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Nickel-containing montmorillonites and chlorites from Brazil, with remarks on schuchardtite

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SUMMARY. Clay-like, hydrous nickel silicates from Niquelandia, Goias, Brazil, and from Jacupiranga, São Paulo, Brazil, are examined by X-ray diffraction, chemical analysis, and thermogravimetric methods. The nickel silicates from Niquelandia are ferric iron montmorillonites, with nickel in the octahedral positions and, to a lesser extent, in interlayer positions. The chemical compositions of samples dried at 110 °C average $(Mg_{0\cdot15}Ni_{0\cdot06}Ca_{0\cdot015}Na_{0\cdot005})$ $(Fe^{III}_{0\cdot92}Fe^{II}_{0\cdot025}Al_{0\cdot55}Mg_{0\cdot37}Ni_{0\cdot22})$ $(Si_{3\cdot88}Al_{0\cdot12})O_{10}(OH)_2(H_2O)_{0\cdot93}$. The layer charge originates largely in the octahedral sheet. The cation-exchange capacities average 107 me/100 g clay (110 °C). These minerals differ from nontronites, in which the layer charge originates mainly in the tetrahedral sheets.

The nickel silicates from Jacupiranga resemble chlorites, with a non-expanding basal spacing of 14·2–14·3 Å. The better crystalline forms give X-ray data in good agreement with a Ia polytype structure, which is consistent with their formation by low-temperature processes. Chemical formulae derived on the basis of $O_{10}(OH)_8$ give an average of 5·47 cations in octahedral positions. Thermogravimetric measurements show up to 4% H_2O lost between 110 and 500 °C. These results suggest a partial vermiculitization of the interlayer sheets. A new method of calculating a structural formula is developed that gives an interlayer composition of the form $R_{1\cdot75}(OH)_{3\cdot75}(H_2O)_{1\cdot14}$, with $(OH+H_2O)/R = 2\cdot80$, which approaches the ratio for a dioctahedral sheet structure.

A comparison of these defect chlorites with available data on schuchardtites shows many similarities; however, schuchardtite is not yet sufficiently well defined for the Jacupiranga chlorites to be given this name.

THE present study extends previous work on fine-grained hydrous nickel-containing silicates by Brindley and Pham Thi Hang (1973) in which serpentine-like and talc-like forms mainly were studied. In the present work, nickel-containing chlorites from Jacupiranga, in the state of São Paulo, Brazil, and nickel-containing montmorillonites from Niquelandia, in the state of Goias, Brazil, are examined. A comprehensive report by Pecora (1944) discussed the geology of the nickel silicate and associated oxide deposits in the region of Niquelandia (previously called São José do Tocantins) and mentioned (p. 275) nickel-bearing vermiculites in the Jacuba deposits of that area. The present samples also came from the Jacuba deposits, but appear to be principally montmorillonites. We have found no similarly detailed report of the Jacupiranga area, but a short description by Felicissimo (1965) refers to the formation of hydrous nickel silicates by lateritic alteration of ultrabasic rocks and the occurrence of nickel vermiculite.

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The question is raised whether the Jacupiranga minerals can be given the name 'schuchardtite', first suggested by Schrauf (1882). It will be shown that there are indeed close similarities but difficulties arise because of inadequate definition of the type material.

Experimental procedures

The minerals under consideration are fine-grained materials that can be examined only by techniques appropriate for clay minerals. Materials for study were selected from crushed samples by hand picking under a binocular microscope with magnifications of 15× to 30×. The minerals have characteristic colours ranging from yellowish-green through various shades of green and bluish-green. Selected materials were examined by X-ray powder diffraction using filtered Cu-$K\alpha$ radiation and usually a scanning speed of 1°(2θ)/min. Thin, oriented layers on glass slides, and quasi-randomly oriented samples in shallow cavities, 10×20×ca 0·3 mm dimensions, in glass slides were used.

Coarse impurities, mainly quartz, were removed by sedimentation after ultrasonic dispersion in water. Magnetic separation was useful in some cases in removing highly magnetic materials, chiefly magnetite and related minerals. Heavy-liquid separations were avoided because of possible alteration of the fine-grained minerals.

Samples that appeared to be monomineralic on the basis of their X-ray diffraction patterns were analysed chemically by using a Perkin-Elmer atomic absorption spectrometer, model 403, and the procedure described by Medlin, Suhr, and Bodkin (1968). Usually 40 mg samples were used. Ferrous iron was determined separately on 100 mg samples by $KMnO_4$ titration after acid dissolution. Thermogravimetric measurements, with parallel X-ray examination, were made by heating duplicate samples of about 100 mg in small platinum crucibles for periods of 2 hr at temperature intervals of about 50 °C. After each heating, the samples were cooled in a desiccator, one sample was used for weight measurements, and the other for X-ray examination. The swelling and shrinking properties of the minerals were examined using oriented samples exposed to water and ethylene glycol, and after various low-temperature heat-treatments.

