

A NEW NICKELIFEROUS MAGNESIUM HYDROXIDE
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ABSTRACT

A new yellow-green nickeliferous magnesium (carbonate?) hydroxide is described from the Cedar Hill serpentinite quarry in southern Lancaster County, Pennsylvania. The ratio of Mg to Ni+Fe is 4 to 1. The x -ray pattern exhibits rhombohedral symmetry and corresponds to the patterns of synthetic nickel hydroxide (II, III) and pyroaurite. The minimal cell constants (hexagonal parameters) are $a=3.12 \text{ \AA}$ and $c=23.19 \text{ \AA}$ or, less commonly, 23.79 \AA . Based on a correspondence of x -ray reflections, unit cell size, and unit cell cation content with $\text{Ni}(\text{OH})_2 \cdot 1/4\text{NiOOH}$, the structure is tentatively considered to be composed of $1/4(\text{Ni}, \text{Fe}) \text{OOH}$ embedded within the laminae of a $\text{Mg}(\text{OH})_2$ rhombohedral lattice, the consequence of which is a c dimension five times that of brucite.

INTRODUCTION

During the summer of 1961, several trips were made to the Cedar Hill serpentinite quarry in southern Lancaster County, Pennsylvania to collect samples of an unknown yellow-green powdery coating which occurs on fractured serpentinite surfaces. During the following year, several x -ray patterns were made, but the material could not be identified from existing patterns in the ASTM file. At that time, a close resemblance was noted to the nickel hydroxide and brucite structures, but an intense low-angle reflection indicated a considerably larger unit cell. In 1963, H. H. Hess (pers. comm.) mentioned an unknown mineral from core samples at Mayaguez, Puerto Rico, for which he had an unidentified x -ray pattern. Upon comparison this pattern was found to be the same as that for the Pennsylvania material (Hess, 1964). Qualitative chemical tests for CO_3 , Ni and water on both samples indicated little CO_3 or Ni, but a considerable quantity of water.

Jambor and Boyle (1964) published mineralogical data for a natural occurrence of a nickel hydroxide mineral from British Columbia. Their x -ray pattern and cell size were very similar to the Pennsylvania material except for a slightly smaller c . This publication provided the impetus for further study of the mineral with considerably less Ni from Cedar Hill, Pennsylvania.

In 1965 ASTM x -ray diffraction data on samples from Langban were published (Smith, 1964) for the pyroaurite and sjögrenite groups (Neumann and Bergstol, Mineral Museum, Oslo, Norway) which match the x -ray patterns of the Pennsylvania samples. The structural, chemical, and optical properties of these Langban samples are taken from previously published data.

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In general, explanations of the mineralogical structure of both synthetic and natural compounds of the Mg-Fe-Ni-Co hydroxides and the carbonate-hydroxides (Table 1) have been approached from two viewpoints, although both have noted a structural relationship with brucite as a fundamental unit. Frondel (1941) proposed a "double cell structure" (doubled a and c dimensions) for naturally occurring rhombohedral and hexagonal variants based on the whole numbers of atoms which are necessary to fulfill the lattice requirements for the particular symmetry involved. In a sense, these might be considered brucite polytypes. On the other hand, Glemser and Einerhand (1950a,b) working with synthetic preparations of nickel hydroxides in varying oxidation states proposed a

