

## A GOLDEN-COLORED, FERRI-NICKEL CHLORITIC MINERAL FROM MORRO DO NIQUEL, MINAS GERAIS, BRAZIL

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**Abstract**—A golden-colored, flaky mineral from Morro do Niquel, Minas Gerais, Brazil, gives an X-ray diffraction pattern of a *I1b* chlorite polytype, with basal spacing  $14.21 \pm 0.02 \text{ \AA}$  and  $b = 9.23 \text{ \AA}$ . Thermogravimetric analysis shows a progressive weight (water) loss up to  $500^\circ\text{C}$ , followed by a rapid weight loss corresponding to dehydroxylation of the interlayer material and a slower weight loss due to dehydroxylation of the 2:1 layer. The structural formula derived from the chemical analysis on the basis of  $\text{O}_{1.0}(\text{OH})_8$ , or total cation valence of +28, shows 5.3 total octahedral cations, i.e. probably 2.3 in the interlayers where normally 3 cations are found. This deficiency together with the appreciable loss of water below  $500^\circ\text{C}$  suggests a partially vermiculitized interlayer. A new method for deriving the interlayer composition gives  $R_{1.67}(\text{OH})_{4.08}(\text{H}_2\text{O})_{0.59}$ , and a ratio  $(\text{OH} + \text{H}_2\text{O})/R = 2.80$ , which approaches that of a dioctahedral interlayer and is consistent with a predominance of  $R^{3+}$  ions. The mineral may resemble the golden, vermiculitized biotite described by Walker and others.

### INTRODUCTION

The geology of the area around Morro do Niquel in the state of Minas Gerais, Brazil, and the genesis of the nickel-bearing silicate ores have been described by Langer (1967). The profile of the mountain shows three principal zones. The lowest zone is a fresh serpentinite which is dense and dark colored and is said to contain principally antigorite. An intermediate zone of strongly weathered and decomposed serpentinite is the mineralized zone. An upper leached zone, which is coarsely porous and consists largely of limonitic cellular quartz and other forms of silica, with occasional remains of the serpentinite, now forms the summit of the mountain. The intermediate zone is of commercial importance and is used extensively for the manufacture of nickel-iron.

The present study is concerned with the mineralogy of the deep brown, earthy material forming the mineralized zone. After crushing and dispersing this material in water, beautiful golden flakes of a chlorite-like mineral were readily separated. The unusual appearance of this material called for a closer examination.

### X-RAY AND THERMAL EXAMINATION

After dispersing the brown earthy material in water in a rotary blender for a few minutes, followed by ultrasonic vibration, two fractions were separated: (1) a coarse fraction which settled quickly, and (2) a much finer fraction which remained in suspension for long periods. Fraction (1) was separated into a coarser fraction (1A) and a somewhat finer fraction (1B), but mineralogically and chemically, these fractions are essentially the same.

### X-ray powder diffraction data

Fractions 1A and 1B, after removal of some minor impurities by hand-picking under the binocular microscope, were examined by X-ray powder diffraction using oriented samples on glass slides and samples lightly packed in shallow cavity holders. A sequence of basal reflections was obtained with  $d(001) = 14.21 \pm 0.02 \text{ \AA}$  and with intensities typical of those given by chlorites; in particular the  $00l$  diffractions,  $l = 1-5$ , were of strong and medium-strong intensity. The sequence was not that of a vermiculite, which normally shows a very strong first order and much weaker higher orders. The general reflections from the quasi-random powders in cavity holders were less distinct, but agreed mainly with the *I1b* polytype diffraction pattern in the classification of Bailey and Brown (1962). Since most, if not all, vermiculites have the *Ia* polytype structure, (see Shirozu and Bailey, 1966, p. 1136) this evidence also points towards chlorite, rather than vermiculite. The  $b$  parameter, based on the  $060$  reflection, is  $9.23 \text{ \AA}$ , a value which is consistent with a trioctahedral layer silicate.

The very fine fraction (2) was examined by allowing a few drops of the aqueous suspension to dry on a glass slide. X-ray powder diffraction again showed the basal reflections of chlorite, but the first reflection was very broad, whereas the others were sharp. Addition of water and of ethylene glycol expanded the first order spacing respectively to  $15.7$  and  $17.0 \text{ \AA}$ , and left the sharp first order chlorite reflection clearly visible. The expanding component is probably a smectite.