Iron-nickel-montmorillonites from Niquelandia, State of Goias

Samples were collected from eight sites in the Jacuba deposits. The principal nickel-containing silicate is a montmorillonite, i.e. a dioctahedral, 2:1 layer silicate with characteristic swelling behaviour and with the layer charge originating largely in the octahedral sheets of the structure.

The separation of pure monomineralic material was difficult and satisfactory materials were obtained from only three of the samples collected. It was evident, however, that similar material was present in the other samples even though materials sufficiently pure to justify chemical analysis were not obtained.

X-ray diffractometer patterns showed basal 00*l* diffractions and *hk* diffraction bands similar to those given by other montmorillonites, but generally the patterns were rather poor. In many cases, only a strong first-order basal reflection was obtained, and only rarely were identifiable higher orders obtained. The 06 diffraction maximum indicated *b* parameters in the range 9·03–9·06 Å for the different samples examined. These values are somewhat larger than 8·95 Å obtained for the *b* parameter of Al, Mg-montmorillonites probably because Fe(III) ions occupy about half the octahedral cation positions (see chemical analyses given later, Table II).

The data in Table I show that the basal spacings under air-dry conditions, 14·4–14·9 Å, diminish to 12·6–13·6 Å when the samples are dried overnight at 110 °C, and to nearly 10 Å when dried at 250 °C overnight. The minerals expand readily in water to about 20 Å, even after drying at 250 °C, and in ethylene glycol they expand to 17·0 Å. These data, combined with the *b* parameter of about 9·05 Å and the chemical data given later, clearly establish these minerals as montmorillonites. In the materials examined we have not found a vermiculite, as mentioned by Pecora (1944), but since he gave no X-ray diffraction data it is possible that his vermiculite was in fact a nickel-containing montmorillonite.

TABLE I. *Basal spacings, in* Å, *of* Fe, Ni-*montmorillonites from Niquelandia, Goias, Brazil, after various treatments, b parameters,* Å, *and colours*

	N1	N2	N8		N1	N2	N8
Air-dry sample	14·4 Å	14·6 Å	14·9 Å	500 °C, overnight	—	—	$9{\cdot}5_5$Å
110 °C, overnight	12·6	13·4	13·6	Water vapour, 5 days	—	—	$9{\cdot}5_8$
Water added	20·4	19·5	19·8				
250 °C, overnight	10·2	10·2	10·0	Air dry, ethylene glycol added	17·0 Å	17·0 Å	17·0
Water added	20·4	18·9	19·7	*b*	9·06	9·05	9·04
Colour (Munsell)	35/6/4	35/7/4	35/7/4				

Chemical analyses, including exchangeable-cation determinations. Table II records the total chemical analyses and formulae of materials dried to constant weight at 110 °C. The values of H_2O+ are weight losses at 1000 °C. The exchangeable cations were determined by measuring the cations displaced by four treatments with excess 1*N* ammonium chloride solution. The K_2O contents, measured only on the total samples, were assumed to come from interlayer cations. The total amounts of CaO exceed slightly the exchangeable amounts; the differences may be due to incomplete replacement by ammonium ions, or to experimental error, but in any case the differences are small and do not affect the conclusions to be drawn. The exchange capacities, in me/100 g clay dried at 110 °C, lie in the range 99–117 and are normal for montmorillonites.

The formulae are calculated on the basis of $O_{10}(OH)_2$ per formula unit, i.e. a total cation valence, including exchangeable cations, of +22. The substitution of Si by Al, or other ions, in tetrahedral sites is small and the minerals are not beidellites. Since the layer charges of nontronites come mainly from tetrahedral substitutions, we prefer to describe these minerals as iron-nickel-montmorillonites.

The formula of sample N2, with 2·00 octahedral cations, agrees closely with the ideal montmorillonite-type formula, but in samples N1 and N8 the octahedral cations, respectively $2{\cdot}08_5$ and $2{\cdot}15_5$, exceed appreciably the ideal value of 2·00. Possibly the exchangeable cations Mg and Ni have not been wholly replaced by ammonium ions and this would lead to excess values for these ions in octahedral positions. However, we note that for sample N8, where the octahedral cations are given as $2{\cdot}15_5$, the exchange capacity is the highest for the three analysed samples.