TABLE 1. COMPARISON OF HYDROXIDES AND CARBONATE-HYDROXIDES

Name/Location	Formula	a Å	c Å	Crystal Symmetry	Reference
Brucite	Mg(OH) ₂	3.11-3.15	4.76-4.78	H	Donnay <i>et al.</i>
Tasmania	Ni(OH) ₂	~3.08	~4.6	H	Williams
Synthetic II, III	Ni(OH) ₂ · ½NiOOH	3.07	23.2	R	Glemser and Einerhand
Synthetic III γ	NiOOH · ¼NiOOH	2.81	8.0	H?	Glemser and Einerhand
Synthetic III α	NiOOH · ¼NiOOH	2.82	20.65	R	Glemser and Einerhand
B. C., Canada	?(Ni, Mg)(OH) ₂ · ¼NiOOH	3.07	22.74	R	Jambor and Boyle
Pa., USA	?Mg(OH) ₂ · ¼(Ni, Fe)OOH	3.118; 3.120	23.19; 23.79	R	
Pyroaurite	(3x)Mg ₆ Fe ₂ (OH) ₁₆ CO ₃ · 4H ₂ O	3.095 (6.19)	23.27 (46.54)	R	Fron del
Hydrotalcite	(3x)Mg ₆ Al ₂ (OH) ₁₆ CO ₃ · H ₂ O	3.065 (6.13)	23.07 (46.14)	R	Fron del
Stichtite	(3x)Mg ₆ Cr ₂ (OH) ₁₆ CO ₃ · 4H ₂ O	3.09 (6.18)	23.19 (46.38)	R	Fron del
Sjögrenite	Mg ₆ Fe ₂ (OH) ₁₆ CO ₃ · 4H ₂ O	3.10	15.57	H	Fron del
Brugnatellite	Mg ₆ Fe(OH) ₁₆ CO ₃ · 4H ₂ O	5.47	15.97	H	Fron del

non-stoichiometric stuffing of "layers" within a rhombohedral (or hexagonal) cell. In such a case, unit cell doubling would not necessarily be required to fulfill symmetry requirements. The x-ray powder patterns, unit cell dimensions, and densities of the hydroxides and carbonate-hydroxides are, in each case, very similar, although the chemical composition varies considerably. It seems logical that both reports are concerned with minor variants on the same structural scheme.

OCCURRENCE, HABIT AND OPTICAL PROPERTIES

The Cedar Hill serpentinite quarry, Lancaster County, Pennsylvania is located ½ mile east of Route 222 just north of the Pennsylvania-Maryland state line. The quarry lies near the northern contact of an elongate serpentinitized ultramafic pluton (Lapham, 1962; McKague, 1964; Lapham and McKague, 1964).

The hydroxide crystallizes in small yellowish-green to brownish-yellow

flakes with a habit similar to that of brucite. Usually the hexagonal crystal outlines cannot be distinguished and the material is a finely divided powder. It is found only in the weathering zone on open fractures and intimately associated with brucite, serpentine, magnesite, and less commonly with dolomite or deweylite. An hexagonal modification resembling sjögrenite rarely may be present, but was not identified with certainty. The origin of this suite of minerals (with the possible exception of brucite) has been described (Lapham, 1961) as the result of leaching of the serpentinite by ground water containing CO_2 , Mg, Si, and minor Fe, Ca and Ni. Another secondary nickeliferous mineral, nickeliferous deweylite (Lapham, 1961) is rarely present, but has not been found associated with the yellow-green hydroxide.

Because brucite and magnesite are intimately intermixed with the yellow-green hydroxide, and also because refractive indices appear to vary among fragments, measurement of the indices of refraction are not considered reliable. The maximum and minimum values obtained are 1.58 and 1.565 (optic sign not determined). Indices of refraction obtained by Frondel (1941) for pyroaurite and sjögrenite range between $\epsilon = 1.54$ and $\omega = 1.57$. The indices which he reported from the hexagonal sjögrenite were higher than from the rhombohedral pyroaurite.

CHEMICAL COMPOSITION

Initial qualitative tests established the presence of considerable water and a questionable amount of CO_3 and Ni. Powdered material effervesces slightly in HCl, but, because of the presence of admixed carbonates, CO_3 in the mineral structure is uncertain. A small amount could be present in view of its similarity to pyroaurite and of the availability of CO_3 . (See "Note Added In Press")

The first analysis (Table 2, col. 1) is a semi-quantitative spectrographic analysis which was obtained to determine the major and minor cations present. Approximately 0.10 grams were handpicked under a binocular microscope and about half this amount used for this analysis. The accuracy range given by Spectrochemical Laboratories, Inc., Pittsburgh, Pennsylvania is plus or minus two times the stated quantity. X-ray patterns of this sample showed the presence of mineral impurities estimated to be not more than 20% serpentine, 5–10% magnesite, and less than 5% dolomite. Brucite was not present in the sample used for chemical analysis.

