COMPOSITIONAL AND STRUCTURAL VARIATIONS IN GARNIERITES

G. SPRINGER

Falconbridge Metallurgical Laboratories, Thornhill, Ontario, Canada L3T 4A8

Abstract

More than thirty samples of magnesium and nickel hydro-silicates from the mineral collection of the Royal Ontario Museum have been examined microscopically, by x-ray diffraction and electron probe microanalysis. The aim of the study was to establish the compositional range of garnierite and its relation to minerals such as pimelite, schuchard-tite, cerolite, nepoute, noumeite and others.

It was found that most of the specimens examined had x-ray diffraction patterns resembling those of serpentine, talc, sepiolite, or mixtures of these. Correspondingly, the compositions were variable with (Mg+Ni)/Si ratios ranging from 3/2 (serpentine) to 3/4 (talc) to 2/3 (sepiolite). Chlorite-type minerals were observed and a nickel-bearing vermiculite was also examined.

The results suggest that, from a macroscopic point of view, one term such as garnierite is adequate as a general name for these hydrosilicates as several species occur usually in an intimately mixed state. Nevertheless, the components of the mixtures can be identified. These are serpentine and its nickel end-member, talc and its nickel analogue willemseite, nickel-bearing sepiolite, nickel-bearing chlorite and nickel-bearing vermiculite. Amorphous and hydrated forms of these also seem to occur.

INTRODUCTION

Hydrous nickel silicates form conspicuous green minerals in many nickeliferous laterite and nickeliferous serpentine deposits. Commonly, the minerals are called garnierites, although it is well recognized that several different species are involved. Some of these species have been defined in the past and names such as genthite, pimelite, nepouite, noumeite, roettisite, connarite, revdanskite, cerolite, schuchardtite and others have been given. The early history of the nomenclature has been reviewed in detail by Pecora et al. (1949) and Faust (1966). Unfortunately many of the older definitions were made entirely on the basis of macroscopic appearance and bulk chemical composition and they are therefore not precise enough by present-day standards.

Applying modern x-ray diffraction techniques, Kato (1961) established that the garnierites from New Caledonia were mixtures of serpentine, talc and chlorite-type minerals. Hotz (1964)

came to a similar conclusion with regard to the nickel silicates from Riddle, Oregon. Very recently Brindley & Hang (1973) carried out a broad survey of many garnierites and concluded that they are usually serpentine-group minerals or talc-like minerals or mixtures of these. The talc-like minerals with basal spacings near 10 Å were considered to be talc monohydrates with the formula $[(Mg,Ni)_{a}Si_{4}O_{10}(OH)_{2}]\cdot H_{2}O$.

The present study is based on a wide variety of nickel hydrosilicate specimens. Extensive use has been made of the electron probe for the analytical determinations in the hope that intergrowth would be on a scale allowing analysis of individual minerals. The study includes vermiculitic and chloritic garnierites which have not been considered in great detail in earlier investigations.

EXPERIMENTAL PROCEDURE AND ANALYSES OF COMPARISON SAMPLES

The samples examined came from the mineral collection of the Royal Ontario Museum, Toronto. Two fragments were taken from each specimen. One was powdered for examination with a Guinier camera or a diffractometer. The other was imbedded in an epoxy resin (Araldite) and a polished thin section was prepared for microscopic and electron probe studies.

The electron probe measurements were carried out with a Cambridge Mark V instrument which has an x-ray take-off angle of 75° . The excitation voltage was 20 kv and the electron beam current at the specimen surface was about 10 na. The low current was chosen because it was found that some of the hydrous silicates appeared to decompose under an electron beam of higher intensity.

The elements detected were Mg, Si, Fe, Ni, and Al, and their $K\alpha$ radiations were measured. MgO, Fe₂SiO₄, a 84% Fe - 16% Ni alloy and Al₂O₃ served as standards. The measured intensity ratios were converted to weight percentages using a modification of the correction procedure described by Springer (1967).

To ascertain that the outlined procedure gave correct answers within the limits of accuracy of at least 2-5% relative to the amount present, a series of related silicates were analyzed. These

		lite	forsterite		talc		serpentines						
wt %	#GP1	Stoich.	#GP2	Stoich.	#15	Stoich.	#17	#18 ·	#21	#22	Stoich.		
Mg0 Fe0	70.9±.5	70.5	57.8±.5		29.8±.4 2.3±.1	31.9	42.0±.9 0.9±.1	43.7±.4 0.8±.1	43.6±.6 1.5±.1	41.7±.7 1.9±.1	43.6		
S 10 H ₂ 02	29.0±.9	29.6	43.6±.3	42.7	62.9±.4 4.8	63.4 4.8	42.2±.6 14.7	43.7±.8 11.3	44.0±.9 10.6	42.1±1.5 14.1	43.4 13.1		
	ŧ			a tor	mic propo	ortions	on basis	of 1 or 4	Si				
St	1.00	1.00	1.00	1.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00		
Mg+Fe H ₂ 0	2.04	2.00	1.96	1.00	2.95 1.04	3.00 1.00	6.00 4.64	6.02 3.44	6.02 3.18	6.06 4.44	6.00 4.00		