TABLE II. *Chemical analyses and structural formulae of nickel-containing montmorillonites. Formulae calculated with respect to oxygen = 11. The exchangeable cations are included in the total analyses*

	N1		N2		N8			
	Total	Exch.	Total	Exch.	Total	Exch.		
SiO_2	55·00	—	55·00	—	53·00	—		
Al_2O_3	6·00	—	9·50	—	8·50	—		
Fe_2O_3	18·30	—	18·79	—	14·42	—		
FeO	n.d.	—	0·37	—	0·52	—		
MgO	5·50	1·23	3·00	1·31	6·00	1·66		
NiO	4·50	1·09	3·50	1·09	6·50	0·92		
CaO	0·30	0·21	0·30	0·22	0·20	0·14		
Na_2O	0·04	0·04	0·02	0·02	0·08	0·05		
K_2O	<0·02	<0·02	<0·02	<0·02	0·02	0·02		
H_2O+ 110° 1000°	7·61	—	8·14	—	8·60	—		
Total	97·27		98·64		97·84		Average	
Si (Tetrahedral)	3·94	4·00	3·88	4·00	3·83	4·00	3·88	4·00
Al (Tetrahedral)	0·06		0·12		0·17		0·12	
Al (Octahedral)	0·45	$2{\cdot}08_5$	0·67	2·00	0·55	$2{\cdot}15_5$	0·55	$2{\cdot}08_5$
Fe(III) (Octahedral)	$0{\cdot}98_5$		$0{\cdot}99_5$		$0{\cdot}78_5$		0·92	
Fe(II) (Octahedral)	—		0·02		0·03		$0{\cdot}02_5$	
Mg (Octahedral)	$0{\cdot}45_5$		0·18		$0{\cdot}46_5$		0·37	
Ni (Octahedral)	$0{\cdot}19_5$		$0{\cdot}13_5$		$0{\cdot}32_5$		0·22	
Mg (Interlayer)	0·13	0·22	0·14	0·22	0·18	0·25	0·15	0·23
Ni (Interlayer)	$0{\cdot}06_5$		0·06		$0{\cdot}05_5$		0·06	
Ca (Interlayer)	0·02		0·02		0·01		$0{\cdot}01_5$	
Na (Interlayer)	$0{\cdot}00_5$		0·00		$0{\cdot}00_5$		$0{\cdot}00_5$	
H_2O	0·81		0·92		1·07		0·93	
	$O_{10}(OH)_2$		$O_{10}(OH)_2$		$O_{10}(OH)_2$		$O_{10}(OH)_2$	
Interlayer charge	0·435		0·44		0·51		0·46	
Exchange capacity, me/100 g clay	99		106		117		107	

The average formula for the three analysed Niquelandia samples is given in Table II, with an interlayer charge +0·46, octahedral layer charge −0·37, octahedral cations $2{\cdot}08_5$, and tetrahedral layer charge −0·12.

Comparison with other data for nickel-montmorillonites. In his study of nickel minerals in the weathered serpentinite at Szklary, Lower Silesia, Ostrowicki (1965, pp. 41–5) described two nickel-containing montmorillonites with 1·75 and 1·42 wt. % NiO, which are much smaller amounts than in the Niquelandia samples. The formulae calculated by Ostrowicki show 2·16 and 2·22 cations in octahedral positions, and interlayer charges of 0·24 and 0·16 relative to a formula unit containing $O_{10}(OH)_2$. Possibly some of the cations placed in octahedral positions belong to interlayer positions. The layer charges would then arise from the octahedral sheets and the minerals would be montmorillonites rather than beidellites. The minerals examined by Ostrowicki contained very little iron, and the nickel ions amount to 0·11 and 0·09 per formula unit containing $O_{10}(OH)_2$.

Nickel-containing chlorites from Jacupiranga, State of São Paulo

Materials were collected from eleven sites in the mine Ribeirão do Joelho, J1–J11, and samples for study were selected as described above. The nickel silicate minerals from this locality resemble chlorite and vermiculite and many are intermediate forms. The similarity of the chlorite and vermiculite crystallizations is such that the intermediate forms are difficult to characterize.

Some samples give X-ray powder diffraction patterns that suggest chlorite-type structures (see fig. 1); they show basal spacings of 14·2–14·3 Å, *b* parameters near 9·21 Å, many *hkl* diffractions, and a sequence of basal intensities similar to those from chlorites. These minerals show no expansion with water and ethylene glycol. In all these respects, they appear to be chlorites. However, mild heat treatments up to 250 °C diminish the basal intensities considerably, the peaks become broadened and somewhat asymmetrical. The minerals are less stable than normal chlorites; some layers may be less stable than others so that low-temperature heating produces some dissimilarity between layers.