The remaining portion of the handpicked sample was then analyzed by quantitative wet chemical analysis for Mg and Ni. Because of the small amount of material, the H_2O and CO_3 content could not be obtained. The major cations present in the powder are Mg, Ni, Si, and Fe. Because all of the silica results from admixed serpentine, a corresponding amount of

Mg was subtracted from analysis 2. Mg, present as dolomite, was subtracted in accordance with the amount of Ca (almost negligible) for stoichiometric dolomite. To correct for magnesite, 2.88% Mg was subtracted, corresponding to 7% magnesite estimated from the *x*-ray pattern. Fortunately, the amount of magnesite present could be seen to be between that of serpentine and dolomite whose amounts are known

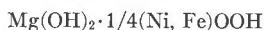
TABLE 2. CHEMICAL ANALYSES OF CEDAR HILL, PENNSYLVANIA, HYDROXIDE

	1	2	3	Atom. Ratio	M ² +M ³ =5	M ² +M ³ =8
Mg	50.00	16.68±2.00	8.31	0.34169	4.039	6.463
Ni	5.00	3.73±0.05	3.73	0.06355	0.752	1.203
Fe	1.00	1.00±2.00	1.00	0.01770	0.209	0.334
Si	5.00					
Al	0.05				5.000	8.000
Co	0.25					
Zn	0.15					
Ca	0.10					
Cr	0.10					
Mn	0.05					
Cu	0.001					

Explanation:

1. Semi-quantitative spectrographic analysis by Spectrochemical Laboratories, Inc., Pittsburgh, Pennsylvania; accuracy range=a factor of two.
2. Quantitative analysis for Ni and Mg by Spectrochemical Laboratories, Inc., Pittsburgh, Pennsylvania.
3. Subtraction from 2. of 8.37% Mg from mineral impurities based on 1. (See text.)

Probable Formula:



within relatively narrow limits, both from the semi-quantitative spectrographic and the *x*-ray analysis. A total of 8.37% Mg was subtracted from analysis 2 by these methods (Table 2, col. 3). Fe was not subtracted because of the possibility of Fe²⁺ substitution for Mg or of oxidized Fe³⁺ as in the carbonate-hydroxides. Unit cell cation contents have been calculated to correspond to both the Glemser and Einerhand (1950a) and Frondel (1941) unit cells (Table 2).

X-RAY DATA

Both powdery and crystallized specimens were handpicked for *x*-ray analysis. The patterns from eight different samples were sufficiently good to yield *d*-spacing and intensity values (Table 3, cols. 2, 3) and could be used to calculate unit cell dimensions (Fig. 1 and Table 3). No difference in the patterns was noted between the crystalline plates and the powder;

however, the darker green flakes have a consistently smaller c than yellow or tan specimens. Increasing Ni, or Ni+Fe, content might be responsible for the darker green. There is no detectable variation in a . The (hkl) indices were calculated on the basis of a hexagonal cell although only those reflections which satisfy rhombohedral symmetry requirements are present. The unit cell dimensions are expressed in terms of a hexagonal cell because direct single crystal evidence for a rhombohedral cell is lacking. The indices in Table 3 are expressed as one-half that of Frondel's doubled unit cell axes.

