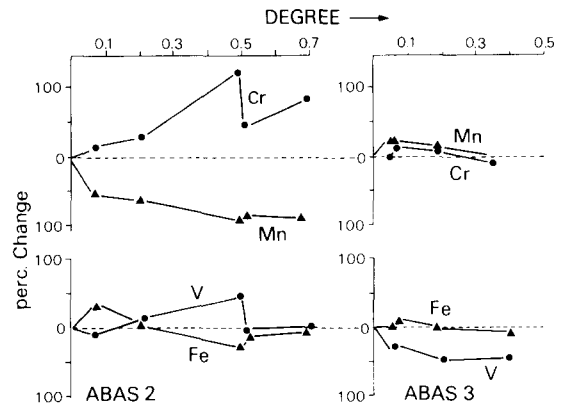

Fig. 5. Percentage change, normalized with respect to Ti, of Mn, Cr, V and Fe (PERC.CHANGE) vs. the degree of chemical alteration (DEGREE) for the profiles ABAS 2 and 3.

transformations of trace metals during weathering of granitic rocks.

When the distributions of Mn and Cr are compared (Fig. 4 and 5), it is seen that these elements can behave antithetically. Mn depletions are accompanied by Cr enrichments, but immobility of Mn is accompanied by immobility of Cr. This can be attributed to the contrasting behaviour of Mn and Cr during redox transformations. Mn depletions and Cr enrichments are both the result of suboxic conditions. Mn will dissolve and remain in solution as Mn(II) and Cr will be effectively scavenged as Cr(III) or coprecipitated with Fe and Al. Therefore, Mn is removed from and Cr is added to the profile. The immobility of both Mn and Cr is the result of oxidizing conditions. Mn will remain essentially immobile because any liberated Mn(II) will be oxidized and precipitated as Mn(IV)-oxyhydroxide. The resistant nature of minerals containing Cr during moderate stages of weathering (Wedepohl, 1969; Koons et al., 1980) results in a distribution of Cr similar to the immobile elements (e.g., Ti, Nb, Zr, Hf, Th). No additions of Cr liberated during more advanced stages of weathering can be expected since $HCrO_4^-$ is very soluble and has a low tendency to adsorb onto surfaces (Van der

Weijden and Reith, 1982). Therefore, the contrasting properties of Mn and Cr can be used to pinpoint the pE level of an alteration suite, but the criterion that Mn be present in a leachable form should be met.

The geochemical distribution of Mn, Cr, V and Fe is shown in Fig. 5 for two selected profiles: ABAS 2 and 3. In the ABAS 2 profile, which we infer to be suboxic, V is enriched, whereas Fe remains practically immobile. In an oxidizing environment (ABAS 3), Fe remains immobile and V is depleted. V is soluble as $H_2VO_4^-$ in an oxidizing environment, whereas it is adsorbed and coprecipitated with Fe under reducing conditions (see Table III). Again this reasoning is valid only if these elements are leachable. For instance, V concentrated in minerals such as ilmenite is unlikely to be affected by redistribution processes.

Assuming that all elements are soluble to some degree, we can deduce a pE level for both profiles. The ABAS 2 weathering suite has a pE level between 7.3 (immobile behaviour of Fe) and 8.2 (immobility of V); the ABAS 3 alteration suite has a pE-value > 10.5 (no addition of Cr). These redox level estimates are supported by field data. The ABAS 2 suite is situated in a forest and comprises relatively unfractured rocks. The period of water–rock interaction is

enough to allow the water to become depleted in oxygen. Note that the abundance of soil-vermiculite (Table I) also points to rather a wet equilibrium system. The ABAS 3 suite is situated along the Ribama Fault (Fig. 1). The fluid content of this very fractured rock is variable and intermittent. Water will flow through at a high rate, resulting in the observed oxidized zones.

It would be interesting to apply this approach to various paleosol data in order to deduce estimates of the paleo oxygen level. Such an approach should be used preferably in conjunction with methods outlined by Holland (1984).

Another interesting multivalent ion is Ce; it will be discussed in the following section on REE.

4.5. Yttrium and the REE

The REE are unique because they have very similar chemical properties and in general show rather a uniform geochemical behaviour. Except for Ce and Eu, these elements are always found in the trivalent state. Ce may be oxidized to the tetravalent state and Eu may be reduced to the bivalent state.

Only a part of the total REE content of granitic rocks is present in the major mineral phases (Alderton et al., 1980). The accessory minerals monazite, xenotime, sphene, zircon and apatite account for the remaining REE content. The crystal structure of these minerals is specific to their REE content; monazite is enriched mainly in light REE (LREE), zircon and xenotime contain mainly heavy REE (HREE), and apatite is enriched in the middle REE (MREE) (Hanson, 1978; Henderson, 1984). With respect to the whole rock, micas are known to have negative Eu anomalies, whereas feldspars have a marked positive Eu anomaly (Alderton et al., 1980). Hence, if any of these minerals is particularly susceptible to any alteration process, then the whole-rock REE pattern may be drastically changed. However, the mobility and the fractionation of REE during various types of alter-

ation processes are still under discussion (e.g., Nesbitt, 1979; Humphris, 1984; Topp et al., 1984, 1986; Butt, 1986).