TABLE 1. ELECTRON PROBE ANALYSES OF COMPARISON MATERIALS*

#GP1, #GP2 synthetic fayalite, forsterite; #15 (ROM 362) talc, Frontenac Co., Ontario; #17 (ROM M19804) lizardite, Madoc Twp., Ontario; #18 (ROM M17371) climo-chrysotile, Deloro Twp., Ontario #21 (ROM M31388) climo-chrysotile, East Broughton Twp., Beauce Co., Quebec; #22 (ROM M28002) ortho-chrysotile, Havelock mine, Swaziland

*Alg03 less than 0.4%, NiO less than 0.2%, HgO by difference from 100%

included four serpentines, a talc specimen and synthetic forsterite and fayalite. The latter two samples were measured against MgO, pure Fe and SiO₂ standards. The measured average concentrations show a reasonably good agreement with stoichiometric compositions (Table 1). The results for water, determined by difference, are naturally affected by the errors in the concentrations of the other components and cannot be considered better than $\pm 2\%$ H₂O. However, within this error margin the water contents also show good agreement. It is notable that the measurements for talc and serpentine spread over a wider range than those for fayalite and forsterite. This indicates that the hydrosilicates are not quite homogeneous. Non-stoichiometry, possibly caused by undulations in the layer structures, may be called upon to explain the scatter, but sub-micron inclusions of amorphous magnesia or silica may also be responsible. The serpentine analyses will be discussed more fully in a forthcoming separate publication by F. J. Wicks, Royal Ontario Museum.

	1	TABLE 2. NICKEL HYDROSILICAT	ES EXAMINED IN THIS STUDY	
Number	Name, Locality	Macroscopic Features	Microscopic Features	Type of Diffraction Pattern
	nepouite, Thio New Caledonia	medium green, crudely hexagonal vermiculitic crystal up to 3mm across and up to 7 mm long	green to yellow-green fibrous crystal, colour-banded and fractured normal to fibres. n>1.55, Δn=0.020-0.040	serpentine (lizardite?)
#2 E 2943	<i>pimelite</i> Frankenstein, Silesia	apple green, massive with conchoidal fracture. Occurs in seams and lenses in weathered rusty brown ultramafic rock.	dark brown, almost opaque	poorly crystalline ser- pentine + poorly crystalline talc
#3 M 6456	pimelite Šaxony, Germany	olive green, very porous, soft with conchoidal fracture	yellowish brown, translucent;cobble- stone pattern of nearly isotropic grains surrounded by fibrous aggregates of highly birefringent material	
#4a 324	<i>garmierite</i> (blue fragment) New Caledonia	medium blue to very dark blue, thin veneer on fractures in specimen 4b	patchy relicts of limonite, veined and surrounded by flaky to fibrous yellowish brown material of low to very high birefringence	dite)
#4b 324	garmierite (green fragment) New Caledonia	medium to dark green, fine colloform aggregates with sub-conchoidal fracture	green to brownish green colloform aggre- gates, n>1.55, An=0.035-0.040	poorly crystalline ser- pentime
#5 M 12800	<i>garnierite</i> Noumea, New Caledonia	dark green, massive with conchoidal fracture; frac- tured and recemented with blue and pale rusty brown veneers on fractures	brownish yellow, translucent, poorly crystalline mass	serpentine (mainly chryso- tile) + talc
#6 E 1420	garnierite Noumea, N. Cal.	apple green, massive, hard with irregular fracture	brown, nearly opaque, dense wispy fi- brous aggregate, mod. to high biref.	sepiolite + minor serpentine + minor talc
#7 M 30328	<i>garmierite</i> Riddle, Oregon	medium green and rusty brown, massive to colloform, hard, with irregular fracture.	olive green botryoidal aggregates, n> 1.55, Δn=0.030-0.040 and patches of fine-grained clear serpentine intergrown with limonite	poorly crystalline ser-
#9 M 24363	garnierite Ufaley, Urals	white to very pale green, very porous, friable	aggregates of opaque grains in yellowish translucent matrix	talc + minor serpentine + quartz
#10 E 2964	<i>schuchardite</i> Frankenstein, Silesia	pale apple green, schistose to massive greasy, slightly porous	cream to light green polycrystalline material intergrown with almost opaque fibrous aggregates	chlorite + talc + quartz
#11 M 12094	schuchardite Frankenstein	apple green, massive to colloform showing both sli- ckensides and irregular fracture	vermicular aggregates in fine-grained matrix, n>1.55, Δn=0.010-0.020	poorly cryst. serpentine + poorly cryst. talc
#12 M 6469	aonnarite Rottis, Voigt- land, Germany	apple green, massive, soft, very porous fragments with conchoidal fracture enclosed in a darker green, massive garnierite with irregular fracture	few yellowish brown semi-translucent flakes with micaceous cleavage in cryp- tocrystalline matrix with low biref.	poorly cryst. serpentine + poorly cryst. talc + quartz
#13 M 15041	rev <i>lanski te</i> Revdansk, Urals	white to pale green and dark brown, schistose, hard, with slickened sides and an irregular fracture	greenish brown, weakly pleochroic fi- brous flakes in matrix of granular qtz.	poorly cryst. serpentine + antigorite + quartz
#14 M 6445	cerolite Chester Co., Penn.	pale buff, massive, soft, with conchoidal fracture	opaque	very poorly cryst. serpen-
#26 M 30386	sepiolite Riddle, Oregon	very pale green, slightly schistose, soft and flaky	light to dark brown, translucent	sepiolite
#27 M 21782	genthite Lancaster Co., Penn.	medium and dark green, thin colloform coating on massive chromite	light green colloform crust, n>1.55, An=0.008-0.010	poorly cryst. serpentine
	nickel silicate Riddle, Oregon (Hanna Mining Co)		foliated material of moderate (second order) birefringence intergrown with amphibole. Some portions amorphous dark brown to opaque aggregates of mi-	chlorite + amphibole. Hand- separated sample #8 mostly chlorite
#43 M 16496	<i>Ni-vermioulite</i> Webster, North Carolina	dark green to brownish green aggregate of fine micaceous flakes	dark brown to opaque aggregates of mi- caceous material, in part transparent with birefringence colours of lower third order	chlorite + talc

