MINERALOGICAL AND CHEMICAL VARIATIONS INDUCED BY TROPICAL WEATHERING OF GRANULITIC ROCKS FROM THE BRAZILIAN BASEMENT

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ABSTRACT Chemical and mineralogical transformations occurring during tropical weathering of granulitic rocks from the Brazilian basement have been studied. Granulite weathering produces either gibbsitic or kaolinitic soil, as well as kaolinitic-gibbsitic soil. The transition from one type to another is abrupt and occurs in very limited areas. The variation in the chemical composition of host-rocks and/or in the drainage conditions seems to account for the above soils variation.

The residual soil is characterized by the almost total disappearance of alkali and alkaline earths and by strong enrichment of some hydrolized elements, like Zr, Ti and Cr. Relationships between ferromagnesian elements and iron both in rocks and in soil have been discussed in detail.

RESUMO Estudaram-se transformações químicas e mineralógicas que ocorrem durante o intemperismo de rochas granulíticas do embasamento brasileiro. O intenso intemperismo produz solos gibbsíticos, cauliniticos ou caulinitico-gibbsíticos. A transição de um tipo para outro é abrupta e ocorre em pequenas áreas, provavelmente devido às variações na composição química da rocha matriz e/ou das condições de drenagem.

O solo residual é caracterizado pelo desaparecimento quase que total dos elementos alcalinos e alcalino-terrosos e pelo forte enriquecimento de alguns elementos hidrolizados, como o Zr, Ti e Cr. Discutiram-se pormenorizadamente relações entre elementos ferro-magnesianos e o ferro, em rochas inalteradas e em solos residuais.

INTRODUCTION Chemical and mineralogical transformations occurring in soil formation under tropical weathering conditions from various types of rock have been widely studied by numerous authors (McLaughlin, 1955; Bonifas, 1959; Delvigne, 1965 and 1967; Fairbairn and Robertson, 1966; Tardy, 1969; Sieffermann, 1969; Haantjens and Blecker, 1970). Weathering of high-grade metamorphic rocks, granulites in particular, has not been studied specifically, although most work deals at least partially with weathering of metamorphic rocks such as gneisses and migmatites (Grant, 1964; Kabata-Pendias and Ryka, 1968; Melfi and Levi, 1971; Levi and Melfi, 1972).

The interesting aspects found when studying granulite weathering are their peculiar structures, the fact that their mineralogical and chemical features may at least affect the type of soil produced, and that large areas of the African and Brazilian shields present granulites as principal country rocks. In addition, it would be interesting to analyze the geochemical behaviour of some elements in the residual soils, taking as the starting point geochemical trends given in recent work (Sighinolfi, 1970 and 1971) on granulites. Thus the aim of this paper is to obtain new mineralogical and chemical data on the tropical weathering of granulites and to investigate the detailed behaviour of elements during the formation of residual soils.

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Parent material and general features of the profile considered Material from a very limited area situated 12 km near Salvador (Bahia, Brazil) was selected for study. This area is situated within the Pedreira Valeria district. Here, the host-rocks belong to the undifferentiated precambrian basement.

PETROLOGY The petrology of this area and the surrounding regions was described by Oliveira (1970) and by Fujimori (1968). According to Oliveira (1970) several types of granulitic rocks occur in which banded "basic" granulites predominate and which show various mineralogical parageneses. The most common granulite consists of the assemblages: quartz-andesite-hornblende-biotite; andesine-hornblende-biotite-hypersthene-diopside and andesite-hypersthene-biotite-magnetite. The diffuse blackening over all the rock types produces a false homogeneity and prevents the rapid field identification of banding in granulites. Three soil profiles developed by weathering of granulites were selected on an elliptic front of approximately 300 m length. Over all the area the zone of weathering extends variably to a maximum depth of 50 m, and most of the soils are composed of coherent, easy to identify, altered rocks. Above this a layer of light-yellow material of variable thickness is found, and is in turn overlain by a more dark horizon which grades into a black organic-rich zone which continues to the surface. The pH measured at different soil levels varies between 4.0 and 6.0. In profiles A and B (Table I) most of the values fall in the range 4.0-5.0, and in that of C between 4.8 and 5.3. Table I reports for each profile the depth at which the samples were collected with the vertical distance given with respect to the contact of the fresh rock with the altered material taken as zero. Sample B10 is an unaltered inclusion above the line of rock weathering.

