CHARACTERISTICS OF SOME WEATHERING PRODUCTS OF CHROMITIC ULTRABASIC ROCKS IN BAHIA STATE, BRAZIL: NONTRONITES, CHLORITES AND CHROMIFEROUS TALC

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Abstract—The study concerns weathering products derived from chromite-rich dunites in the region of Campo-Formoso. In the zone where the weathered rock retains its initial structure, brown, pink and green colors predominate; they are closely related with the presence of weathering-produced iron and chrome silicates.

The climate of this area of moderate altitude is tropical with a rainfall of 880 mm.

About fifty samples have been collected and studied by chemical analysis, atomic absorption, direct reading spectrometry, X-ray diffraction, electron microscopy and Mossbauer spectrometry.

The most salient clay minerals are:

- 1. a pink chromiferous chlorite, containing about 8% of CrO₃ in the form of Cr⁶⁺;
- 2. bright green coloured chromiferous nontronite containing up to 11 % Cr₂O₃;
- 3. other minerals showing a much lower content of chromium: a 1 % Cr \mathcal{O}_3 talc, and a 1 % Cr \mathcal{O}_3 chrysotile. The main conclusion that can be drawn from this study is that high-Cr clay minerals can be found in the field.

INTRODUCTION

In the northwest of the state of Bahia (Brazil) near Campo-Formoso, there are several areas with weathering products up to 10 m in thickness derived from chromite-rich Precambrian dunites.

These rocks, worked by the FERBASA Mining Co., were described by many authors (Branner, 1910; Moraes-Rego, 1931; Mello, 1937; Paiva, 1942; Souza, 1942; Johnston and Souza, 1943; Guimaraes, 1956; Kegel, 1964; Griffon, 1964; Poesche, 1965; Mascarenhas, 1969).

The chromite bearing area is situated between 600 and 700 meters (a.s.l.). The climate is tropical with a mean annual rainfall of about 600 mm. Mean annual temperature is 27°C (max. 38°, min. 16°C). The vegetation is a thorny, xerophile savanna forest.

THE CHROMITE MINE OF CAMPO-FORMOSO

The dunite outcrops of the area of Campo-Formoso form an almost continuous line along a hill front where the rainfall exceeds the mean annual precipitation. In this way, the ultrabasic rock area is always wet, and that is the reason for the thickness of the weathering zone which cannot be correlated with the mean annual precipitation.

Description of the weathering zone

A continuous profile shows the following horizons:

- 1. An upper layer of non-chromitic coarse material carried down from the neighbouring hills, ranging from 4 to 6 meters thick.
- 2. Around 6 meters deep, the weathering material derived from the dunite begins, mostly with preserved struc-

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The hard, non-weathered bedrock is generally found at a depth ranging from 15 to 20 meters.

Usually the colors are brownish and reddish in the upper part of the weathering material; in the lower part the bluish, pink and greenish hues predominate.

Near the bed-rock the moisture content is very high due to infiltration of water.

The sampling

More than fifty samples of weathered rock with preserved structure have been collected and studied by chemical analysis, atomic absorption, direct reading spectrometry, X-ray diffraction, electron microscopy and Mössbauer spectrometry.

A dozen of the samples were pure clay minerals with a high amount of chromium and some nickel. The structure of some of them has been ascertained by means of Mössbauer spectrometry.

THE CLAY MINERALS OF CAMPO-FORMOSO

The larger part of the alteration material of the Campo-Formoso mine is made up of chlorites and montmorillonites; in some places talc can be found; chrysotile and kaolinite are rarely observed.

The chlorite minerals

Chlorites occur both as pinkish-violet or greenish masses. The first type is a high chrome-bearing variety, the second a nickeliferous iron-chlorite. The two minerals can be found associated in the same alteration material, but mostly mixed up with montmorillonite and chromite. Very pure samples, sometimes found in form of distinct tabular crystals, have been used for the analytic and structural determinations.

a) The pinkish-violet chlorite

This mineral occurs in the form of massive aggregates easily scratched with the nail; it shows the following characteristics:

