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## On the new mineral theophrastite, a nickel hydroxide, from Unst, Shetland, Scotland

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**ABSTRACT.** The new mineral theophrastite,  $\text{Ni}(\text{OH})_2$ , from Unst, is Mg-bearing and occurs associated with a very poorly crystalline Ni-containing mixed hydroxide of the pyroaurite type and/or zaratite on chromitite. X-ray powder diffraction data show a shift in  $d$  spacing toward brucite compared with pure  $\text{Ni}(\text{OH})_2$ . Infrared, thermal, chemical, optical, and physical data are presented together with indexed powder data for fifteen lines ranging from  $d$  4.66 Å to 0.90 Å. The solid-solution series brucite-theophrastite is briefly discussed.

SEVEN Heddle specimens\* of chromitite from Hagdale Quarry, Unst, held in the Scottish Mineral Collection, are partially encrusted with 'emerald-nickel' and zaratite according to Heddle (1901). Macpherson and Livingstone (1974) demonstrated this material to be a mixture of nickel hydroxide,  $\text{Ni}(\text{OH})_2$ , and zaratite. Recent work on this assemblage indicates the nickel hydroxide to be Mg-bearing theophrastite, mixed on a sub-micron scale with a very poorly crystalline Ni-containing mixed-hydroxide of the pyroaurite type and/or zaratite.

The natural occurrence of nickel hydroxide was first reported by Williams (1960) although no mineral name was given to the compound. In late 1979 a submission was made by the above authors of this paper to the IMA, endeavouring to establish a mineral name for the compound  $(\text{Ni},\text{Mg})(\text{OH})_2$ . The material investigated came from Hagdale, Unst, and although associated with a nickel-

containing mixed-hydroxide or zaratite from which it could not be separated, a detailed investigation fully characterized the mixture. By submitting to the IMA a priority date was established for the Unst material, however, two months after that date another submission was received for pure  $\text{Ni}(\text{OH})_2$  from Greece, by Th. Marcopoulos and M. Economou. In the vote the Unst material and name were narrowly defeated in favour of the Greek  $\text{Ni}(\text{OH})_2$ , which is now known as theophrastite.† Difficulties arose in trying to establish a joint publication with the Greek authors and hence the Unst data are presented separately herewith under the name theophrastite.

On the chromitite surfaces two colour variants, though mineralogically similar, are present: the first is a bright emerald-green, gel-like, clear coating whereas the second is pale blue-green and 'opaque'. A single chromitite specimen invested with gel-like and 'opaque' theophrastite, lacks (according to the Museum register entry) detailed locality information and is simply labelled 'zaratite-Canada' (RSM No. 1890-114-1976). This specimen is almost identical to the one from Hagdale Quarry (and is possibly a duplicate) where the gel-like and 'opaque' material collectively cover an area of approximately 60 cm<sup>2</sup>.

The Hagdale specimens contain minor aragonite, chlorite, and goethite together with scarce citron-yellow reevesite and honessite (Bish and Livingstone, 1981) and very rare pentlandite and heazlewoodite.

\* RSM Nos. 303.2,4,5,6; 338.109 and 493.b1 and b2.

† Now published: Marcopoulos and Economou (1981).



FIG. 1. Scanning electron micrograph showing plates of theophrastrite blue-green sample from Hagdale, Unst.

**Physical and optical properties.** Both colour types are devoid of any detectable cleavage or fracture and electron microscopy demonstrates that the Hagdale blue-green type possesses a platy morphology (fig. 1). The lustre is dull for the blue-green variety and resinous for the gel-like material. The Mohs hardness for both varieties is 2 and they possess the same greenish-white streak and specific gravity, which is 3.6. The latter value is considerably lower than that of theophrastrite from Vermion, Greece (4.00) or synthetic  $\text{Ni}(\text{OH})_2$  (3.95) and reflects the considerable amount of mixed-hydroxide and/or zaratite (sp. gr. c.2.6) in the material. Optically only one refractive index for each variety could be obtained:  $n$  1.66 (blue-green) and  $n$  1.613 (emerald-green). In transmitted light, grains are obscurely platy to fibrous and non-pleochroic. No fluorescence was observed when examined under long- or short-wave ultra-violet light. Using hot, very dilute 5% v/v HCl both varieties are rapidly dissolved.