TABLE 3. COMPOSITE X-RAY PATTERNS FOR NICKEL (MAGNESIUM) HYDROXIDE

1		2				3		4		5		
I (est.)	d Å	I (est.)	d Å (meas.)	d Å (calc.)	(hkl)	I (est.)	d Å	I (est.)	d Å	I/I ₁	d Å	(hkl)
vs	7.7	100	7.75	7.73	003	100	7.87	10	7.59	100	7.77	006
s	3.85	55	3.86 (5)	3.865	006	50	3.96 (5)	6	3.79	80	3.89	0.0.12
w	2.63							$\frac{1}{2}$	2.77			
s	2.56	18	2.62 (3)	2.629	012	25	2.63 (5)	6	2.585	50	2.62	024
								$\frac{1}{2}$	2.41			
s	2.31	25	2.330	$\left\{ \begin{array}{l} 2.334 \\ 2.319 \end{array} \right\}$	$\left\{ \begin{array}{l} 015 \\ 0.0.10 \end{array} \right\}$	~ 20	2.36 (5)	5	2.296	50	2.33	0.2.10
vW	2.09							$\frac{1}{2}$	2.06			
s	2.03	25	1.975	1.976	018	25	1.99 (5)	4	1.946	50	1.97	0.2.6
		?	1.92	1.932	0.0.12							
w	1.75	4	1.758	1.759	1.0.10	5-15	~ 1.79	1	1.73	10	1.76	$\left\{ \begin{array}{l} 2.0.20 \\ 1.0.25 \end{array} \right\}$
w	1.66	4	1.658	1.661	0.1.11	4	1.685	1	1.64	10	1.66	0.2.22
s	1.53	10	1.559	$\left\{ \begin{array}{l} 1.559 \\ 1.556 \end{array} \right\}$	$\left\{ \begin{array}{l} 110 \\ 111 \end{array} \right\}$	5	1.560	3	1.536	20	1.55	$\left\{ \begin{array}{l} 220 \\ 3.0.15 \end{array} \right\}$
s	1.50	12	1.523	1.528	113	8	1.53 (4)	3	1.507	20	1.52	226
$a = 3.07$			$a = 3.198 \pm .01$			$a = 3.120$		$a = 3.07$			$a = 6.20$	
$c = 23.2$			$c = 23.190 \pm .01$			$c = 23.79$		$c = 22.74$			$c = 46.6$	

1. Ni(OH)₂· $\frac{1}{2}$ NiOOH (II, III) (Glemser and Einerhand, 1950).

2. Cedar Hill, Pennsylvania; avg. of 5.

3. Cedar Hill, Pennsylvania; avg. of 3, interleaved with brucite $a = 3.14$, $c = 4.74$ ($\times 5 = 23.70$).

4. British Columbia (Jambor and Boyle, 1964).

5. Pyroaurite, Langban (by Neumann and Bergstol, in Smith, 1964).

The Pennsylvania x-ray analysis, the data of Jambor and Boyle (1964), the new ASTM data of Neumann and Bergstol (Smith, 1964), and that of Glemser and Einerhand (1950a,b) are essentially in agreement both with regard to estimated intensities and to d-spacings. The cell size of the Pennsylvania material is, however, somewhat closer to the nickel hydroxide (II, III) of Glemser and Einerhand (1950b). Of the two c distances found in the Pennsylvania samples, the smaller cell dimension appears to be the more common (Table 3, col. 2, Fig. 1). Comparisons of c variations among the hydroxides are illustrated in Fig. 1. For purposes of comparing c expansion (or contraction) the c of the simple hexagonal

hydroxides of Ni and Mg possessing a brucite structure have been multiplied by 5. Unit cell dimensions of the pyroaurite and sjögrenite groups are compared in Table 1. These comparisons emphasize the closely related structures of these rather diverse compounds. Arrows between c dimensions (Fig. 1) illustrate the range found by Glemser and Einerhand (1950b) for nickel hydroxide, the c increasing with increasing oxygen content. In addition, extent of hydration and cation or anion group substitution would also be expected to influence the cell size.

Details of the x -ray patterns vary somewhat from specimen to specimen. A small angular line broadening appears to be characteristic, but is most pronounced in patterns from less well crystallized powder. In these,

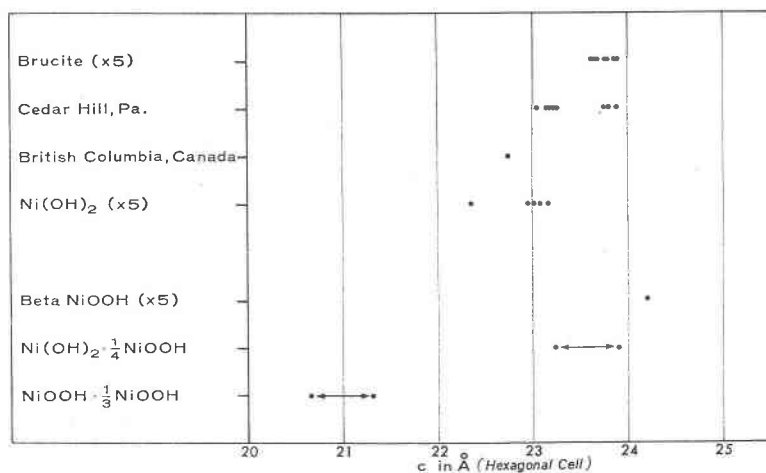


FIG. 1. Comparison of c unit cell dimensions.