TABLE 2. NICKEL HYDROSILICATES EXAMINED IN THIS STUDY

GENERAL DESCRIPTION OF SAMPLES EXAMINED

Table 2 lists the specimens investigated and their names and localities as found on the museum labels. Many older species names appear and some of the samples came from the type localities of these minerals. However, because the older descriptions are too general it was uncertain that the specimens were representative of the original materials.

Brief notes on the macroscopic and microscopic appearances are provided in Table 2. As may be seen, many of the nickel hydrosilicates are bright apple green to greenish white, soft clay-like materials with a waxy luster and, indeed, similar terms can be found often in the original accounts. It was frequently mentioned that these silicates were translucent or even opaque and comparable observations were made on many of the samples in Table 2. Only in two cases was it possible to decide with some certainty that the specimens in Table 2 resembled those described previously by other authors. The two specimens were schuchardtite (#11) and genthite (#27). The latter was described as grape-like clusters coating chromite (Faust 1966), whilst the schuchardtite agrees with the description of Spangenberg (1938) who stated that it occurred as bent packets of sheets and as vermiculitic aggregates resembling distorted piles of coins.

The types of x-ray diffraction patterns obtained are marked in Table 2. Most common are serpentine and talc-like patterns, but sepiolite, chlorite and vermiculite patterns have also been recognized. The patterns from serpentine and talc-like minerals (7 and 10 Å basal reflections) have recently been discussed by Brindley & Hang (1973) and reference is made to their analysis. The patterns showing lines due to chlorite, vermiculite or sepiolite were found to be similar in their general appearance: mixtures of two or three species rather than pure substances were usually indicated; furthermore, diffraction lines were mostly diffuse, suggesting that the average crystalline size was very small or the structures very disordered. Both chlorite and vermiculite yield strong basal reflections at about 14 Å and the two were distinguished by heating to 600°C which reduces the 14 Å spacing of vermiculite but enhances the intensity of the chlorite reflection. Montmorillonites also have basal reflections at 14 Å but these increase to higher values on treatment with water or glycerol; no indication could be found of a mineral with such properties.

NICKEL HYDROSILICATES WITH SERPENTINE, TALC OR SEPIOLITE-TYPE STRUCTURES

Minerals of this group contain Mg and Si as major cations, with little Fe or Al. The electron probe analyses are listed in Table 3 and are plotted in the triangular Mg-(Fe+Ni)-Si diagram of Figure 1. This figure also contains information about the x-ray diffraction properties of these materials and their original names, and indicates the positions of the solid solution series extending between serpentine, talc and sepiolite and their corresponding nickel analogues.