**X-ray data.** As reported by Macpherson and Livingstone (1974) X-ray powder data agree closely with those for synthetic  $\text{Ni}(\text{OH})_2$ . However, if numerous minute fragments are X-rayed individually then appreciable deviation from synthetic  $\text{Ni}(\text{OH})_2$   $d$  values may be observed, the shift being towards larger values. A solid-solution series would seem to exist between brucite and theophrastrite, for both are hexagonal and possess the same space group  $P\bar{3}m1$ . Natta and Passerini (1928) demonstrated that the synthetic compound  $(\text{Ni},\text{Mg})(\text{OH})_2$  50 mol. %  $\text{Ni}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  had cell parameters intermediate between those of synthetic  $\text{Ni}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ , and the cell parameters are functions of the changing Ni:Mg ratio throughout the series (G. W. Brindley, pers. comm., 1981). Thus the X-ray powder pattern can be used to estimate composition. A small bulk sample of blue-green Unst theophrastrite was prepared and

TABLE I. X-ray data for blue-green theophrastrite from Hagdale, Unst, Shetland

$I_{\text{est.}}$	$d_{\text{meas.}}$	$d_{\text{calc.}}$	hkl
90	4.666	4.666	001
60	2.712	2.712	100
100	2.348	2.345	101
70	1.768	1.768	102
70	1.564	1.565	110
50	1.482	1.484	111
30	1.351	1.349	103
30	1.300	1.300	112
20	1.171	1.172	202
5	1.103	1.103	113
5	1.073	1.073	104
10	1.023	1.022	203
15	0.998	1.001	211
15	0.937	0.938	212
10	0.902	0.904	300

Cu-K $\alpha$ , 114.6 mm diameter camera, Ni filter, estimated intensities. The data were indexed on a hexagonal cell,  $a = 3.131$ ,  $c = 4.666\text{\AA}$ ,  $V = 39.61\text{\AA}^3$ .

X-rayed and  $d$  spacings together with cell parameters, are presented in Table I. Tiny single fragments from both the 'Canadian' and Unst samples were also X-rayed and the fragments then analysed under the electron probe microanalyser for Mg and these results are given in Table II. Using the  $c$  value of the bulk sample, together with those for pure  $\text{Ni}(\text{OH})_2$  (4.605 $\text{\AA}$ ) and brucite (4.769 $\text{\AA}$ ) the Unst theophrastrite composition could be expressed as  $(\text{Ni}_{62.8}\text{Mg}_{37.2})(\text{OH})_2$ . Likewise, from Table II the  $c$  parameters indicate a range from  $(\text{Ni}_{88.4}\text{Mg}_{11.6})(\text{OH})_2$  to  $(\text{Mg}_{57.9}\text{Ni}_{42.1})(\text{OH})_2$ . Considerable discrepancies arise between the calculated MgO contents for the above compositions and the values determined by electron probe microanalysis. These are doubtless due to difficulties encountered in probing very small areas plus sample inhomogeneities.

The possibility that the theophrastrite is randomly interstratified with a mixed-hydroxide mineral of the pyroaurite type cannot be dis-

TABLE II. Variation of cell parameters with MgO content (determined by EPMA) of four individual theophrastrite-zaratite fragments

	$a$	$c$	% MgO
Blue-green Unst	3.128	4.700	7.6
Blue-green 'Canada'	3.125	4.624	3.5
Gel-like Unst	3.112	4.625	5.5
Gel-like 'Canada'	3.117	4.625	0.3

TABLE III. EPMA of blue-green and emerald-green theophrasite-zaratite grains from 'Canada' and Unst

	1	2	3	ave.	4	5	6	7	8	9	ave.	10	11	12	13	14
NiO	72.8	72.0	66.9	70.5	66.5	66.1	56.7	56.7	56.0	54.0	55.5	65.2	64.1	63.0	58.6	35.5
MgO	2.4	3.0	5.1	3.5	7.6	7.9	7.3	—	0.3	—	0.3	5.7	5.5	5.7	0.7	19.1
FeO	—	—	—	—	0.1	—	—	—	—	—	—	0.1	—	0.5	—	8.7
CuO	—	—	—	—	0.9	1.1	0.7	—	—	—	—	0.8	1.1	1.8	1.2	0.7
SiO <sub>2</sub>	0.2	0.3	—	0.2	0.2	0.1	0.3	—	0.2	0.2	0.2	—	0.2	0.3	0.2	1.4
SO <sub>3</sub>	0.5	0.6	0.8	0.6	1.1	0.8	1.4	7.5	6.4	5.0	6.3	0.8	0.6	0.7	1.3	0.6
	75.9	75.9	72.8	74.8	76.4	76.1	66.2	64.5	63.1*	59.3†	62.3	72.6	71.5	72.0	62.0	66.1‡

\* Includes 0.2% CaO † includes 0.1% CaO ‡ includes 0.1% Cr<sub>2</sub>O<sub>3</sub>.1-3 'Canada', No. 1890-114-1976, blue-green theophrasite-zaratite. Single spot analysis (defocused beam) on separate grains from 2-3 mg. sample analysed for H<sub>2</sub>O and CO<sub>2</sub>: H<sub>2</sub>O = 20.6%, CO<sub>2</sub> = 3.9%, total 24.5%.

ave. Mean of 1-3.