Other samples give diffraction patterns with a sequence of basal intensities, 001 very strong, 002 and 003 weak, 004 and 005 medium intensity, which point to vermiculite rather than to chlorite. The basal spacing is about 14·2–14·3 Å. In some cases, there is very little change in basal spacing and basal intensities with addition of water and ethylene glycol, and with heating up to 400 °C; the mineral begins to collapse to a spacing of about 10 Å at 500 °C. In other cases, the mineral expands to about 16 Å in ethylene glycol, to about 14·5 Å in water, and collapses to about 10 Å at around 400 °C. The vermiculitic character, therefore, is somewhat variable among these materials.

Weak reflections from spacings of about 28 Å have been observed from some samples, and these spacings may vary with addition of ethylene glycol and with mild heat treatments. These materials are probably quasi-regular interstratifications of chlorite and vermiculite layers. One such sample gave a weak third-order reflection from the long spacing, but generally only weak and rather broad first-order reflections were obtained so that the precise nature of the interstratifications was not clear. (The second-order reflection corresponds to the normal 14 Å reflection and is not informative as regards interstratification.)

X-ray diffraction data and polytype structure of the chlorite-like minerals. Fig. 1 shows diffraction patterns for two samples, J6 and J11, and for comparison the pattern of a magnesium chlorite from Omeo, Victoria, Australia (see Brindley and Chang, 1974), which has the IIb polytype structure. The results for the nickel-containing chlorites agree well with the data of Bailey and Brown (1962) for the Ia polytype structure. Other nickel-containing chlorites, for example J5 and J5A mentioned later, give very similar Ia-type patterns but also show weak reflections from a 28 Å spacing. Evidently the interstratification that produces the 28 Å spacing does not inhibit the Ia polytype arrangement.

Samples that resemble vermiculite, e.g. J3 and J8, also give diffraction patterns that indicate the Ia polytype structure. Shirozu and Bailey (1966, p. 1133) stated 'vermiculites . . . studied to date all have the same type of structural layer . . . designated Ia'. It appears that chlorite and vermiculite layers are sufficiently similar that they can be interstratified without seriously modifying the Ia polytype diffraction pattern.

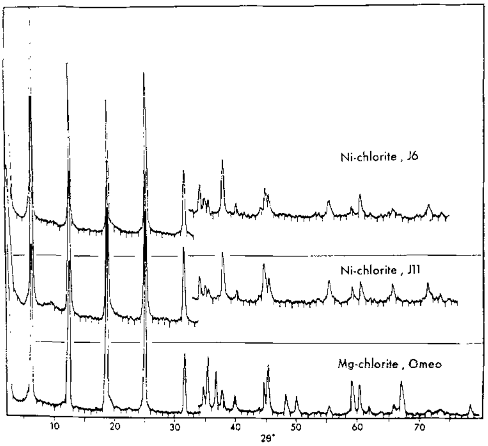

FIG. 1. X-ray powder diffraction patterns for two nickel chlorites, J6 and J11, from Jacupiranga, São Paulo, Brazil, and a magnesium chlorite from Omeo, Victoria, Australia. J6 and J11 have Ia polytype structure, the Omeo chlorite has IIb polytype structure. Filtered Cu-$K\alpha$ radiation, recorded at 1° (2θ)/min.

Table III lists the observed and calculated lattice spacings for the sample J11; the sample J6 gives practically identical data. The observed values were obtained from a pattern recorded at 0·5 °(2θ)/min and calibrated with respect to a silicon standard. The pattern was indexed by comparison with the data of Bailey and Brown (1962, p. 839). The unit cell parameters were determined initially by using the relations $d(001) = c \sin \beta$, $6d(060) = b$, $d(200) = (a/2) \sin \beta$, and β was obtained from $20l$, $20\bar{l}$ pairs with $l = 2, 4, 6$. Refined parameters were obtained using the least squares refinement computer programme of Evans, Appleman, and Handwerker (1963). The final values were: a 5·322, b 9·223, c 14·356 Å; β 97° 4′.

The occurrence of the Ia polytype structure is interesting in that Bailey and Brown (1962, p. 845) and Hayes (1970, p. 287) have concluded that this structure type is likely to form in geologic environments with lower temperature–pressure energy levels than are required for the more frequently observed IIb polytype structures. The Ia structure type is consistent with the formation of these hydrous nickel silicates by lateritic weathering processes.