Figure 1 and Table 3 reveal that all the measured compositions lie in the range bounded by the serpentine and the sepiolite series. Despite this large over-all scatter the compositional variations within one sample are mostly not much larger than expected from the statistics of x-ray counting. Note that for #7 and #13 where two phases were detected optically, two correspondingly different compositions were found by electron probe analysis.

The compositional findings corroborate the x-ray diffraction results which indicate that most nickel hydrosilicates are mixtures of talc-like and serpentine-like phases. Sepiolite can also occur in these associations. It is evident that specimens with a high Si/(Mg+Ni) ratio contain sepiolite, and that specimens with a low Si/(Mg+Ni) ratio mostly contain only serpentine whilst specimens with intermediate composi-

wt %	#1	#2	#3	#4a	#4b	#5	#6	#7	#7	#9	#11	#12	#13	#13	#14	#26	#27
S102	33.8	51.2	47.8	39.1	39.8	48.6	56.9	42.5	43.0	42.3	50.9	39.2	43.4	46.7	51.7	46.6	33.1
Fe0 ²	0.06	0.01	1.52	5.29	0.00	1.01	0.04	0.48	3.39	0.08	0.21	0.00	1.45	0.91	0.93	0.00	0.00
NIO	58.5	31.3	13.9	3.99	51.6	19.4	17.3	43.6	6.07	10.7	29.8	34.9	0.56	33.0	0.08	5.75	40.9
MgO	1.11	14.8	28.2	36.2	4.06	24.1	17.3	7.44	36.4	15.8	16.3	2.30	40.9	9.78	31.4	18.1	10.1
H_0	6.5	2.7	8.5	15.4	4.5	6.9	8.5	6.0	11.1	31.1	2.3	23.6	12.7	8.9	15.9	29.1	15.9
···2-					•	- ** -			n hacia	of / 5	4		-				
						atomic	propor	tions u	n basis	of 4 S							
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Fe		_	0.09	0.44	-	0.04	_	0.04	0.23	-	-	· -	0.12	0.07	0.07	0.00	
Ni	5.59	1.95	0.96	0.31	4.18	1.30	0.98	1.06	0.46	0.82	1.90	2.85	0.05	2.26		0.41	4.00
Mg	0.17	1.73	3.51	5.53	0.62	2.98	1.82	3.30	5.07	2.22	1.90	0.35	5.60	1.25	3.61	2.31	1.80
Mg+Fe+N		3.68	4.56	6.28	4.80	4.32	2.80	4.40	5.76	3.04	3.80	3.20	5.77	3.58	3.68	2.72	5.80
H_0	2.56	0.72	2.36	5.24	1.56	1.92	1.96	1.88	3.41	9.72	0.72	8.00	3.87	2.53	3.87	8.39	6.39
<u>Z</u> .																	

TABLE 3. ELECTRON PROBE ANALYSES OF GARNIERITES WITH SERPENTINE, TALC, OR SEPIOLITE-TYPE STRUCTURES*

*All Fe assumed to be ferrous. H20 by difference from 100%, excluding 0-0.9% Al203

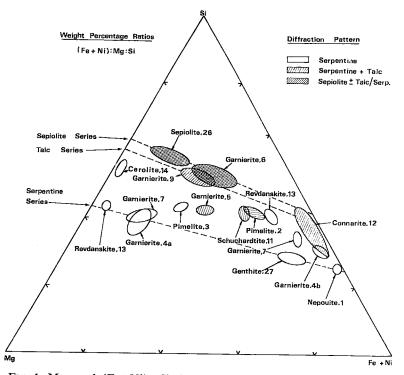


FIG. 1. Measured (Fe+Ni): Si: Mg ratios for garnierites with serpentine, talc, or sepiolite-type x-ray diffraction patterns.

tions consist of mixtures of talc and serpentine, according to x-ray results. In some intermediate cases, however, no such mixtures were noticeable. Possibly x-ray amorphous material was present to give the observed compositional data. Structural defects with unoccupied octahedral or tetrahedral positions as, for example, encountered in the mineral stevensite, may also play a part. It is hoped that a current systematic examination of garnierite from a particular deposit will produce evidence to decide on this question.

As the electron probe analyses are of volumes only a few micrometers in size, the various phases must be mixed at least on that scale. High-resolution electron micrographs by Uyeda *et al.* (1973) indicate that intermixing of 7- and 10 Å-type hydrosilicates occurs even on the scale of individual atomic layers.