4-6 Hagdale, Unst, No. 303-2, blue-green theophrasite-zaratite. Single spot analysis (focused beam) on separate grains.

7-9 'Canada', No. 1890-114-1976, emerald-green, gel-like theophrasite-zaratite. Single spot analysis (defocused beam) on separate grains from 2-3 mg. sample analysed for H<sub>2</sub>O and CO<sub>2</sub>: H<sub>2</sub>O = 21.5%, CO<sub>2</sub> = 20.6%, total 42.1%.

ave. Mean of 7-9.

10-14 Hagdale, Unst, No. 303-2, emerald-green, gel-like theophrasite-zaratite. Single spot analysis (focused beam) on separate grains.

counted, for examination of some powder photographs of the Hagdale material reveals the presence of a very broad and diffuse line between 7 and 8Å. Calculations for a random interstratification of 4.8Å and 7.8Å material show that significant amounts (up to 20%) of the 7.8Å component may be present before large shifts in  $d_{001}$  occur (J. Hower, pers. comm., 1981). Because of the similarity in structure between the elementary hydroxides and the pyroaurite and carboydite structures, such interstratifications are very likely. These interstratifications should be formed in environments with a finite but limited concentration of trivalent cations and a high concentration of divalent cations. The minerals coalingite and coalingite-K (Mumpton *et al.*, 1965) are examples of partially ordered interstratifications of brucite and pyroaurite-type layers (Pastor-Rodriguez and Taylor, 1971).

*Chemical data.* Although Williams (1960) reported the first natural occurrence of Ni(OH)<sub>2</sub> and demonstrated its authenticity by X-ray powder diffraction, he was unable to ascertain the chemistry. Likewise, the Unst theophrasite cannot be analysed in the pure state for it is variably intermixed with sub-micron mixed-hydroxide and/or zaratite and possibly an amorphous nickel sulphate. Bulk samples of 2 to 3 mg of both the 'Canadian' blue-green and gel-like material were handpicked and analysed for H<sub>2</sub>O and CO<sub>2</sub>. From these two small bulk samples numerous grains were randomly selected for electron probe microanalysis using a defocused beam. Single spot analyses, utilizing a focused beam, were performed on grains selected from the chromitite surfaces and all the results are collated in Table III. The electronprobe

used was a Cambridge Instruments Microscan V with standardization on Ni, Fe, and Cu metals, periclase for Mg, and pyrite for S. Salient features of the analyses are NiO contents considerably lower than the theoretical value 80.6% NiO for Ni(OH)<sub>2</sub>, high water and CO<sub>2</sub> values, and appreciable magnesium and SO<sub>3</sub>. Inhomogeneity of both the Unst and 'Canadian' specimens is clearly demonstrable.

In her study of zaratite Isaacs (1963) showed that a complete solid solution series exists between NiCO<sub>3</sub> and MgCO<sub>3</sub> and it is noteworthy that the Unst zaratite does contain appreciable magnesium (Table IV). Availability of magnesium in the Ni-bearing solutions from which zaratite and theophrasite crystallized, plus the well-established

TABLE IV. EPMA of emerald-green, gel-like zaratite from Hagdale, Unst (wt %)

	1	2	3	4
NiO	54.3	52.7	54.5	48.3
MgO	2.5	2.6	2.8	4.1
FeO	0.2	—	—	—
CoO	0.8	1.0	1.1	0.1
CuO	0.3	0.2	—	0.3
SiO <sub>2</sub>	0.2	—	0.2	0.8
SO <sub>3</sub>	1.1	1.1	0.3	4.9
	59.4	57.6	58.9	58.5

Single spot analysis on separate grains, each grain gave powder pattern of zaratite only.

RSM Nos. 1-3, 303.4; 4, 303.6.

ability to readily substitute for Ni, combined with the *d* spacing shift, noted previously, are very strong indications that Mg has most probably entered the theophrastite structure. Of the Unst gel-like material one analysis (no. 14) shows that substitution by Mg has taken place to a high degree and suggests natural compositions intermediate between theophrastite and brucite. With reference to fig. 1 the EDS attachment showed, unquestionably, that Mg in considerable quantities is present in the plates of Unst theophrastite. Optical spectroscopy for both colour types determined the presence of Ni<sup>2+</sup> only.