Table I — Sample position in relation to the contact between fresh granulite and overlaying residual soil

	Profile A		Profile B		Profile C	
	Sample number	Distance from the contact, m	Sample number	Distance from the contact, m	Sample number	Distance from the contact, m
Fresh granulite	A1	25	B1	20	C5	30
	A2	20	B2	10	C7	20
	A3	10	B5	1	C6	15
	A4	1	B3	0.2	C10	2.5
	A5	0.03	B10	*	C1	1
Residual soil					C11	0.1
	A9	0.1	B6	0.8	C2	0.5
	A5	1	B4	1.2	C8	1
	A10	1.5	B9	3	C3	3
	A6	2.5	B7	4	C4	4
	A11	3.5	B8	4.5	C12	6
	A7	5	B10	5	C13	12
					C14	15

*Boulder of fresh rock found in the residual soil at 3 meters above the contact

CLIMATIC CONDITIONS Climatic conditions are very steady and are characterized by very high rainfall (up to 1,800 mm) and by an average temperature of 25°C.

DRAINAGE Field observations supported by the mineralogical and chemical data of this work suggest that alteration has occurred under conditions of very strong drainage.

ANALYTICAL METHODS Major elements were determined by AA spectroscopy using the decomposition procedure described by Bernas (1968) and modified by the authors in some details. Each sample was analyzed in duplicate. The analytical error for major elements can be evaluated as in Bernas (1968). V, Cu, Zr, Ni and Co were determined by optical spectrography by methods described by Sighinolfi (1966 and 1968). Cr and Zn were determined by AA spectroscopy following Belt (1964). The analytical error for most of the trace elements is estimated to be 10%. Standardization for all the elements was made using the USGS rock standards to obtain calibration curves.

ANALYTICAL RESULTS AND DISCUSSION MINERALOGY OF RESIDUAL SOIL

According to the X-ray analysis the residual soil has as main secondary minerals either gibbsite or kaolinite, as well as a mixture of both minerals (Fig. 1). Goethite and a

Figure 1 — Diffractograms of orientated clay layers of Samples A7, B8 and 14C. *Gib*: gibbsite; *Q*: quartz; *Goe*: goethite; *M-V*: mixed-layered mica-vermiculite and *K*: kaolin

Figure 2 — Electron micrograph of a kaolinitic material from profile C showing tubes of halloysite associated with plates of kaolinite

mixed-layer mica-vermiculite were found frequently. The latter is derived probably from the biotite. Halloysite was identified with electron microscope analysis and seems to be also one of the main components of the residual soil (Fig. 2). Quartz was identified in all samples. According to the Fig. 1 the mineralogical composition of the residual soil varies abruptly over very limited areas. Thus the gibbsite content, which can be used as weathering index (Moniz and Jackson, 1967) presented a wide variation, from zero to 52% (Table II). The variation in the chemical composition of the host-rocks and/or in the drainage conditions seems to account for the above mineralogical variation.

Table II — Gibbsite content of some residual soils determined by DTA method

Sample	Gibbsite, %	Sample	Gibbsite, %	Sample	Gibbsite, %
A10	17	B6	24	C8	9
A6	44	B4	31	C4	33
A11	43	B7	52	C12	0
A7	34	B8	21	C14	0

CHEMICAL DATA 16 samples of fresh rock and 19 samples of altered material were analyzed for major and trace elements, and the results are reported in Table III and IV. Averages and dispersion data for all the elements in rocks and soil are also reported. The values of the coefficient of variation (*C* per cent) demonstrate that chemical heterogeneity characterizes the granulitic parent material. Furthermore, a still stronger dispersion of main and trace elements in the residual soil is demonstrated.