Chemical analyses and structural formulae. Table IV lists these data for the samples J6, J11, J5, and J5A. The colours[1] of these samples are: J6, yellow green-yellow, 30/8/4; J11, yellowish green-yellow, 32·5/7/4; J5, greenish yellow, 27·5/8/4; J5A, yellowish green-yellow, 32·5/8/4. Table IV also gives data for three schuchardtites and one chlorite taken from the literature, namely from Schrauf (1882), Starkl (1883),

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[1] The colours of the ground powders are matched against those in the Munsell Book of Color, Munsell Color Company, Inc., Baltimore, MD. (1929). The numbers have the following significance: hue/lightness/chroma.

and Ostrowicki (1965). The formulae are calculated on the assumption that the minerals have the chlorite type of structure with anion composition $O_{10}(OH)_8$ and total cation valence +28 per formula unit. On this basis the water content ideally is 4 H_2O per formula unit. For the Jacupiranga samples the water contents range from 4·24–4·53; for the schuchardtites, the water contents are generally close to 4·00.

TABLE III. *X-ray powder diffraction data for nickel-containing chlorite from Jacupiranga, sample J11. $I_{obs.}$ = peak intensities*

d_{obs}	d_{calc}*	I_{obs}	*hkl*	d_{obs}	d_{calc}*	I_{obs}	*hkl*
14·25 Å	14·247 Å	100	001	1·888 Å	1·8848 Å	½	$20\bar{6}$
7·13	7·124	60	002	1·867	1·8620	½	027
4·75	4·749	65	003	1·7208	1·7201	½	151
4·575	4·584	4	110	1·6675	1·6667	5	206
3·560	3·5618	80	004	1·5691	1·5687	2	$20\bar{8}$
2·848	2·8494	32	005	1·5371	1·5371	5	060
2·639	2·6411	6	200	1·527	1·5279	1½	330
2·602?	2·5833	1½	131	1·503	1·5025	1	062
2·581	2·5821	3	$20\bar{2}$	1·4377	1·4381	1½	$20\bar{9}$
2·543	2·5414	1½	201	1·4250	1·4247	4	0.0·10
2·382	2·3826	12	202	1·3246	1·3244	4	139
2·259	2·2585	1½	$20\bar{4}$		1·3205		400
2·069	2·0680	1½	$20\bar{5}$	1·3167	—	1	
2·033	2·0353	8	007	1·2907	—	2	
2·006	2·0066	3½	204	1·1876	—	1	
	2·0061		$13\bar{5}$	1·1314	—	½	

* Calculated from cell parameters: *a* 5·322, *b* 9·223, *c* 14·356, *β* 97° 4′.

When the tetrahedral cation positions are filled, the remaining cations (other than Ca, Na, K) placed in octahedral positions are always considerably less than 6·00. In the Jacupiranga samples, the octahedral cations range 5·40–5·53, and for the schuchardtites 5·18–5·62.

When these results for the Jacupiranga samples are considered in relation to the evidence that they may have vermiculitic layers interstratified with chlorite layers, then the chemical data are seen to point in the same direction, and the validity of deriving formulae on the basis of a total cation valence of +28 becomes questionable.

Combined thermogravimetric and X-ray diffraction data. Fig. 2 shows the percentage weight loss of samples J6 and J11, calculated with respect to sample weight at 110 °C, plotted against temperature *T*, °C, for progressive 2 hr heatings. Fig. 2 also shows similar data for a magnesian chlorite from Omeo, Victoria, Australia, for which heating periods of 10 hr were used. The composition of this chlorite $(Si_{2\cdot66}Al_{1\cdot34})(Al_{1\cdot44}Fe_{0\cdot015}Mg_{4\cdot485})\,O_{10\cdot02}(OH)_{7\cdot98}$, agrees almost perfectly with the ideal chlorite formula. The basal spacings of the heated chlorites also are plotted in fig. 2, and the temperature ranges are shown within which the modified structures, formed after the main weight loss around 550 °C, are observed.

There are several striking differences as well as some similarities between the two sets of data in fig. 2. The steep rise in weight loss of the magnesian chlorite occurs at slightly lower temperatures, 500 to 560 °C, than the corresponding rise for the

TABLE IV. *Chemical analyses and structural formulae for nickel silicates from Jacupiranga, São Paulo, Brazil, three samples described as schuchardtites, and one additional nickeloan silicate*