Thus the coarse and the fine fractions are dominantly chlorite, but a smectite also is present in

the fine fraction. The latter is a very small fraction of the whole material and has not been studied further.

#### Combined thermogravimetric and X-ray measurements

Samples of the 1A and 1B fractions of about 100 mg were contained in small platinum crucibles for weight measurements. Samples for X-ray measurements were dispersed in water and 'slurried' on to Vycor plates which could be heated to 1100°C without noticeable reaction with the samples. The samples were well oriented, and by careful handling were not seriously changed by the repeated handling necessary for the heating and diffraction study.

All four samples, two in crucibles and two on Vycor plates, were given identical heat treatment, namely 3-hr periods at temperature intervals about 40–60°C apart, followed by cooling in a desiccator. Weighings were repeated several times to check for rehydration in the atmosphere, which appeared to be small and insufficient to modify seriously the resulting thermogravimetric curves. X-ray data were obtained by placing the still-warm Vycor slides quickly into a closed chamber on the diffractometer together with fresh Drierite.

The X-ray and thermogravimetric data are summarized in Fig. 1, left-hand diagram, where they are compared with similar data for a white magnesian chlorite of composition  $(\text{Mg}_{4.48} \text{Fe}_{0.01} \text{Al}_{1.44}) (\text{Al}_{1.34} \text{Si}_{2.66}) \text{O}_{10.02} (\text{OH})_{7.98}$ , right-hand diagram, previously studied, (Brindley and Chang, 1974). The weight loss data are expressed as percentages of sample weight after drying at 110°C.

There are many similarities between the data for the golden-colored chlorite and for the magnesian chlorite, but two dissimilarities are worth mentioning. The golden chlorite shows a progressive weight loss up to 2.1 per cent at 500°C, whereas the magnesian chlorite shows a loss of no more than 0.3 per cent. Possibly the interlayer hydroxide sheets of the golden chlorite contain some molecular  $\text{H}_2\text{O}$  which is more easily lost than the water derived from hydroxyl ions. The main loss of hydroxyl water occurs sharply at about 500°C from both kinds of chlorite.

The basal spacing of the golden chlorite remains essentially constant at  $14.21 \pm 0.02 \text{ \AA}$  up to 500°C. At 544°C, after completion of the first stage of dehydroxylation, the 001 reflection increases markedly in intensity, the 002, 003, 004, 005 intensities decrease, and the basal spacing decreases to about 13.9 Å. The magnesian chlorite shows essentially the same intensity and spacing changes. However, above 700°C the basal spacing of the golden-colored chlorite rapidly diminishes, and also becomes highly irregular, because only the first order reflection persists. For this reason, the basal spacing curves above 700°C are shown by dashed lines in Fig. 1, left-hand diagram. In fact, the basal spacing of the finer-grained 1B fraction diminishes to about 9.5 Å, whereas the coarse-grained

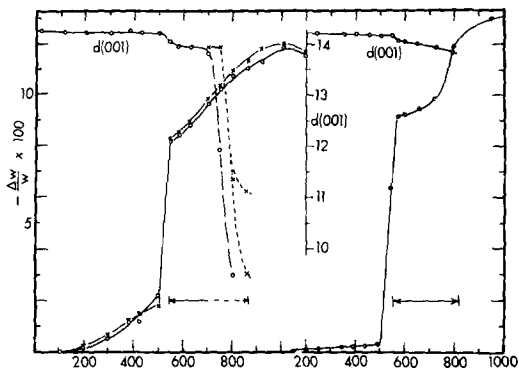


Fig. 1. Percentage weight loss with respect to weight of material dried at 110°C, plotted against temperature  $T$ °C. Also basal spacing  $d(001)$ , Å, plotted against temperature. Left-hand diagram—golden, chloritic mineral; circles and crosses correspond respectively to fractions 1A and 1B mentioned in the text. Right-hand diagram—a magnesian chlorite. Arrows indicate temperature ranges in which the modified chlorite structures following dehydroxylation of the interlayer materials are observed. Dashed lines indicate non-regular basal spacings.

1A fraction seems to show two spacings around 11.1 and 9.5 Å.