Several authors (see Kato 1961) have noted a high water content of garnierites and Brindley & Hang (1973) have concluded that talc occurs in a hydrated form $[Mg_3Si_4O_{10}(OH)_2]$ +H₂O. The present analyses in Table 3 are not accurate enough to contribute much to a further clarification of this problem. However, they do not indicate water contents that are consistently higher than the stoichiometric $H_2O:SiO_2$ ratios of 1:4 for talc and 4:4 for serpentine, assuming that mixtures of the two minerals are present. Since the samples have been subjected to a high vacuum and to some heating during electron probe examination it is possible that more water has been extracted from the materials than by the heating to 110°C that is done for chemical analyses. It appears, therefore, that the monohydrate postulated by Brindley & Hang (1973) is not noticeable by electron probe methods.

Attention is drawn to the fact that sample #11, which was recognized by its optical appearance as the typical schuchardtite of Spangenberg (1938), belongs to the serpentine-talc group of garnierites both with respect to composition and diffraction properties; it is not a chlorite.

CHLORITIC NICKEL HYDROSILICATES

Chloritic nickel hydrosilicates clearly differ from the aforementioned group of garnierites in their diffraction characteristics and their composition, especially in their high alumina content, although it frequently is difficult to make a distinction on the basis of macroscopic appearance.

The first nickeliferous silicate which was generally presumed to belong to the chlorite group is schuchardtite. Material from Frankenstein, Silesia has been described in detail by Spangenberg (1938) and a sample from that deposit was available for the present examination (#10). Optically the material appeared fine-grained and poly-crystalline (Table 2) and the x-ray diffraction pattern (Table 2) indicated the presence of talc and quartz as well as chlorite. The sample was fairly uniform in composition and an average analysis is listed in Table 4. The analysis cannot be explained on the basis of either the talc or the chlorite/serpentine formula, but it can be concluded, in accordance with the diffraction results, that the sample is a sub-micron mixture of chlorite, talc and possibly quartz. This is analogous to the above-described garnierites which are mixtures of talc or sepiolite with serpentine.

TABLE 4. ELECTRON PROBE ANALYSES OF GARNIERITES CONTAINING MINERALS WITH

	#10	#33	← ────────────────────────────────────									
wt %			talc	. mixt	ures of	talc a	nd chlo	rite c	hlorite			
S10,	35.7	31.3	62.1	43.0	39.2	37.5	35.9	33.4	32.5	27.2		
A1203	8.86	18.3	-	4.53	10.4	9.49	7.09	8.03	15.3	17.9		
Fe0	3.12	5.63	1,99	3,60	4.12	4.55	7.81	10.5	3.19	11.5		
NiO	20.8	0.25	0.37	13.4	5.83	4.80	10.4	12.8	0.39	13.4		
Mg0	16.4	30.8	29.8	25.0	27.0	26.7	22.2	26.2	33.5	17.2		
H ₂ 0	15.1	13.8	5.78	10.5	13.5	17.0	16.7	9.12	15.2	12.8		
			a tomi c	propor	tions o	n basis	s of S1+	- <u>1</u> A1=4				
Si A1 IV A1 VI	3.49 0.51 0.51	2.97 1.03 1.03	4.00	3.76 0.24 0.24	3.46 0.54 0.54	3.48 0.52 0.52	3.59 0.41 0.41	3.50 0.50 0.50	3.13 0.87 0.87	2.88		
Fe Ni	0.26	0.45	0.11 0.02	0.26	0.30	0.36	0.66	0.93	0.26	1.0		
Mg Σ	2.39 4.78	4.36 5.86	2.86 2.99	3.27 4.71	3.55 4.80	3.70 4.94	3.31 5.21	4.10	4.81 5.97	2.73		
^H 2 ⁰	4.88	4.37	1.24	3.08	3.93	5.28	5.52	3.17	4.85	4.49		
Σ=Σ (Α	1VI+Fe	•N1+Mg)										

#10 Frankenstein, Silesia (schu	chardtite); #33 Riddle, Oregon
#43 Webster, North Carolina	#30 "nimite", Barberton, Transvaal
*All Fe assumed to be ferrous.	H ₂ 0 by difference from 100%.

A portion of a specimen (#33) from Riddle, Oregon, gave chlorite patterns with some additional lines due to amphibole and vermiculite. A hand-picked fraction consisting of flaky, greenish white material, showed only chlorite lines. Glycolation or heat treatment of this fraction did not produce changes in intensity or position of the 14 Å reflection and confusion with montmorillonite or vermiculite can therefore be excluded. Crystalline and amorphous portions could be distinguished under the microscope but electron probe analyses revealed no appreciable differences in composition between these parts. An average analysis is shown in Table 4 and indicates that the ratio (Mg+Fe+Ni+Al^{vi}): (Si+Al^{IV}) is 5.86:4 and therefore is close to that of chlorite (6:4).