*Infrared and thermal studies.* Infrared spectra obtained on a Nicolet Fourier Transform Infrared Spectrometer using KBr pellets reveal the presence of both free and hydrogen-bonded OH groups, H<sub>2</sub>O, CO<sub>3</sub>, and SO<sub>4</sub> in the emerald-green material. Results for the Hagdale blue-green material are

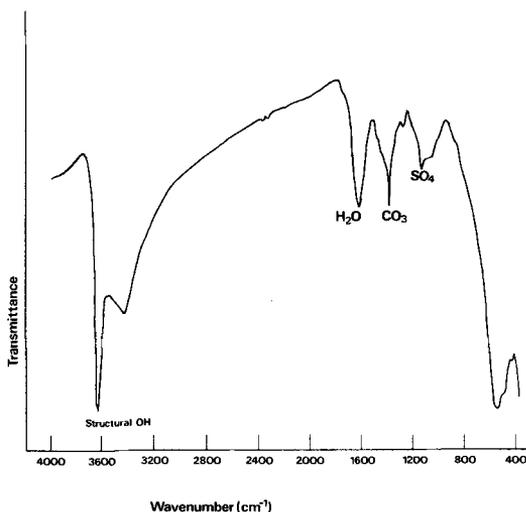


FIG. 2. Infrared absorption spectrum of Hagdale blue-green theophrastite-mixed-hydroxide-zaratite material.

similar (fig. 2) although the H<sub>2</sub>O and CO<sub>3</sub> absorptions are not as pronounced. The very sharp OH stretch absorption at about 3650 cm<sup>-1</sup> is characteristic of Ni(OH)<sub>2</sub>. The CO<sub>3</sub><sup>2-</sup> absorption band at about 1390 cm<sup>-1</sup> in both spectra is characteristic of pyroaurite-type mixed-hydroxides but is about 40 cm<sup>-1</sup> higher than is typically observed in well-crystallized mixed-hydroxides. The SO<sub>4</sub><sup>2-</sup> absorption band at 1200 cm<sup>-1</sup> is typical of carbohydrite-type mixed-hydroxides. These absorptions due to carbonate and sulphate provide further confirmation that the theophrastite is intimately

mixed with very poorly crystalline mixed-hydroxides.

Evolved gas analysis for the Hagdale blue-green theophrastite-mixed-hydroxide samples, using a 1.7 mg sample, shows that the CO<sub>2</sub> is sharply evolved with a peak at 285 °C. (A heating rate of 15 °C/min. was used and the evolved CO<sub>2</sub> swept with a N<sub>2</sub>/O<sub>2</sub> mixture flowing at 300 ml/min.) Synthetic technical-grade zaratite (NiCO<sub>3</sub> · 2Ni(OH)<sub>2</sub>) showed a virtually identical sharp evolution of CO<sub>2</sub> peaking at 280 °C. Thermogravimetric analysis of laboratory grade Ni(OH)<sub>2</sub> revealed that the main OH loss occurs sharply between 240–306 °C and thereafter tails off gradually and is not complete until approximately 700 °C. A 1 mg blue-green Hagdale sample showed a 1.5% weight loss up to 300 °C followed by a sharp loss to 380 °C and again a gradual tail-off to 700 °C. Heating tiny fragments of the Hagdale material for 10 minutes at 300, 350, and 400 °C and X-raying the products shows that at 400 °C breakdown to NiO is complete.

*Conclusions.* The hydroxide minerals from Unst are intimate mixtures of theophrastite and mixed-hydroxides of the pyroaurite- and carbohydrite-types. Theophrastite has variable amounts of Mg-for-Ni substitution, which is reflected in small but measurable changes in the X-ray powder patterns. Infrared spectra are typical of Ni(OH)<sub>2</sub> but show, in addition, absorptions characteristic of pyroaurite- and carbohydrite-type mixed-hydroxides. A broad, weak line in the X-ray patterns between 7 and 8 Å is due to a very poorly crystalline pyroaurite-type mineral, but we cannot rule out the occurrence of mixed-hydroxides randomly interstratified with the Ni(OH)<sub>2</sub>. The poor crystallinity of the pyroaurite-type mineral is likely due in part to the lower layer charge of the mineral; chemical analyses reveal a very small concentration of trivalent cations, which are required to give the mixed-hydroxides a positive layer charge.

The Unst theophrastite clearly formed via the breakdown of the rare primary Ni-bearing sulphides in the deposit, heazlewoodite, and pentlandite, as a bright green gel-like halo has been observed around a heazlewoodite grain. The scarcity of theophrastite in the Unst deposits is doubtless related to the restricted availability of Ni ions and a restricted supply of trivalent cations.

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