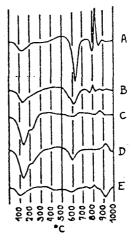
- 1. X-ray powder data, listed in Table 1, are similar to those obtained for chlorites by many authors (Brown, 1961; Brindley, 1951; Caillère and Hénin, 1963); there is no change in the powder diagram after glycerol treatment (Fig. 2). After heat treatment at 490°C an intensified 14 kX, and a 2.81 Å spacing can be observed, whilst most of the other spacings disappear.
- 2. Differential thermal curves show endothermic reactions at 630 and 790°C followed by a small exothermic peak at 800°C (Fig. 1).
- 3. The C.E.C. is 18 me/100 g, mostly saturated by Mg⁺⁺.
- 4. Mossbauer spectrometry shows that 19% of the iron exists in Fe³⁺ form in tetrahedral coordination, whilst 81% is situated in an unique position in the Fe⁺⁺ form.
- 5. The presence of Cr⁶⁺ has been confirmed (a) by the pink coloration produced with diphenyl carbazide after fusion with strontium metaborate, and (b) by X-ray electron spectroscopy (ESCA) in Professor Wey's laboratory. The latter test indicated more than 90% of the chromium to be in the hexavalent state. Because of the small ionic radius of Cr⁶⁺, it is assumed to be in tetrahedral coordination.

Table 1. Lattice spacings and estimated intensities in powder diagrams of high and low chromium substituted chlorites

	1	SCF 1		SCF 2	
	IIUM	LOV CHRON CHLOI	HIGH CHROMIUM CHLORITE		
h k l	1	d	I	đ	
001	30	14.4	41	14.4	
002	100	7.18	. 100	7.18	
003	100	4.795	100	4.80	
02; 11				4.63	
004	100	3.59	100	3.59	
005	100	2.87	30	2.87	
200	<1	2.645			
13 <u>1</u> , 202	<1	2.59	14	2.59	
132, 201	1	2.54	29	2.55	
$132, 20\overline{3}$	1	2.44	21	2.45	
202, 006	7	2.387	, 12	2.387	
$132, 20\overline{4}$	3	2.265	9	2.265	
007. 205	34	2.04	14	2.04	
135, 204	8	2.01	31	2.01	
$135, 20\overline{6}$	1	1.890	9	1.890	
136, 205	1	1.830	8	1.830	
008	6	1.788			
009	9	1.587			
137, 208	6	1.575	16	1.575	
060, 331, 331	2	1.536	29	1.536	
062, 331			9	1.502	
0, 0, 10	32	1.428	4	1.428	
139, 208	5	1.402	12	1.402	
400	i	1.315	6	1.330	
0, 0, 11	i	1.299	3	1.299	
, , , , ,	-		9	1.293	
	1	1.228	4	1.228	
0, 0, 12	21	1.190	4	1.190	

Fig. 1. Differential thermal curves

- (A) Low chromiferous chlorite (SCF 1)
- (B) High chromiferous chlorite (SCF 2)
- (C) Volkonskoite (SCF 4)
- (D) Chromiferous nontronite (SCF 5)
- (E) Low chromiferous talc (SCF 13)



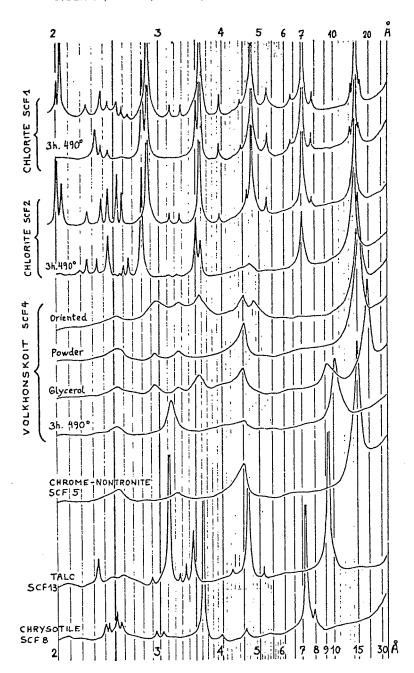


Fig. 2. X-ray diffraction diagrams of chrome substituted minerals from Campo-Formoso

6. With the chemical analysis (Table 2) and the preceding indications the following structure seems the most plausible:

$$\begin{array}{c} (\mathrm{Si}_{3.06}\,\mathrm{Cr^{6+}}_{0.46}\,\,\mathrm{Al}_{0.47}\,\mathrm{Fe^{+++}}_{0.01}) \\ (\mathrm{Mg}_{4.53}\,\mathrm{Al}_{0.74}\,\mathrm{Fe^{++}}_{0.06}\,\mathrm{Ni}_{0.03}) \\ \mathrm{O}_{10}(\mathrm{OH})_{8}\,\mathrm{M^{+}}_{0.21} \end{array}$$

The theoretical C.E.C. calculated from this structure (21 me/100 g) is near the experimental data (18 me/100 g).