Estimates of gain and loss for main elements in the weathering within the three profiles, calculated as suggested by Krauskopf (1967, p. 103), are reported in Table V. These calculations were made on the assumption commonly retained (see for example Craig and Loughnan, 1964) that alumina does not change appreciably under normal weathering conditions. Nevertheless, a partial loss of alumina under conditions of very strong drainage and appropriate pH must be considered (see for example Delvigne, 1965; Hendricks and Whitting, 1968).

Table III—Chemical composition of fresh granulite

	A1	A2	A3	A4	A8	B1	B2	B3	B5
SiO ₂	55.36	55.92	55.99	53.38	60.06	53.51	51.81	53.96	55.25
TiO ₂	1.91	1.83	1.32	2.24	0.50	0.77	0.86	0.71	0.73
Al ₂ O ₃	14.37	15.91	15.44	15.91	18.05	17.60	16.85	17.27	15.73
Fe ₂ O ₃	0.09	0.71	1.17	0.38	1.47	1.99	2.51	1.59	1.84
FeO	10.81	10.48	9.48	11.25	6.27	8.99	8.98	7.86	8.71
MnO	0.082	0.086	0.108	0.132	0.061	0.116	0.142	0.126	0.140
MgO	3.18	2.18	2.63	3.75	1.58	5.11	4.18	4.32	4.25
CaO	5.75	4.78	4.83	6.75	4.82	9.21	9.02	8.30	6.95
Na ₂ O	3.17	3.22	3.72	2.83	4.07	0.75	3.20	3.30	3.04
K ₂ O	3.72	3.75	3.74	2.45	2.53	0.81	1.25	1.24	2.03
H ₂ O ⁺	0.00	0.00	0.10	0.00	1.03	0.00	0.13	0.23	0.12
Total	98.44	98.86	98.45	99.07	100.44	98.86	98.93	98.91	98.79
Total Fe*	12.09	12.34	11.69	12.87	8.43	11.97	12.48	10.31	11.51
Trace elements (ppm)									
V	36	74	60	118	54	170	235	137	150
Cu	100	145	117	126	92	107	117	103	130
Zr	180	800	690	510	230	76	157	155	203
Ni	10	23	36	47	16	21	41	34	31
Co	6	13	16	21	9	23	31	17	24
Cr	50	45	89	102	33	65	148	183	96
Zn	131	130	110	135	54	116	142	95	101

	B10	C1	C5	C6	C7	C10	C11	$\bar{X}$	C, %
SiO ₂	56.70	52.86	52.92	55.91	45.44	47.99	54.59	53.95	6.3
TiO ₂	0.98	0.72	0.85	1.02	0.30	0.60	0.50	0.99	56.6
Al ₂ O ₃	17.95	16.77	16.99	18.99	20.89	16.25	16.91	17.99	9.0
Fe ₂ O ₃	2.54	0.67	1.92	1.04	3.39	1.09	2.78	1.55	106.8
FeO	5.42	11.15	9.35	7.09	9.38	11.18	6.96	8.96	20.3
MnO	0.056	0.134	0.147	0.066	0.194	0.177	0.118	0.12	33.2
MgO	2.22	4.40	4.32	3.54	5.20	8.64	3.79	3.95	41.2
CaO	2.72	7.24	7.28	4.24	9.58	8.39	7.02	6.68	29.8
Na ₂ O	3.57	3.02	3.53	3.33	3.72	3.29	2.55	3.14	23.5
K ₂ O	4.15	0.84	1.02	2.54	1.11	0.86	1.38	2.09	5.1
H ₂ O ⁺	2.63	0.94	0.08	0.51	0.48	0.00	1.92	0.51	151.6
Total	98.94	98.74	98.41	98.28	99.68	98.47	98.52		
Total Fe*	8.56	13.05	12.30	8.91	13.80	13.50	10.51	11.52	14.8
Trace elements (ppm)									
V	95	155	180	142	190	210	153	135	43.0
Cu	147	125	117	100	72	113	73	111	19.4
Zr	71	97	102	90	125	70	110	229	99.8
Ni	20	30	18	20	28	16	18	25.6	39.8
Co	16	20	21	16	19	20	17	18.1	32.5
Cr	40	113	68	62	100	91	83	85.5	46.6
Zn	77	106	125	98	92	119	84	107	22.1