also, the higher order reflections tend to be weak or absent. This type of lattice disorder (or "roughened" lattice planes: "aufgerauhte Netzebenen") was also noted by Glemser and Einerhand (1950b, p. 44) as characteristic of their nickel hydroxides. Among the minerals of the pyroaurite and sjögrenite groups, the intensities and symmetry from the x -ray reflections appear to correspond most closely to pyroaurite from Langban (Fron del, 1941, Fig. 1).

DISCUSSION

The Pennsylvania material is characterized by rhombohedral lattice reflections and a minimal unit cell (hexagonal parameters) of $a = 3.12 \text{ \AA}$ and a $c = 23.19 \text{ \AA}$ or 23.79 \AA . The a dimension remains constant. It is the same as that of brucite (unless a doubled cell is required) and corresponds to a 3.12 \AA separation of adjacent protons in the same plane (Elleman and

Williams, 1956). Color changes suggest that the smaller c may correlate with increased Ni, or Ni+Fe. The lack of larger and well-crystallized specimens, slight line broadening, and weak or absent high order reflections may be an indication of short range internal disorder, or of stacking faults. The major cation is Mg with a lesser amount of Ni and possibly a minor amount of Fe, although Fe could be incorporated in the mineral impurities present in the analyzed samples. The major anion group is OH, presumably with H₂O and possibly CO₃. The ratio of Mg to Ni+Fe is 4 to 1.

Rhombohedral compounds with approximately the same cell dimensions as the Pennsylvania specimens (Table 1) are Co(OH)₂·1/4CoOH, Ni(OH)₂·1/4NiOOH, the British Columbia nickel hydroxide (which contains only a minor amount of Mg, Jambor, personal communication), pyroaurite, hydrotalcite, and stichtite. The last two can be omitted from chemical identity by a lack of Al and Cr, respectively. The first three are chiefly Co or Ni, rather than Mg, compounds. Pyroaurite, a carbonate-hydroxide, contains about 6 times the amount of Fe present in the Pennsylvania samples. Thus, on a chemical basis, the nickeliferous magnesium (carbonate ?) hydroxide described here represents a different species. On the other hand, the same fundamental structural scheme is indicated for all these minerals, suggesting the possibility of at least limited cation substitutions of Mg, Ni, Fe, and, in addition, Co (Feitknecht, in Glemser and Einerhand, 1950b) and possible anion substitutions of O, (OH), and CO₃. Some structural scheme which satisfies these possibilities should be sought.

The data of Glemser and Einerhand (1950a,b) show that variations in degree of cation oxidation exist which do not readily conform to any stoichiometric rhombohedral arrangement. They were further able to correlate this oxidation with minor changes in c and with density variations. However, the actual size of the cell, about 23 Å for nickel hydroxide (II, III), varies with the degree of oxidation; for example, alpha NiOOH (NiOOH·1/3NiOOH) has a c of approximately 20.6 Å and gamma NiOOH a c of about 8 Å (Table 1). From calculated and theoretical density comparisons, they concluded that the NiOOH was embedded in a disorderly manner between Ni(OH)₂ laminae (Glemser and Einerhand, 1950b, p. 45), and would not yield lattice reflections upon x-ray examination. Working with the pyroaurite group, Frondel (1941) attacked the problem from a normal stoichiometric basis and calculated that a double cell ($a=6.2$ Å and $c=46.4$ Å) was necessary in order to place whole numbers of atoms on all the lattice points utilizing hexagonal coordinates for the rhombohedral cell. Thus, in part, the problem to be resolved is whether or not the cations lie on the lattice points of a rhombohedral cell. The work of Glemser and Einerhand (1950a,b), the presence of a trace of