	Jacupiranga samples				1	2	3	4
	J6	J11	J5	J5A				
SiO_2	35·0	34·58	36·0	36·0	33·79	33·89	38·47	37·48
Al_2O_3	14·55	17·01	12·4	13·6	15·47	14·88	11·28	12·68
Fe_2O_3	6·22	4·22	8·53	4·55	4·01	3·90	3·22	2·73
FeO	0·25	0·35	0·29	0·58	3·26	3·62	0·44	0·71
MgO	24·4	23·3	22·0	22·5	25·87	24·15	19·03	29·71
NiO	5·50	7·50	7·00	8·00	5·16	5·78	7·51	2·93
CaO	0·16	0·11	0·25	0·40	1·38	1·50	0·08	0·18
K_2O	tr.	tr.	0·02	0·06	—	—	0·07	0·02
Na_2O	tr.	tr.	0·04	0·12	—	—	0·14	0·01
H_2O+	13·41	13·92	12·90	13·32	11·54	12·37	11·12	10·96
H_2O-	—	—	—	—	—	—	8·41	2·14
Total	99·49	100·99	99·43	99·13	100·48	100·09	99·77	99·55
Si	3·40	3·33	3·53	3·55	3·23	3·30	3·97	3·55
Al	0·60	0·67	0·47	0·45	0·77	0·70	0·03	0·45
Al	1·06$_5$	1·26$_5$	0·96	1·12	0·97$_5$	1·00$_5$	1·34	0·96$_5$
Fe(III)	0·45$_5$	0·30$_5$	0·62	0·34	0·29	0·28$_5$	0·25	0·19$_5$
Fe(II)	0·02	0·03	0·02	0·05	0·26	0·29$_5$	0·04	0·05$_5$
Mg	3·54	3·35	3·22	3·30	3·69	3·51	2·93	4·19$_5$
Ni	0·43	0·58	0·55	0·63	0·40	0·45$_5$	0·62$_5$	0·22
Σ Oct	5·51	5·53	5·40	5·46	5·61$_5$	5·54$_5$	5·18$_5$	5·63
Ca	0·02	0·01	0·02	0·04	0·14	0·16	0·01	0·02
Na	—	—	0·01	0·02	—	—	0·03	—
K	—	—	—	0·01	—	—	0·01	—
O,OH	10,8	10,8	10,8	10,8	10·31, 7·38	10,8	10·16, 7·68	10·53, 6·94
H_2O	0·35	0·48	0·23	0·38	0	0·015	0	0

1. Schrauf, 1882 } Gläserndorf, Silesia; schuchardtite.
2. Starkl, 1883 }
3. } Ostrowicki, 1965; Szklary, Silesia { schuchardtite.
4. } { chlorite.

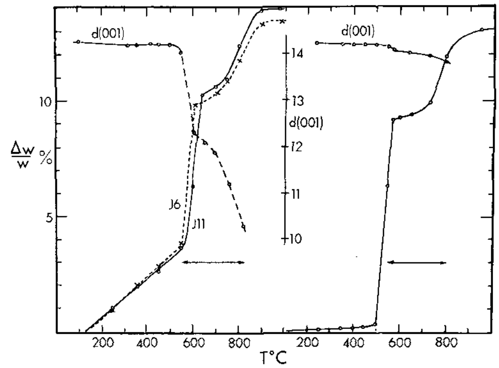

FIG. 2. Percentage weight loss and basal spacings d_{001}, Å, vs. temperature, for J6 and J11 nickel chlorites (left), and magnesium chlorite from Omeo (right). Horizontal arrows indicate ranges of temperature in which modified structures exist, prior to high-temperature recrystallization.

nickel-containing chlorites at 550 to 620 °C. This difference reflects the difference of heating conditions, 2 hr period for the nickel silicates, 10 hr periods for the magnesian silicate, and is of no basic significance for the discussions that follow.

The high-temperature weight losses from about 600 to 900 °C follow similar S-shaped curves for the two kinds of chlorites. They arise from the dehydroxylation of the 2:1 layers, which presumably are similar processes in the two kinds of minerals.

The low-temperature weight-loss data are strikingly dissimilar. The magnesian chlorite shows almost negligible weight loss up to 550 °C where dehydroxylation of the interlayer hydroxide material takes place rapidly. This behaviour is typical of normal well-crystallized chlorites. The nickel chlorites show a progressive weight loss from 110 ° to 550 °C, which could arise from hydrous vermiculitic interlayer material.

A second major difference concerns the basal spacings and intensities after various heatings. Above 550 °C, the magnesian chlorite gives the well-known modified form with greatly increased 001 intensity and little change of basal spacing, first shown and explained by Brindley and Ali (1950), and also a long spacing of about 27 Å, recently discussed by Brindley and Chang (1974). The nickel silicates above 600 °C show a rapid diminution of basal spacing and of 001 intensity, and no development of a long spacing. These results for the nickel silicates are consistent with vermiculitic layers, which diminish in spacing almost to 10 Å when heated from 500 to 800 °C. In fig. 2, the basal spacing curve for the nickel silicates above 500 °C is shown by a dashed line because only a first-order reflection is observed and the absence of higher orders probably indicates considerable disorder and precludes a more detailed study.