A sample from Webster, North Carolina (#43), was originally labelled Ni-vermiculite (see Table 2). An apparently true nickeliferous vermiculite had previously been described from that locality by Ross & Shannon (1926) but the present samples, although soft and micaceous, showed x-ray diffraction patterns that indicated mixtures of chlorite and talc. Neither treatment with glycerol nor heating to 600°C affected the basal reflection at 14 Å. Electron probe analysis identified some portions as talc and others as chlorite; in both cases the nickel content was only 0.3%. Highly nickeliferous material (up to 10% Ni) was found to be optically opaque and according to the analyses listed in Table 4 seems to be a mixture of talc and chlorite.

A nickel-rich chlorite was analyzed for comparison. The sample came from Barberton, Transvaal and was supposed to contain pure nimite (de Waal 1970). As the analysis in Table 4 shows, there is close agreement with the composition of stoichiometric chlorite.

A nickel-rich septechlorite has recently been described by Maksimovic (1972). It is considered a nickel analogue of amesite, for which the name nimesite has been suggested. Unfortunately the detection of a 7 Å layer mineral in the presence of a chlorite is difficult by x-ray diffraction. Nevertheless the intensity ratios observed for the presently-studied samples were such that not more than traces of nimesite or related material can have been present.

VERMICULITIC NICKEL HYDROSILICATES

When examining the museum specimens of garnieritic minerals listed in Table 2, no clear indication could be found of hydrosilicates that are montmorillonitic or vermiculitic in structure. That such minerals exist however, is apparent from the literature. Faust (1966) established that the majority of his garnieritic materials consisted of pimelite, which he claimed to belong to the montmorillonite group. However, Slansky (1955) found that a pimelite from Bohemia was not montmorillonitic and his x-ray patterns suggest that it was a nickeliferous talc. The results reported earlier in this report support the contention that pimelite, even from the type locality, is not a montmorillonite.

Schneider (1970) reported that most of the nickel hydrosilicates in a Saxonian deposit were vermiculites. Four samples of this material were kindly provided by Dr. Schneider and are now in the Royal Ontario Museum Collection (ROM numbers M32842/5). They came from Obercallenberg, near Hohenstein-Ernstthal, District of

TABLE 5. ANALYSES OF VERMICULITES Obercallenberg(electron probe) #34, Kipiponi, Kenya #126 avg. #403-5 electron probe chem.t ^{5 10}2 35.2 38.1 38.8 35.7 A1 203 13.3 12.0 14.6 14.8 T102 1.21 1.2 Fe₂03 6.79 Fe0 0.51 5.23 Fe 3.95 5.07 NIO 7.09 2.39 0.15 MaO 21.4 26.0 24.2 25.0 CaO 0.74 0.83 0.09 н,0 15.0* 15.4* 13.4* 19.18 atomic proportions** 2.71 1.29 0.04 SI 2.77 2.92 2.85 1.15 1.08 AT VI. 0.12 --Ti Fe³⁺ Fe²⁺ Ni 0.07 0.07 0.29 0.09 0.40 0.39 0.15 0.24 0.45 0.15 0.01 Mq 2.11 2.40 2.47 2.52 Mgi Cai+Ki 0.40 0.48 0.06 0.07 0.02 H20 4.86 4.04 3.98 3,29

*H₂O by difference from 100%; #34 also contains 0.26% K₂O

**Si+Al^{IV}=4 Al^{VI}+Ni+Fe+Mg=3 with remainder of mono- and divalent ions in interlayers (Mg^{ℓ} , Ca^{ℓ} , K^{ℓ}). Fe²⁺/Fe³⁺ ratio adjusted to give a total of 11 oxygen anions.

+Chemical analysis by L.L. James, Falconbridge Metallurgical Labs.

Karl-Marx-Stadt, German Democratic Republic. The vermiculite material had been carefully removed from the soil-like weathering product of serpentinite. It had been dispersed in water, then sieved and dried at 80°C. The fraction 60-100 μ m, a micaceous olive to apple green powder, was available for examination (samples #403, 404, 405 and 126). Acicular particles of medium birefringence (up to lower second order) were visible in the polished thin section. Under the microscope the particles were colourless except for sample #126 where they were slightly greenish yellow. The x-ray diffraction patterns were of vermiculite, but in #405 additional lines due to amphibole were visible. Treatment with glycerol did not shift the 14 Å reflection to higher values, but heating to 600°C replaced it by a broad, low-intensity peak at 12 Å.

Samples #403, #404 and #405 had similar compositions with an average nickel content of 1.9% Ni. Sample #126 contained 5.2% Ni. In all cases, however, the composition was close to that of a vermiculite (see Table 5).