The percentage change of elements, relative to TiO_2, as a function of the degree of alteration, is shown in Fig. 6. No significant trends are apparent for Y and the REE although Y and Yb show a tendency to become depleted (Fig. 6a and h, respec.). The decrease of these elements may reflect a somewhat lower stability of xenotime (HREE-rich) compared to monazite (LREE-rich) or may indicate that HREE are more soluble than LREE. Cantrell and Byrne (1987) have shown that complexation of REE smoothly increases as a function of atomic number and that an increase in solubility is expected to follow this trend. In addition, Michard et al. (1987) did indeed find spring waters enriched in HREE originating in a granitic area. Therefore, it is likely that the tendency of Y and Yb to become depleted during weathering can be attributed to their aqueous solubility.

However, the intensively altered residual soils on the SPDS granite show that the REE are both mobilized and fractionated (Fig. 7). The fractionation results from an initial distribution of the REE in both leachable and residual mineralogical sites. REE concentrated in resistate phases do not become easily enriched in the residual soils, whereas REE in leachable phases such as plagioclase, K-feldspar and apatite are easily liberated and consequently may be enriched in the residual soils. The weathering of apatite and the subsequent concentration by sorption processes lead to a relative enrichment of the MREE in the residual soils. This enrichment in MREE of the final weathering product is enhanced by the resistance of zircon, xenotime and monazite to weathering, being minerals that contain preferentially LREE and HREE. Relative to other REE, Eu as Eu(II) is preferentially incorporated in feldspar during magmatic processes (Alderton et al., 1980) and is consequently easily liberated and concentrated in the residual soils (Fig. 7). Notice that Topp et al. (1984) needed "a com-
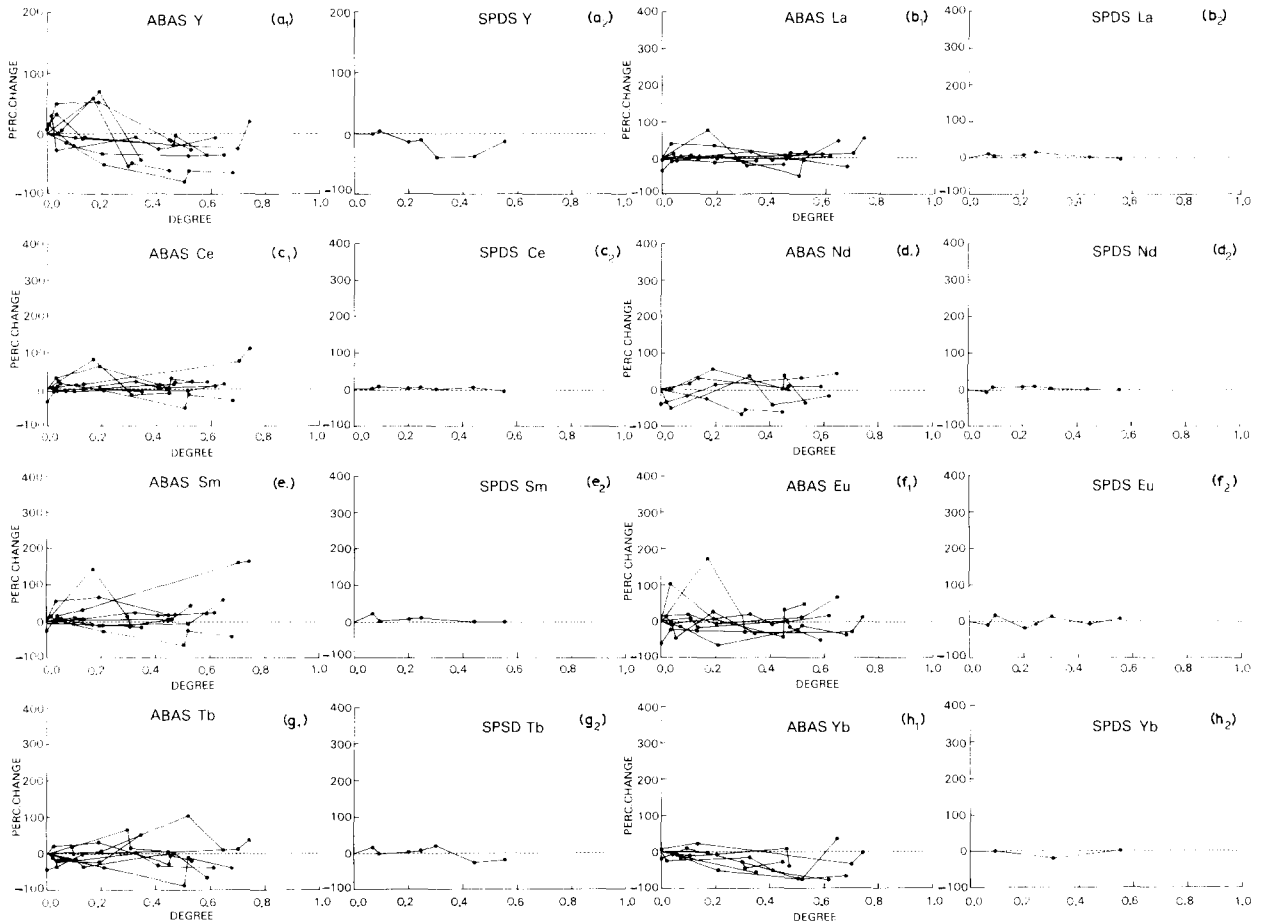
Fig. 6. Percentage change, normalized with respect to Ti, of Y and the REE (PERC.CHANGE) vs. the degree of chemical alteration (DEGREE).