Tentative models for partially vermiculitized nickel chlorites

Homogeneous model. The simplest model is a homogeneous structure with normal 2:1 layers of composition $R_3T_4O_{10}(OH)_2$, where R and T signify cations respectively in octahedral and tetrahedral positions, and with defective hydrated interlayers of composition $R_p(OH)_a(H_2O)_b$. The high-temperature water loss (above about 500 °C) will be attributed to decomposition of hydroxyls and the low-temperature water loss (110 to 500 °C) to the $(H_2O)_b$ in the hydrated interlayers. The formula for the mineral can then be written:

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

where H.T. and L.T. signify high temperature and low temperature respectively. Three equations can be written from which p, a, and b can be determined. For the sample J6, the three equations are:

$$\text{(Total cations)/Oxygen} = (7+p)/(11+\tfrac{1}{2}a) = 9{\cdot}51/14 \text{ (from Table IV)}$$

$$\text{(Total water)/Oxygen} = (1+\tfrac{1}{2}a+b)/(11+\tfrac{1}{2}a) = 4{\cdot}36/14 \text{ (from Table IV)}$$

$$\text{(Total water)}/H_2O_{\mathrm{L.T.}} = (1+\tfrac{1}{2}a+b)/b = 13{\cdot}41/3{\cdot}8 \text{ (from curve J6, fig. 2)}$$

From these equations, we obtain $p = 1{\cdot}75$, $a = 3{\cdot}75$, $b = 1{\cdot}14$. The average interlayer composition, per formula unit, is $R_{1\cdot75}(OH)_{3\cdot75}(H_2O)_{1\cdot14}$. The interlayer cations are considerably less than the value 3 of the normal chlorite composition. The ratio

$(OH+H_2O)/R = 4{\cdot}89/1{\cdot}75 = 2{\cdot}80$. This value approximates to what would be expected for a dioctahedral sheet (cf. gibbsite, for which $OH/Al = 3{\cdot}0$) but the numbers of ions, $1{\cdot}75(R^{2+},R^{3+})$ and $4{\cdot}89(OH,H_2O)$, are such that the interlayer must be very defective.

This method of calculating a formula can be compared with those commonly employed by considering its application to a normal chlorite, for which $p = 3$, $a = 6$, $b = 0$. Then the first equation reduces to (Total cations)/oxygen $= (7+p)/(11+\frac{1}{2}a) = 10/14$ and therefore corresponds to the procedure in which the number of cations per formula unit is normalized with respect to 14 oxygens, or to a total cation valence of +28.

For the defective chlorite composition, the structural formula is obtained from the generalized composition:

$$R_3T_4O_{10}(OH)_2+R_{1\cdot75}(OH)_{3\cdot75}(H_2O)_{1\cdot14} = R_{4\cdot75}T_4O_{10}(OH)_{5\cdot75}(H_2O)_{1\cdot14}$$

by normalizing the cations to give a total cation valence of +25·75. The final formula becomes

$$(Si_{3\cdot13}Al_{0\cdot87})(Al_{0\cdot66}Fe^{3+}_{0\cdot42}Fe^{2+}_{0\cdot02}Mg_{3\cdot25}Ni_{0\cdot40})O_{10}(OH)_{5\cdot75}(H_2O)_{1\cdot14}.$$

Very similar results can be calculated for samples J11, J5, and J5A.

Inhomogeneous models. Many such models can be devised containing normal chlorite interlayers and hydrous interlayers. The *average* interlayer composition will be the composition calculated for the homogeneous case. No useful purpose is served by considering inhomogeneous models in detail, but one case can be considered briefly, namely a model with 50 % of hydroxide interlayers, $R_3(OH)_6$, and 50 % of hydrous layers, the composition of which is easily shown to be $R_{0\cdot50}(OH)_{1\cdot50}(H_2O)_{2\cdot28}$. In this formula, $R_{0\cdot50}$ is comparable to the value found in vermiculites, but in vermiculites R is co-ordinated only to water molecules. Since the number of cations is now too small to develop a brucite-like interlayer, a more likely arrangement can be written $[R_{0\cdot50}(OH)_{1\cdot50}(H_2O)_{1\cdot50}](H_2O)_{0\cdot78}$, i.e. octahedral co-ordination of OH and H_2O around each R cation, with additional water filling the interlayers.

From these considerations, we see that the chemical constitution of the Jacupiranga minerals and the manner in which the water is lost, shown in fig. 2, can be reconciled with a chlorite-like arrangement of 2:1 layers with interlayers we call 'vermiculitized' layers. The analysis shows that various proportions of normal hydroxide interlayers and vermiculitized interlayers will give an over-all composition consistent with the analytical data and also with the occasional observation of long spacing reflections.