It has been assumed for the formulae in Table 5 that Ni occupies octahedral sites in the talc layers of the vermiculite structure rather than interlayer sites. The basis for this assumption is that treatment with 1N MgCl₂ for three weeks at 60-70°C led to only a minimal exchange of nickel for magnesium (1-3% of total nickel content). Commonly only the interlayer ions are exchangeable.

In order to establish the reliability of electron probe determinations for materials with a high, relatively loosely bound water content, the welldefined vermiculite from Kipiponi, Kenya, which has been described in some detail by Brydon & Turner (1972), was analyzed. As a chemical analysis given by the latter authors referred to completely dehydrated material it was repeated using a sample from the same locality; this same sample was subjected to the electron probe measurements. The agreement among the results summarized in Table 5 is not unreasonable considering that the material contained impurities, notably apatite, which make the wet chemical analyses somewhat uncertain.

Attention is drawn to the fact that the water content required to bring the analysis total to 100% is less than the ideal number of 4.5-5.5 H₂O molecules (referred to 4 octahedral cations). This indicates that materials with loosely bound water seem to release more of it during electron probe analysis than by heating to 110°C as required for chemical analysis. As mentioned previously, the serpentine- and talc-like garnierites also show this effect and therefore appear to belong to the same category of hydrous compounds.

Nomenclature

There seems to be no justification for applying special names to any of the mixed nickelmagnesium hydrosilicates; the term garnierite used by field geologists for greenish nickel-bearing hydrosilicates is adequate (Caillière 1936; Pecora *et al.* 1949). On the basis of the present study, garnierites can be defined more specifically as nickel-magnesium hydrosilicates, with or without alumina contents, having x-ray diffraction patterns typical for serpentine, talc, sepiolite, chlorite, vermiculite or mixtures of these.

Names for crystallographically and chemically well-defined end-members are undoubtedly in order. The nickel analogues of talc and chrysotile have been named willemseite (de Waal 1970) and pecoraite (Faust *et al.* 1969), respectively. Although Maksimovic (1973) has recently suggested that nepouite be redefined and this name be given to a mineral which he has identified as the nickel analogue of lizardite, de Waal (1970) had already proposed retaining nepouite as a general term for the nickel serpentines. However, many authors have regarded nepouite as a chlorite in the past (Spangenberg 1938; Winchell 1951; Phillips 1964) and in order to prevent confusion it may be advisable to avoid this name in future.

Even if all the nickel-rich analogues of the serpentine varieties had been recognized and named, a general name for a nickel end-member. Ni₃Si₂O₅(OH)₄ having a serpentine structure but for which structural variety cannot be specified would still be desirable. Thus, a given garnierite can often be identified as being very nickel-rich and having a serpentine structure, but determination of the exact varietal form is impossible because of low crystallinity or the presence of impurities. Specimens #1 and #27described above are cases in point. This new name would therefore designate the whole group of minerals comprising pecoraite, the nickel analogues of lizardite, and possibly antigorite, in the same way as serpentine is a general name covering chrysotile, lizardite and antigorite. The name nickel-serpentine had originally been suggested when part of this study was published for the first time (G. Springer, F. J. Wicks, 24th In-Montreal, ternational Geological Congress, 1972). However, it was realized subsequently that this name might be misunderstood to mean a nickeliferous serpentine with a predominant magnesia content and consequently, a more neutral term was chosen. The new name proposed to the IMA Commission on New Minerals and Mineral Names was disapproved because the Commission considered it unnecessary (personal communication, D. C. Harris, Canadian Representative).

In the Russian literature nickel-free mixtures of serpentine and talc are commonly called cerolites (kerolites). This term, therefore, has a similar general meaning as garnierite and, as Brindley & Hang (1973) point out, should not be used as a mineral name in a strict sense.

Maksimovic (1966, 1973) allocates the name B-kerolite to a hydrated form of talc which seems to be identical to the talc monohydrate of Brindley & Hang (1973). The nickel-rich analogue of this is called pimelite by Maksimovic and can be considered a hydrated form of willemseite. Since the specimens studied by the aforementioned authors were contaminated by 7 Å layer minerals and were poorly crystalline, it is not certain that the greater water content is not also due to contamination. The shift in the basal spacing of talc from 9.2 to 10 Å, which is usually observed for this kind of material and attributed to the effects of additional water molecules in the structure, can be interpreted alternatively as being caused by an extremely small particle size (Reynolds 1968). Hopefully

the discovery of well-crystallized samples will resolve these uncertainties.

Sepiolite in which magnesium is almost completely replaced by nickel has not yet been described in the literature but will undoubtedly be found.

A nickel-bearing chlorite with the ideal formula $Ni_3Si_2O_5(OH)_4$ has been named nimite by de Waal (1970) and it seems unnecessary to retain names like schuchardtite or nepouite.