This high Cr⁶⁺-bearing chlorite shows some similarities with the minerals studied and called kämmererite and kotschubeite by Lapham (1958).

b) The green, low chromium-substituted chlorite

This mineral can easily be found in the form of distinct tabular greenish transparent crystals of centimeter size.

The X-ray powder data are similar to those obtained with the preceding chlorite (Table 1) but after heat treatment most of the *hkl* spacings remain (Fig. 2). The differential thermal curve compared with the preceding shows similar but intensified endo- and exothermic reactions.

The structure established with the chemical analysis (Table 2)

$$\begin{array}{c} (Si_{3.40}\,Al_{0.49}\,Fe^{\,+\,+\,+}_{0.11}) \\ (Mg_{4.60}\,Al_{0.95}\,Fe^{\,+\,+}_{0.28}\,Ni_{0.07}\,Cr^{\,+\,+\,+}_{0.02}) \\ O_{10}(OH)_8\,M^{\,+}_{0.07} \end{array}$$

can be taken as possible: Mossbauer spectrometry shows that 28% of the iron is located in tetrahedral sites in the Fe⁺⁺⁺ form, whilst 72% exists in Fe⁺⁺ form in a unique position. The experimental C.E.C. (13 me/100 g) of this mineral is only produced by a grinding effect.

The montmorillonites

In the montmorillonitic weathering material with preserved structure the colors vary from reddish-brown to bright emerald green. The first hue can be correlated with iron-rich chromiferous nontronites, the second with high chrome-bearing volkonskoite varieties. Both minerals are frequently found in association with the preceding chlorites, with iron oxides and hydroxides and with chromite. Some very pure samples have been used for the structural characterization.

a) The chromiferous nontronites

The best typical samples of these minerals show dark brown-greenish colors, as for SCF 5.

The X-ray diagram (Fig. 2) of this sample is typical of montmorillonite; its differential thermal curve shows a small endothermic reaction at 610°C and an exothermic peak at 925°C (Fig. 1, C).

Table 2. Chemical analyses of chromiferous minerals of Campo-Formoso (in % after the sample was dried at 110°C).

- (A) Low chromiferous chlorite (SCF 1)
- (B) High chromiferous chlorite (SCF2)
- (C) Volkonskoite (SCF 4)
- (D) Chromiferous nontronite (SCF 5)
- (E) Low chromiferous talc (SCF 13)
- (F) Low chromiferous chrysotile (SCF 8)

	A	В	С	D	E	F
SiO ₂	36.0	34.4	49.3	45.2	61.4	39.9
Al ₂ O ₃	13.0	11.6	9.6	7.9	0.8	1.63
MgO	32.0	34.4	4.47	3.52	27.2	34.0
CaO	< 0.2	< 0.2	0.2	< 0.2	< 0.2	< 0.2
Fe ₂ O ₃	1.55	0.2	15.2	30.7	n.d.	0.2
FeO	3.55	0.8	n.d.	n.d.	3.0	9.35
CrO ₃	n.d.	8.61	n.d.	n.d.	n.d.	n.d.
Cr ₂ O ₃	0.2	n.d.	11.0	3.2	1.6	1.22
NiO	0.9	0.4	0.8	1.4	< 0.1	0.23
Mn ₃ O ₄	0.06	0.01	0.08	0.15	0.15	0.13
TiO ₂	0.07	< 0.05	0.16	0.20	0.05	0.15
Na ₂ O	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
K ₂ O	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
P_2O_5	0.10	0.13	0.10	0.07	0.12	0.11
+ H ₂ O	11.94	9.3	8.1	7.72	5.05	12.7
Σ	99.37	99.91	99.01	100.06	99.37	99.62
-H ₂ O	0.7	0.9	14.0	13.6	1.2	2.7
T me. %	13	18	81	87	16	2.3

The structure established with the chemical analysis (Table 2)

$$\begin{array}{l} \text{[(Si}_{3.32} \text{ Al}_{0.68}\text{) (Fe}^{+}_{1.69} ^{+}\text{C}{r}^{+}_{0.19} ^{+}\text{Mg}_{0.25} \text{ Ni}_{0.08}\text{)} \\ \text{O}_{10}\text{(OH)}_{2}\text{]} \text{M}^{+}_{0.37} \end{array}$$

can be taken as plausible: the theoretical C.E.C. calculated from this structure (87.6 me %) is in agreement with the experimental data (87 me %).