At higher temperatures, above 860°C for the finer material and above 920°C for the coarser material, recrystallization occurs with a spinel phase as the main product. After 5 hr at 1100°C, the spinel phase is sufficiently well crystallized so that the  $a$  parameter can be measured. The value obtained,  $a = 8.175 \text{ \AA}$ , is intermediate between the parameters of  $\text{MgAl}_2\text{O}_4$ ,  $a = 8.103 \text{ \AA}$ , and of  $\text{MgFe}_2\text{O}_4$ ,  $a = 8.383 \text{ \AA}$ . By assuming the iron to be wholly ferric and taking a linear variation of  $a$  with Fe(III) content, the estimated compositions of the spinel phase is  $\text{Mg}(\text{Al}_{1.48} \text{Fe}_{0.52})\text{O}_4$ . The coarse fraction of the golden chlorite also showed evidence for enstatite formation at 1100°C, but the data were not entirely conclusive.

#### CHEMICAL ANALYSIS AND STRUCTURAL FORMULA

Chemical analyses of samples 1A and 1B have been made using a Perkin Elmer atomic absorption spectrometer, model 403, on 40 mg samples dried at 110°C, then heated for 5 hr at 1100°C to obtain the ignition loss which is taken to be the  $\text{H}_2\text{O} +$  content of the samples. The FeO contents were determined separately on samples of about 400 mg by acid dissolution and potassium permanganate titration.\* The analytical results are given in Table 1.

#### Derivation of structural formulae by conventional procedures

Structural formulae of chlorites are usually derived on the basis of the ideal formula  $R_6T_4O_{10}(\text{OH})_8$  where  $R$  and  $T$  represent cations in octahedral and tetrahedral cation sites. There are three ways of using this general formula in conjunction with a chemical analysis, namely to assume (a) total cations = 10, (b) total anions = 18, (c) anion valence = cation valence = 28.

\* We are indebted to Mr. J. B. Bodkin, Chief Analyst, Mineral Constitution Laboratory for the FeO determinations.

Table 1. Chemical analyses and structural formulae of Samples 1A, 1B, of the golden-colored chlorite from Morro do Niquel, Minas Gerais, Brazil

	Weight %		Formulae, based on O = 14				
	1A	1B	1A		1B		
SiO <sub>2</sub>	34.50	33.60	Si	3.36	4.00	3.31	4.00
Al <sub>2</sub> O <sub>3</sub>	15.05	14.35	Al	0.64		0.69	
Fe <sub>2</sub> O <sub>3</sub>	12.05	14.40	Al	1.08 <sub>5</sub>	5.31 <sub>5</sub>	0.98	5.30
			Fe(III)	0.88		1.07	
FeO	3.07	2.17	Fe(II)	0.25		0.18	
MgO	18.12	17.75	Mg	2.63		2.61	
NiO	6.01	5.75	Ni	0.47		0.46	
CaO	0.09	0.10	Ca	0.01		0.01	
			K	0.00		0.01	
K <sub>2</sub> O	0.02	0.07					
			O	14.00		14.00	
Na <sub>2</sub> O	0.00	0.00	H <sub>2</sub> O	3.90		3.91	
H <sub>2</sub> O+*	12.01	11.86	O	10.10		10.09	
Total	100.92	100.05	OH	7.80		7.82	

\* Weight loss of material dried at 110° and heated 5 hr at 1100°C.

If the mineral approximates the ideal composition, it makes little difference which of these methods is used. The formula of the magnesian chlorite, already quoted, which was derived by method (b), illustrates such a case: total cations = 9.93, total anions = 18.00, total valence = 28.02.

Foster (1962) made an extensive study of chlorite structural formulae using 154 carefully selected chlorite analyses. Her calculations were based on method (c). In the present case, when method (c) is used, the results (see Table 1) give total octahedral cations 5.31<sub>5</sub> and 5.30, and H<sub>2</sub>O 3.90 and 3.91 respectively for the two samples. The H<sub>2</sub>O values are only slightly less than the ideal value of 4 corresponding to the anion composition O<sub>10</sub>(OH)<sub>8</sub>, which is equivalent to O<sub>14</sub>.4H<sub>2</sub>O, but the octahedral cations are markedly deficient compared with the ideal value of 6. Foster also found many chlorites deficient in octahedral cations; in fact 32 gave values less than 5.80 with the lowest value 5.46.