Apart from the mention by Spangenberg (1938), an expandable, montmorillonitic nickel silicate has not yet been identified with certainty as far as the present author is aware. Unforunately, the name pimelite is very often associated with this type of substance and not only with the above-mentioned talc-type minerals. The nickel - bearing vermiculites described hitherto are chemically not sufficiently close to a pure nickel end-member to warrant introduction of a new name.

ACKNOWLEDGEMENTS

The close cooperation with the Royal Ontario Museum is gratefully acknowledged, but the author is solely responsible for all the data and interpretations present. Thanks are also due to management and staff of Falconbridge Metallurgical Laboratories for their support. Miss B. McFarland, Mr. C. Kozak and Mr. L. L. James deserve to be mentioned especially. Drs. E. G. Haldemann and A. R. Graham are thanked for valuable literature references.

References

- BRINDLEY, G. W. & PHAM THI HANG (1973): The nature of garnierites I. Clays Clay Minerals 21, 27-40.
- BRYDON, J. E. & TURNER, A. C. (1972): The nature of Kenya vermiculite and its aluminum hydroxide complexes. *Clays Clay Minerals* 20, 1-11.
- CAILLIÈRE, S. (1936): Contribution à l'étude des minéraux des serpentines. Bull. Soc. franc. Miner. Crist. 59, 307-308.
- DE WAAL, S. A. (1970): Willemseite, a nickel-rich talc. Amer. Mineral. 55, 31-42.
- _____ (1970): Nimite, a nickel-rich chlorite. Amer. Mineral. 55, 18-30.
- FAUST, G. T. (1966): The hydrous nickel-magnesium silicates — the garnierite group. Amer. Mineral. 51, 279-298.
- FAHEY, J. J., MASON, B. & DWORNIK, E. J. (1969): Pecoraite, Ni₈Si₄O₁₀(OH)₈, nickel analog of clinochrysotile, formed in the Wolf Creek Meteorite. Science 165, 59-60.
- Horz, P. E. (1964): Nickeliferous laterites in southwestern Oregon and northwestern California. *Econ. Geol.* 59, 355-396.
- KATO, T. (1961): A study of the so-called garnierite

from New Caledonia. Mineral. J. Japan 3, 107-121.

- MAKSIMOVIC, Z. (1966): β-kerolite-pimelite series from Goles Mountain, Yugoslavia. Proc. Internat. Clay Conf. Jerusalem, Israel.
 - (1972): Nimesite a new septechlorite from a bauxite deposit near Megara (Greece). Bull. Sci. Sect. A Yougosl. — 1972, 1066, 224-226.
 - dite-nepouite. Zapiski Vses. Mineralog. Obshch 102, 143-149 (Transl. by M. Fleischer, U.S. Geol. Survey, Washington).
- PECORA, W. T., HOBBS, S. W. & MURATA, K. J. (1949): Variations in garnierite from the nickel deposit near Riddle, Oregon. *Econ. Geol.* 44, 13-23.
- PHILIPS, W. R. (1964): A numerical system of classification for chlorites and septechlorites. *Mineral. Mag.* 33, 1114-1124.
- REYNOLDS, R. C. (1968): The effect of particle size on apparent lattice spacings. Acta Cryst. A24, 319-320.
- Ross, C. S. & SHANNON, E. V. (1926): Nickelifer-

ous vermiculite and serpentine from Webster, North Carolina. Amer. Mineral. 11, 90-93.

- SCHNEIDER, H. (1970): Ein Nickelchlorite aus den hydrosilikatischen Nickelerzen im Sächsischen Granulitgebirge. Ber. deutsch. Ges. geol. Wiss.— B—Miner. Lagerstaettenf. 15, 55-60.
- SLANSKY, E. (1955): A contribution to the knowledge of the Ni-hydrosilicates from Kremze in southern Bohemia, Univ. Carolina, Geol. 1, 1-28
- SPANGENBERG, K. (1938): Die wasserhaltigen Nickelsilikate. Zentralbl. Miner. Geol., Palaeont. Abt. A., 360-364. See also Naturwiss. 1938, 578-579.
- SPRINGER, G. (1967): Die Berechnung von Korrekturen fuer die quantitative Elektronenstrahl-Mikroanalyse. Fortschr. Mineral. 45, 103-124.
- UYEDA, N., PHAM THI HANG & BRINDLEY, G. W. (1973) The nature of garnierites — II. Clays Clay Minerals 21, 41-50.
- WINCHELL, A. W. & WINCHELL, H. (1951): Elements of Optical Mineralogy. Part II. John Wiley, New York.
- Manuscript received February 1974, emended June 1974.