b) The volkonskoite

This beautiful bright emerald green mineral can easily be found in the Campo-Formoso mine. Its X-ray diagram (Fig. 2) differs only slightly from that of the preceding lower chrome substituted nontronites. The differential thermal curve (Fig. 1, D) differs from the preceding by the absence of the endothermic peak around 600°C, and an advanced exothermic reaction: 890°C. The C.E.C. is somewhat smaller than that of the lower chrome substituted nontronites: 80 me %. Mossbauer spectrometry shows that all the iron is located in ocathedral coordination in Fe⁺⁺⁺ form. With the chemical data (Table 2) and all the preceding indications the following structure can be suggested:

$$[(\mathrm{Si}_{3.54}\,\mathrm{Al}_{0.46})(\mathrm{Fe}_{0.82}^{++}\mathrm{Cr}_{0.62}^{++}\mathrm{Al}_{0.35}\,\mathrm{Mg}_{0.32}\,\mathrm{Ni}_{0.05})\,\mathrm{O}_{10}(\mathrm{OH})_2]\,\mathrm{M}_{0.35}^{+}$$

The theoretical C.E.C. calculated from this structure (86 me %) differs only slightly from the experimental determination.

This high chrome-bearing mineral can be compared with those described as "Wolkhonskoit" by Kersten (1938) and McConnell (1954). They can be located, with the precedent chromiferous nontronites, in a continuous sequence nontronite - volkonskoite in which the octahedral substitutions by chromium seem to be possible. This octahedral location of chromium was previously noted by Saynal et al. (1969).

The low chrome-substituted minerals: talc and chrysotile

In the deeper part of the dunite weathering zone talc and chrysotile occur, both mixed with chlorite. These minerals show only a low chromium content (Table 2). Pure samples (Fig. 2) have been used for the analytical and structural determinations.

The chrysotile, mostly in form of grey-bluish fibrous aggregates, with a low C.E.C. (2.25 me/100 g) is principally a ferrous mineral. The structure of the unit-cell-layer is the following:

$$[(\mathrm{Si}_{3.89}\mathrm{Al}_{0.09}\mathrm{Fe}_{0.02}^{+,+})(\mathrm{Mg}_{4.99}\mathrm{Fe}_{0.75}^{+,+}\mathrm{Al}_{0.1}\mathrm{Cr}_{0.09}^{+,+}\mathrm{Ni}_{0.02})\mathrm{O}_{10}(\mathrm{OH})_8]\mathrm{M}_{0.017}^+$$

The greenish or yellow semi-transparent talc with a C.E.C. of 16 me/ 100 g is also a ferrous mineral. The following structure seems the most plausible:

$$[(Si_{3.98}Al_{0.02})(Mg_{2.63}Fe_{0.15}^{+}Cr_{0.08}^{++}Al_{0.04})O_{10}(OH)_{2}]$$

The kaolins sometimes found associated with the montmorillonites do not show chromium in their structure.

INTERPRETATION AND CONCLUSIONS

Three points can be drawn from this study:

1) The clay minerals which form during the hydrothermal alteration and weathering of the chromite-rich ultrabasic rocks of Campo-Formoso can be classified according to their chromium content as follows:

volkonskoite - nontronite > chlorites > talc and chrysotile > kaolinites. Volkonskoites, often having a bright emerald green color, can contain up to 11% Cr₂O₃. Pinkish-violet chlorites can contain up to 8% CrO₃.

- 2) The Campo-Formoso mine shows in its altered part, an upper zone rich in minerals of the volkonskoite nontronite series, and a lower zone where the chlorites mixed with a small amount of talc and chrysotile become the dominant alteration product. In the upper zone, weathering predominates; nontronites and volkonskoites are formed in a humid and cation-saturated environment. This is an essential factor in the neoformation of all the montmorillonites (Gastuche and Herbillon, 1962; Millot, 1964; Segalen, 1965; Pédro and Lubin, 1968; Paquet, 1969; Sieffermann, 1969; Tardy, 1969). The lower chlorite, talc and chrysotile zone results from an hypogene alteration process. In the upper zone where the weathering is superimposed on the earlier hypogene alteration, the nontronites and volkonskoites appear as the most stable products in the supergene physico-chemical conditions.
 - 3) The bedrock with a density close to 3, shows chromium contents ranging from values

of 20 to 48% (expressed as Cr_2O_3). Weathered samples with preserved structures and densities varying between 1.2 and 2 derived from these same rocks, contain from 3 to 10% of chromium (expressed as Cr_2O_3).

It can be concluded that during the weathering of these chromium-rich rocks, under tropical climate, only 5 to 35% of the initial chromium content of the rocks are refixed in the neoformed products; 95 to 65% are finally removed.

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