These low values of octahedral cations occur particularly in iron-rich chlorites. Foster considered that in the formation of these chlorites, Fe<sup>3+</sup> ions are incorporated as original constituents. This is contrary to the view that Fe<sup>3+</sup> ions arise from oxidation of initial Fe<sup>2+</sup> ions, with an accompanying loss of "water" by (OH)<sup>-</sup> becoming O<sup>2-</sup>. She considered that if Fe<sup>3+</sup> ions are present in octahedral positions in excess of the number required to balance Al replacements of Si in tetrahedral positions, then a charge balance is established by diminishing the number of R<sup>2+</sup> ions in octahedral sites. This balancing mechanism can be expressed as follows:

$$\frac{1}{2}[R^{3+}(\text{octahedral}) - R^{3+}(\text{tetrahedral})] = 6 - \sum R(\text{octahedral})$$

In the present case, for analysis 1A,  $\frac{1}{2}[R^{3+}(\text{octahedral}) - R^{3+}(\text{tetrahedral})] = \frac{1}{2}[1.965 - 0.64] = 0.66$ , and  $6 - \sum R(\text{octahedral}) = 6 - 5.31_5 = 0.68_5$ . The significance of this agreement, however, must not be over-exaggerated. In fact, it is an arithmetical neces-

sity, but it does provide a possible 'explanation' for the low total of octahedral cations in these chlorites. We can say that in the process of formation, the mineral becomes over-populated with R<sup>3+</sup> ions and the charge balance is taken care of by omitting R<sup>2+</sup> octahedral ions. In fact, the interlayer composition, taken from the results of Table 1, is (R<sup>2+</sup>, R<sup>3+</sup>)<sub>2.31</sub>(OH)<sub>6</sub> with 0.69 cation vacancies, and with a ratio (OH)/R = 2.60 which is intermediate between di- and trioctahedral compositions. These results show that this chlorite is considerably deficient in its interlayer composition.

#### Derivation of a structural formula for defective chlorites

Certain features of the thermal behavior of the chlorite studied here are not explained by the conventional formulae given in Table 1, namely the appreciable loss of water prior to the rapid dehydroxylation at 500°C. A low-temperature loss of water from some chlorites was recognized by Foster (1962, p. 45) as follows: "The temperatures at which H<sub>2</sub>O(-) is usually determined, 100° or 110°C, were fixed long before thermal analysis techniques were developed. Studies of chlorites by such techniques show that adsorbed water, H<sub>2</sub>O(-), continues to be given off to temperatures as high as 500°C." To the writers, this statement raises serious questions. Can adsorbed water be retained to 500°C? Should such water be considered as part of the structure of the mineral? In the case of vermiculite, molecular water entirely replaces the interlayer hydroxyls of chlorite. A partially vermiculitized chlorite may contain such water in place of hydroxyl anions. The chlorite under study has been shown to be defective in interlayer cations. It seems worth considering whether the water liberated up to 500°C may form part of the interlayer arrangement.

Let us consider that the 2:1 layers have a normal composition, R<sub>3</sub>T<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>, and the interlayers have a composition R<sub>p</sub>(OH)<sub>a</sub>(H<sub>2</sub>O)<sub>b</sub>, and that water lost above 500°C, high-temperature water, H<sub>2</sub>O<sub>H.T.</sub>, comes from hydroxyl units, and water lost between 110° and 500°C, low-temperature water, H<sub>2</sub>O<sub>L.T.</sub>, comes from

the defective interlayers. Then the overall composition is the following:

$$R_3T_4O_{11}(H_2O_{H.T.}) + R_pO_{a/2}(H_2O_{H.T.})_{a/2}(H_2O_{L.T.})_b \\ = R_{3+p}T_4O_{11+(a/2)}(H_2O_{H.T.})_{1+a/2}H_2O_{L.T.})_b$$

Three independent equations are required to determine  $p$ ,  $a$ , and  $b$ , and these are as follows, where the numerical values relate to the sample 1A in Table 1 and Figure 1:

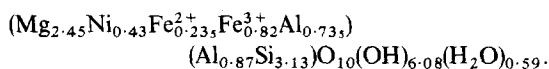
$$\frac{\text{Total cations}}{\text{oxygen}} = \frac{7+p}{11+(a/2)} = \frac{9.315}{14} = 0.665 \\ \text{(from Table 1)}$$

$$\frac{\text{Total water}}{\text{oxygen}} = \frac{1+(a/2)+b}{11+(a/2)} = \frac{3.90}{14} = 0.278 \\ \text{(from Table 1)}$$

$$\frac{\text{Total water}}{(H_2O)_{L.T.}} = \frac{1+(a/2)+b}{b} = \frac{12.0}{1.95} = 6.15 \\ \text{(from Figure 1)}$$

These equations give  $a = 4.08$ ,  $b = 0.59$ ,  $p = 1.67$ . The interlayer material has the composition  $R_{1.67}(OH)_{4.08}H_2O_{0.59}$  which is seriously deficient in cations as compared with the normal interlayer composition,  $R_3(OH)_6$ . In the present case, the ratio  $(OH + H_2O)/R = 4.67/1.67 = 2.80$ , which is closer to a dioctahedral composition, cf.  $Al(OH)_3$ , gibbsite, than a trioctahedral composition as in  $Mg(OH)_2$ , brucite.