mon transport mechanism" for Sr and Eu to explain their data. We suggest that a common plagioclase source for both Sr and Eu and subsequent concentration by sorption form a more likely scenario for their similar behaviour. The enrichment of these elements, with respect to TiO_2, cannot be caused by an accumulation of resistant minerals, but must result from sorption and coprecipitation processes (Fig. 3; see Section 4.3 on residual soils). The REE are probably contained in both Fe-rich and P-rich phases. Coprecipitation of REE with P phases (amorphous and crystalline) during continental weathering has been reported to occur (Sawka et al., 1986) and the affinity of REE for Mn- and Fe-oxyhydroxides has been estab-

lished (Fleet, 1984).

The process of selective leaching and subsequent concentration in secondary phases may account for the observed fractionation, but probably does not explain the pronounced depletion of Ce with respect to La and Nd. This depletion is related to the redox chemistry of Ce. Upon weathering Ce(III) is oxidized to Ce(IV) and will consequently behave in rather an immobile way, because CeO_2 has a very limited solubility. As a consequence Ce, with respect to La and Nd, is preferentially retained in the weathering suite and is consequently less enriched in the residual soils.

For comparison the ash-altered-to-clay rhyolite ratio reported by Zielinski (1982) is also

Residual soil/Fresh rock

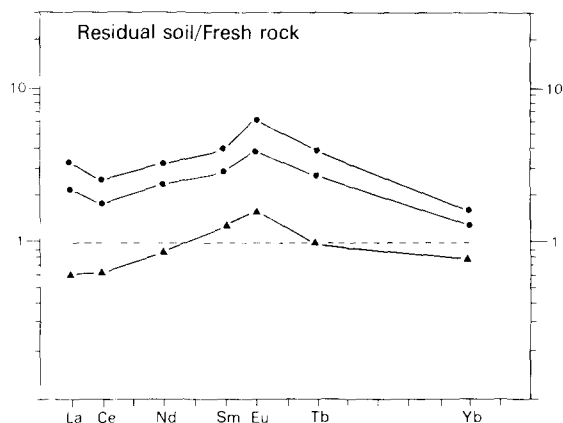La Ce   Nd   Sm Eu   Tb   Yb

Fig. 7. Ratio of residual soils to unaltered rock [*dots* = SPDS granite data; *triangles* = rhyolite data of Zielinski (1982)]. (Notice the difference between this figure and Fig. 3, because here no correction has been made for the collapse.)

presented in Fig. 7. The similar shape of the distributions over the SPDS granite and the weathering suite on the rhyolite, suggest that the proposed scenario may well apply to most rocks containing REE in both resistate and leachable phases.

5. Conclusions

Gibbsite, quartz and kaolinite prevail in the residual soil mineralogy despite the temperature climatic setting. Although the presence of distinct iron minerals could not be deduced from X-ray diffractograms, these minerals are certainly present. These X-ray-amorphous phases and surface coatings are of major importance for trace-metal behaviour.

Mass-balance calculations have been used to determine element mobility in granitic rocks during weathering. Mobilities are calculated from geochemical data normalized with respect to Ti in the fresh parent rock. The introduced parameter DEGREE, which reflects the degree of chemical alteration, has shown itself to be a reliable progress variable. Diagrams in which DEGREE vs. PERC.CHANGE are plotted on the abscissa and ordinate, respectively, provide a firm basis for assessing element mobility.

Elements that remained immobile during incipient and moderate stages of weathering were Fe, Al, Zr, Hf, Th, Nb, Sc and the REE. However, Zr and Hf were the only elements that showed no mobility under extreme alteration stages. Elements that consistently tended to be lost during moderate weathering were Na, Ca, K, Mg, Si, Sr, Ba and P. The elements lost were mainly derived from leachable minerals such as feldspars, micas and apatites. Structural H_2O was the only component that was consistently enriched during progressive alteration.

Redox transformations were important in the determination of element mobility. The geochemical behaviour of Mn, Cr, V, Fe and Ce is very dependent on the redox state of a weathering system. These redox transformations can be useful to set limits on the oxidation state of a weathering suite.

The REE were not significantly mobilized during incipient and moderate stages of weathering, but could be mobilized and fractionated during intense weathering. The fractionation of the REE can be attributed to selective leaching of rocks containing both stable and unstable minerals. REE in weatherable minerals will be preferentially released and subsequently concentrated so as to yield supergene enrichments.

Acknowledgements

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