*Calculated as Fe₂O₃

Table IV — Chemical composition of residual soils

	A5	A9	A10	A11	A6	A7	B4	B6	B7	B8
SiO ₂	41.51	43.12	44.24	36.93	31.94	30.56	35.65	44.20	36.63	38.98
TiO ₂	2.73	0.98	1.04	1.08	2.86	3.42	0.71	0.26	0.69	0.93
Al ₂ O ₃	25.32	30.06	26.62	29.75	28.92	29.17	34.34	30.95	32.53	34.02
Fe ₂ O ₃	9.14	5.59	6.88	7.56	16.73	15.17	5.45	3.71	6.33	7.00
FeO	2.55	0.66	0.61	0.55	0.79	2.08	1.50	1.26	0.20	0.19
MnO	0.048	0.022	0.023	0.024	0.070	0.056	0.036	0.051	0.030	0.018
MgO	1.25	0.49	1.16	0.43	tr	tr	1.09	0.70	0.23	0.23
CaO	0.95	tr	0.71	tr	tr	tr	tr	1.40	tr	tr
Na ₂ O	0.69	0.54	0.40	0.20	tr	tr	0.20	1.87	0.20	0.20
K ₂ O ₊	2.07	3.70	4.17	2.61	0.10	0.31	0.90	1.80	0.57	0.10
H ₂ O	13.25	13.33	13.42	20.17	17.58	18.47	18.56	12.55	20.74	17.48
Total	99.54	98.49	99.27	99.30	98.99	99.24	98.44	98.75	98.15	99.15
Total Fe*	11.97	6.32	7.56	8.17	17.61	17.48	7.11	5.11	6.55	7.21
Trace elements (ppm)										
V	145	68	102	75	225	250	91	95	102	96
Cu	37	16	18	15	15	17	37	24	37	43
Zr	2000	620	1200	690	1250	2500	250	94	305	330
Ni	42	19	31	11	11	19	29	11	18	31
Co	22	9	9	4	5	13	9	7	5	8
Cr	130	64	220	79	197	140	96	85	110	nd
Zn	nd	138	175	108	nd	188	131	123	nd	nd

	B9	C2	C3	C4	C8	C12	C13	C14	X	C, %
SiO ₂	44.57	26.44	43.88	39.96	40.17	36.89	27.55	36.25	37.75	15.0
TiO ₂	0.41	0.73	3.78	3.83	2.64	1.53	4.33	3.50	21.97	70.3
Al ₂ O ₃	28.51	36.03	22.52	24.32	30.81	30.05	26.68	31.64	29.57	12.0
Fe ₂ O ₃	1.85	13.44	8.35	15.30	10.22	17.00	25.83	13.55	10.50	56.9
FeO	1.24	0.23	2.07	1.76	0.46	0.18	0.00	0.00	0.91	87.9
MnO	0.026	0.065	0.100	0.087	0.070	0.024	0.11	0.095	0.05	60.0
MgO	0.58	0.46	1.77	tr	0.37	tr	tr	tr	0.50	100.0
CaO	tr	tr	tr	tr	tr	tr	0.46	tr	0.23	170.8
Na ₂ O	tr	tr	tr	tr	0.20	tr	tr	0.20	0.28	157.1
K ₂ O	2.12	0.66	1.96	0.12	0.37	tr	0.36	tr	1.22	106.6
H ₂ O	19.29	22.31	14.76	13.55	14.57	13.67	13.02	13.36	16.11	19.7
Total	98.60	100.36	99.19	98.93	99.88	99.34	98.24	98.59		
Total Fe*	3.23	13.70	10.64	17.25	10.73	17.20	25.83	13.55	11.51	50.7
Trace elements (ppm)										
V	57	240	120	206	200	233	175	197	149	44.9
Cu	25	47	50	21	84	56	70	41	36.3	54.7
Zr	460	125	2000	3000	202	360	2500	940	1046	90.5
Ni	18	35	36	15	333	10	14	18	22.3	45.9
Co	13	18	22	9	14	5	2	11	10.3	56.7
Cr	60	236	75	181	73	nd	620	138	156	86.8
Zn	133	nd	281	147	nd	nd	nd	169	157	32.4