The total composition according to this model is  $R_{4.67}T_4O_{10}(OH)_{6.08}(H_2O)_{0.59}$ . The structural formula evaluated with respect to a total cation valence of 26.08, in place of the usual value 28.0, is the following:



The distribution of the octahedral ions between the 2:1 layer and the interlayer can only be guessed, but if  $(Mg_{2.45}Al_{0.55})$  goes into the 2:1 layer, then  $(Ni_{0.43}Fe_{0.23}^{2+}, Fe_{0.82}^{3+}Al_{0.185})$  goes into the interlayer, which then contains  $1.00_5R^{3+}$  ions and  $0.66_5R^{2+}$  ions. The predominance of trivalent cations is consistent with the ratio  $(OH + H_2O)/R$  approaching 3 rather than 2.

#### Comparison of the two models

The conventional procedure for calculating the formula has given an interlayer composition with  $2.31(R^{2+}, R^{3+})$  cations,  $6(OH)$  ions and a ratio  $OH/R = 2.60$ . The deficiency of cations below the normal value of 3 is attributed to an over-population of  $R^{3+}$  ions compensated by vacant cation sites.

The second and new procedure, which takes account of the low-temperature loss of water by supposing that molecular water is present in the interlayers (vermiculitized interlayers), gives  $1.67(R^{2+}, R^{3+})$  cations,  $4.08(OH)$  ions,  $0.59 H_2O$  molecules, and a ratio  $(OH + H_2O)/R = 2.80$ .

Because this chlorite is clearly deficient in cations, there are no strong grounds for preferring a method of

calculation which assumes an ideal formula as regards the O, OH anions. The supposition of a partially hydrous interlayer seems preferable, and the resulting ratio  $(OH + H_2O)/R = 2.80$ , which approximates to a gibbsite-like situation, is probably a better description of the mineral.

#### DISCUSSION

The unusual color of the chloritic mineral under consideration raises the question whether similar minerals have been described previously. In *The System of Mineralogy of James Dwight Dana*, 6th Edition, (E. S. Dana, 1903), the section on chlorites mentions a variety of stilpnomelane called chalcodite, forming velvety coatings of brass-like appearance, and yellow varieties resembling mosaic gold, and gives a reference to work by Genth. The Genth Collection of Minerals in this university contained three samples marked chalcodite, which have indeed a golden, flaky appearance. Their X-ray powder patterns, however, agreed generally but not in detail with that of stilpnomelane (Eggleton and Bailey, 1965; Eggleton, 1972), and they were clearly not chlorites.

The appearance of the golden flakes of chlorite is reminiscent of a description given by Walker (1949) of glistening, golden-yellow flakes of biotites partially transformed towards vermiculite. Chemical analyses of the original biotite and of the altered weathered biotite indicated almost complete oxidation of initial FeO (21.23 per cent) to  $Fe_2O_3$  (18.88 per cent) considerable loss of  $K_2O$ , 7.17 per cent down to 3.66 per cent, an increase of  $H_2O$ , 3.03–6.70 per cent. Although Walker's vermiculitized biotite and our vermiculitized chlorite are not identical materials, nevertheless it is possible that both are minerals in a state of incomplete alteration towards vermiculite; in both cases the color may be a consequence of the incomplete conversion. There is an extensive literature on the weathering of biotites which is scarcely relevant to the chloritic mineral considered here, but it may be noted that Wilson (1966) described the development of an aluminian vermiculite-chlorite, with the interlayer positions 'occupied by islands of hydroxo-aquo-aluminum', and cleavage sections showing a pale yellowish-brown color and in a later study (Wilson, 1970) he refers to a pale brown or golden-yellow color.

In this study, the primary interest was the nature of the nickel-containing silicates at Morro do Niquel, and the occurrence there of a nickel-containing chlorite or chloritic mineral of unusual color had not previously been reported.

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