Mg in the British Columbia nickel hydroxide (Jambor and Boyle, 1964), and the cation content of the Pennsylvania material indicate that at least limited non-stoichiometry is one solution to the problem of rhombohedral symmetry requirements. Evidence of slight disorder tends to support this conclusion. On the other hand, in his study of the carbonate-hydroxides Frondel (1941) did note the possibility of a defect structure (the substitution of Fe^{3+} for Mg^{2+}) as well as the probability of random stacking parallel to (0001) of either hexagonal types or of mixed rhombohedral and hexagonal types of layers. His single crystal data did not provide any confirmation of a doubled cell, but did provide evidence of random stacking arrangements (although his Rutherglen pyroaurite yielded a perfect single-crystal Laue photograph).

The ratio of 4 to 1 for Mg to Ni+Fe in the Pennsylvania samples supports the analytical data and unit cell proposed by Feitknecht (in Glemser and Einerhand, 1950a) and by Glemser and Einerhand (1950b). For example, the structural formula of nickel hydroxide (II,III) contains five cations, approximately one of which is oxidized depending on the exact amount of non-stoichiometric NiOOH . The 23 Å cell of nickel hydroxide (II, III) corresponds to five times the c of the $\text{Ni}(\text{OH})_2$, or brucite, structure. Similarly, there is a correspondence between the 20.6 Å c of $3\text{NiOOH}\cdot\text{NiOOH}$ (alpha type) and four times the c of alpha NiOOH , assuming the necessary lattice expansion resulting from oxidation. The same situation exists for the cobalt hydroxides. Assuming that the Ni and Fe in the Pennsylvania samples are oxidized to a 3+ valence, then they are in agreement with the cation ratios of the nickel and cobalt hydroxide structures. A consequence of this agreement would be that the c dimension of 23 Å is the result of $1/4(\text{Ni,Fe})\text{OOH}$ embedded in a disordered fashion within a rhombohedral $\text{Mg}(\text{OH})_2$ lattice. Because of the similarity in occurrence and x-ray data between these hydroxides and the carbonate-hydroxides of the pyroaurite group, a non-stoichiometric, oxidized layer should be considered in further investigations of the carbonate-hydroxides. Although CO_3 is not required for this structure, additional analyses for CO_3 in samples of the same type as the British Columbia and Pennsylvania minerals might provide additional evidence for a structural equivalence with the pyroaurite group.

Until complete chemical analyses are available, a name cannot be applied to the Pennsylvania material. It may be that all of these compounds can be considered as polytypes of the brucite structure with as yet undefined limits of cation and anion substitution. On the other hand, pyroaurite with an apparent minimal c of 23 Å is firmly established for both the group and mineral name. Consequently, for the time being, the Cedar Hill, Pennsylvania material might best be considered as a nickeliferous polytype of brucite.

ACKNOWLEDGMENTS

The author is especially grateful to John Jambor who supplied samples of the British Columbia material for comparison, translations of the Glemser and Einerhand articles, and suggestions regarding the possible inter-relationship of these minerals. Michael Fleischer kindly considered the problem of nomenclature and concurred that no new name should be applied at this time. The work was carried out at the Pennsylvania Geological Survey as part of a comprehensive project on the serpentinites of Pennsylvania.

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NOTE ADDED IN PRESS

Since this report was completed, two Cedar Hill specimens were submitted by Mr. Edward Carvalho, Wilmington, Del. for identification. Mr. Carvalho has kindly donated these specimens for the Pennsylvania Geological Survey mineral collection. One contains hexagonal, colorless single crystal plates of pyroaurite (x-ray identification) about 0.2 mm thick which effervesce strongly in 1.0 normal HCl acid. The other specimen contains a few hexagonal single crystals of the green Ni-hydroxide described here. These do not react to 1.0 normal HCl acid. Thus these samples support the contention that carbonate is not an essential constituent of the green Ni-hydroxide and that carbonate is not required for this structure.