*Calculated as Fe₂O₃

Data of Tables III, IV and V show that an extensive removal of soluble components as alkalis and alkaline earths has occurred during weathering. Magnesium, calcium and sodium were depleted up to 90% by weight; loss of potassium was more limited (50-70%). Considering the absolute averages, the strong increase of alumina, ferric iron and water in soil is accompanied by an obvious concentration of some elements, like Ti, Zr, V, Cr, usually characterizing sesquioxide weathering products (see for example Short, 1961; Melfi and Levi, 1968; Sinclair, 1967; Oertel and Giles, 1967). Generally, there is no progressive gain or loss of elements from the base of the profile to the top as would be expected during continual weathering. Particularly local concentration of ferric or aluminium oxides which may be due to the original composition of the rock and/or to peculiar physico-chemical conditions of local weathering have produced fluctuations independently from its location in the profile. The presence of microenvironmental conditions responsible for the formation of various types of soil may be shown by considering the behaviour of titania. In profiles *A* and *B* titania exhibits definite mobility relative to alumina (Table V) while the contrary occurs in the profile *C*. Provided titanium forms $\text{Ti}(\text{OH})_4$ when it is released from magnetite, biotite and pyroxene of the parent granulites, and considering that Kovalenko and Nestorovich (1952) report this compound as soluble at pH below 5 while alumina is precipitated at value above 4 (profiles *A* and *B* have pH between 4 and 5), local movement of titanium relative to alumina is possible.

Table V — Weathering balance of the main elements within the various profiles

	Profile A			Profile B			Profile C		
	Fresh granulite	Residual soil	Gains and losses, %	Fresh granulite	Residual soil	Gains and losses, %	Fresh granulite	Residual soil	Gains and losses, %
SiO_2	56.13	38.05	—62	54.25	40.00	—60	51.61	35.88	—57
TiO_2	1.56	2.02	—27	0.81	0.60	—60	0.66	2.90	+173
Al_2O_3	15.94	28.31	—	17.10	31.87	—	17.97	28.87	—
Fe_2O_3	0.76	10.18	+651	2.10	4.87	+24	1.82	14.81	+400
FeO	9.66	1.21	—93	7.99	0.87	—94	9.19	0.67	—95
MnO	0.09	0.04	—78	0.13	0.03	—85	0.14	0.06	—71
MgO	2.66	0.57	—88	4.01	0.57	—92	4.98	0.40	—95
CaO	5.38	0.31	—97	7.24	0.32	—98	7.29	0.10	—99
Na_2O	3.40	0.32	—94	2.77	0.50	—90	3.24	0.09	—98
K_2O	3.24	2.16	—63	1.90	1.10	—69	1.29	0.51	—75
H_2O^+	0.23	16.04	+3865	0.62	17.72	+1424	0.65	15.03	+1335
Total loss		44%			47%			38%	

Variations in geochemical trends induced by weathering As was seen by the *C* per cent data reported in Tables III and IV, weathering produced an increased dispersion of almost all the elements (water and ferric iron behave of course contrarily even though can vary much more in granulites in consequence of local metamorphic conditions of O_2 and H_2O pressure). This implies that weathering must influence relationships between elements, which geochemical trends were influenced or established should be investigate. On the basis of the average content in rocks and soils, the geochemical balance for the

various elements can be schematized as follow:

$$\text{in weathering material} \left\{ \begin{array}{l} \text{Zr, Ti (strong), Cr, Zr, V (medium or low) enrichment;} \\ \text{Cu (strong), Mn, Co (medium or low) loss.} \end{array} \right.$$

Let us test both in fresh rocks and in soils the relationships between some ferromagnesian elements (chromium, zinc, vanadium and manganese) and iron (Fig. 3). These elements are commonly associated with iron in magmatic rocks (Raber *et al.*, 1963; Gruza, 1965) as well as in granulitic rocks (Sighinolfi, 1970 and 1971).