A comparison of the Jacupiranga nickel chlorites with related minerals

A nickel chlorite from Barberton, S. Africa, studied by De Waal (1970), which he named nimite, has a IIb polytype structure and a composition in agreement with the normal chlorite formula. It contains 29·49 wt % NiO, and has 2·616 Ni ions in octahedral positions, with a total of 5·891 ions in these positions. The thermal behaviour of nimite is similar to that of other well-crystallized chlorites, with maintenance of the basal spacing up to temperatures of about 800 °C, where recrystallization occurs, and with great enhancement of the 001 intensity around 600 °C when dehydroxylation commences. The Jacupiranga nickel chlorites differ from nimite in the same respects as they differ from the magnesian chlorite from Omeo, Victoria.

A nickel-containing pennine from New Caledonia has been described by Montoya and Baur (1963). The X-ray powder data of this mineral indicate a IIb polytype structure. The mineral contains 3·2 wt. % NiO and the loss of weight on heating at 400 °C is 1·7 %, and from 400 to 900 °C an additional 11·1 %; these results indicate that the mineral studied was a normal chlorite.

Table IV compares the chemical analyses and formulae of the Jacupiranga chlorites with corresponding data for three schuchardtites analysed by Schrauf (1882), who first proposed this name, Starkl (1883), and Ostrowicki (1965); Gläserndorf (50° 36′ N., 17° 11′ E.) and Szklary are probably merely the German and Polish names for the same locality. There are obvious similarities between the chemical data for these materials and especially between the numbers of octahedrally co-ordinated cations. Ostrowicki gave X-ray powder diffraction data for three samples of schuchardtite and all are consistent with the Ia polytype structure. In a short discussion of schuchardtites, Spangenberg (1938) mentioned similarities of the X-ray powder patterns with those of chlorite and antigorite, but gave no details.

It appears that schuchardtites have more low-temperature water than normal chlorites. Thus, Starkl (1883) measured the loss of water up to 300 °C and found a loss at 300 °C that exceeded that at 100 °C by 3·79 %. Ostrowicki (1965, p. 66) recorded a loss of 4·30 % between 115 and 510 °C, and 11·12 % between 115 and 1000 °C. Spangenberg (1938) noted that material dried at 110 °C contains more than 2 H_2O that is gradually given off up to 300 °C, while the main thermal loss[1] of 2 H_2O occurs between 400 and 550 °C.

The final column of Table IV gives data by Ostrowicki for a nickel-containing chlorite, also from Szklary, which gave a IIb diffraction pattern and a considerable (about 2 %) weight loss between normal temperatures and 100 °C. The octahedral cation number, 5·63, is the highest in Table IV. This sample, therefore, may not be quite comparable with the others presented in Table IV.

Schneider (1970) described a nickel chlorite from the Granulitgebirge, Saxony, which contains 1·11 wt % NiO, or 0·08 Ni ions per $O_{10}(OH)_8$. He remarks that 'nickel chlorites' from this region, previously described by Jubelt, are mainly nickel-containing vermiculites and interstratified vermiculite-chlorites, and that only one out of about 50 samples was a pure chlorite. Schneider gives a weight-loss vs temperature curve for a vermiculite-chlorite that is rather similar to the curves given here for the Jacupiranga minerals.

Concluding remarks

We conclude that the data for the Jacupiranga samples are very similar to the data of Schrauf, Starkl, and Ostrowicki for schuchardtites. The similarity covers the chemical analyses and formulae, the thermogravimetric data particularly as regards the loss of water up to about 500 °C, and the Ia polytype structure. The present study considers particularly the number of octahedral cations and water contents. The data

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[1] Spangenberg does not explain exactly the meaning of his description, but presumably these amounts of water correspond to the usual formula involving $O_{10}(OH)_8$.

are shown to be consistent with the presence of vermiculite-like, or vermiculitized layers and this conclusion is supported by X-ray evidence showing the presence of long spacings near 28 Å in some samples, and the structural deterioration of the minerals at temperatures up to around 300 °C.

The present conclusions are indeed similar to those of Ostrowicki (1965, p. 91) who considered that schuchardtite is nearer to a vermiculite than a chlorite. In an extended summary in English he expressed his conclusion as follows: 'Between minerals from these groups there exist transitional forms of various degrees of alteration from clinochlore through talcochlorite to vermiculite (schuchardtite), which presumably at Szklary is not a final product of weathering'. We agree especially with the statement that these minerals may be 'transitional forms'.

We hesitate to label the Jacupiranga minerals as schuchardtites mainly because the type material was insufficiently defined. However, since these minerals appear to be in some way intermediate between chlorite and vermiculite, either by interlayering or by defective compositions, there is a question whether a particular name is justified. The situation might be clarified if samples from the type locality could be obtained for detailed study.

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