To test correlation grade between elements correlation coefficient r for some pairs of elements in fresh rocks and residual soil was calculated; the results are reported on the figures. As can be seen on Fig. 3, a general correlation ferromagnesian-iron in fresh rocks may be considered to exist. In soil, chromium, vanadium and zinc maintain or establish closer relationships with iron (limitation of these assertions for zinc are due to scarce number of Zn data in soil) whereas manganese seems vary independently from iron. In addition, as can be seen on Fig. 3 and as indicated by average contents, chromium, zinc and vanadium are concentrated and manganese impoverished in soil with respect to iron. The independence of Mn and Fe in the soil can be easily explained by considering that manganese requires higher oxidation condition and higher pH to precipitate than iron or if both elements form colloidal oxides during the first stage of weathering (in this case unlikely) they must be stable under different conditions (Krauskopf, 1957 and 1967, p. 268; Hem, 1960a and 1960b).

Particular oxidation conditions would also explain the concentration of vanadium and chromium in soil: contrary to Mn, the oxidized form, for example $(\text{VO}_3)^{2-}$ and $(\text{CrO}_4)^{2-}$, of these two elements are more soluble. Therefore limited oxidation conditions during the first stage of weathering can account for the results obtained for Mn, V and Cr in soil.

Fig. 4 shows relationships between Ni, Co and Cr, elements which normally show good correlations in any type of crystalline rock. The correlation Ni-Cr, fairly closed in granulites, disappears completely in soil, whereas Ni and Co increase their correlation in soil, although Co is clearly removed relative to Ni during alteration. Ni^{2+} and Co^{2+} are oxidized only under high Eh conditions so that they remain in solution. But there is a tendency for Ni to be retained in some silicate (see the behaviour of Ni in alteration of ultrabasic rocks) and this explains the partial removal of Co relative to Ni in soil.

Relationships between three typical hydrolized elements, Zr, Cr and Ti, are shown on Fig. 5; their mutual correlation increases markedly in altered materials, underlining the influence of some physico-chemical factor, such as ionic potential and possibly adsorption phenomena in establishing definite geochemical trends. Zirconium shows the strongest absolute rate of increase in concentration in soils: here its average content is more than four times that in granulites. This does not agree with the results of the isoalumina calculations, from which it would seem that loss of material during weathering should not exceed 50 per cent. Two explanations can be proposed:

a) Because the residual soil is produced by "mature" weathering (Haantjens and Bleeker, 1970) and under strong drainage conditions, a partial loss of alumina could be considered (Delvigne, 1965; Lelong, 1967; Hendricks and Whittig, 1968). This of course would cause an indirect enrichment of some less mobile elements such as Zr. At this point it must be remembered that geochemistry of zirconium in exogenic cycle is not well known.

Figure 3 — Relationships between Cr, Zn, V and MnO contents with the total Fe content, calculated as Fe_2O_3 , of both fresh granulite and residual soil derived from it

Figure 4 — Relationships between Cr and Co contents with the Ni content of both fresh granulite and residual soil derived from it

Figure 5 — Relationships between Cr and TiO₂ contents with the Zr content of both fresh granulite and residual soil derived from it

b) Owing to the great dispersion shown by Zr both in rocks and in soil, it may be possible that a bias was introduced during sample collection which influenced the average contents. It seems more plausible that the two factors acted together.

CONCLUSIONS 1) Tropical weathering of granulitic rocks under conditions of very strong drainage produced either gibbsitic or kaolinitic soil, as well as kaolinitic-gibbsitic soil. The transition from one soil type to another is abrupt and occurs in very limited areas. The variation in the chemical composition of horst-rocks and/or in the drainage conditions seems to account for the soil type variation.

2) Almost total disappearance of alkali and alkaline earths (up to 90%) and enrichment of hydrolisate elements characterize the residual soils formed. The abnormal enrichment of some elements, like Zr, suggests that alteration may have progressed not under isoalumina conditions but partial removal of Al may have occurred.

3) Weathering has influenced geochemical trends in soils, in particular the relationships between the ferromagnesians Cr, Zn, V, Mn and Fe. In soil, Mn is partially depleted and loses its correlation with Fe, whereas Cr, Zn and V maintain or increase the correlation with Fe.

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