

PARAOTWAYITE, A NEW NICKEL HYDROXIDE MINERAL FROM WESTERN AUSTRALIA

ERNEST H. NICKEL AND JAMES GRAHAM

Division of Minerals and Geochemistry, CSIRO, Private Bag, P.O., Wembley, W.A. 6014, Australia

ABSTRACT

Paraotwayite, a new mineral species from the Otway nickel occurrence in the Pilbara region of Western Australia, occurs as green fibrous masses and cross-fibre veinlets in a mineral assemblage consisting largely of millerite and nickeloan chrysotile. Its composition corresponds to $\text{Ni}(\text{OH})_{2-x}(\text{SO}_4, \text{CO}_3)_{0.5x}$, with $x \sim 0.6$. The mineral is monoclinic, with a 7.89(1), b 2.96(1), and c 13.63(3) Å, β 91.1(2)°, $V = 318 \text{ Å}^3$; $Z = 6$. Its strongest five X-ray powder-diffraction lines [d in Å(hkl)] are: 6.81(10)(002), 5.083(8)(102), 3.859(5)(103,201), 2.946(4)(010,203) and 2.239(8)(212,014). Its density is 3.30 (meas.) and 3.520 g/cm³ (calc.); its hardness VHN₂₀ is 223. In transmitted light, paraotwayite is weakly pleochroic from bluish green to yellowish green; it has parallel extinction and is length-slow. Indices of refraction are 1.705 (n_{max}) and 1.655 (n_{min}). The name reflects the mineral's close compositional and physical similarity to otwayite.

Keywords: paraotwayite, otwayite, new mineral species, nickel minerals, electron-microprobe analyses, X-ray data, Pilbara region, Australia.

SOMMAIRE

La paraotwayite, nouvelle espèce minérale du gîte de nickel Otway, dans la région de Pilbara en Australie occidentale, se présente en agrégats de fibres vertes et en veinules à fibres transversales dans un assemblage de millerite et de chrysotile nickelifère. Sa composition répond à $\text{Ni}(\text{OH})_{2-x}(\text{SO}_4, \text{CO}_3)_{0.5x}$, pour une valeur de x d'environ 0.6. C'est un minéral monoclinique, a 7.89(1), b 2.96(1), c 13.63(3) Å, β 91.1(2)°, $V = 318 \text{ Å}^3$, pour $Z = 6$. Les cinq raies les plus intenses du cliché de poudre [d en Å(hkl)] sont: 6.81(10)(002), 5.083(8)(102), 3.859(5)(103,201), 2.946(4)(010,203) et 2.239(8)(212,014). Densité 3.30 (mesurée), 3.520 (calculée); dureté VHN₂₀ 223. En lumière transmise, la paraotwayite est faiblement pléochroïque du vert bleuâtre au vert jaunâtre; elle possède une extinction parallèle et un allongement positif. Ses indices de réfraction sont 1.705 (n_{max}) et 1.655 (n_{min}). Son nom rappelle sa grande ressemblance à la otwayite, tant en composition qu'en propriétés physiques.

(Traduit par la Rédaction)

Mots-clés: paraotwayite, otwayite, nouvelle espèce minérale, minéraux nickelifères, analyses à la microsonde électronique, données de diffraction X, région de Pilbara, Australie.

INTRODUCTION

The small Otway nickel deposit in the Pilbara

region of Western Australia (Nickel *et al.* 1979) has already been the source of two new nickel minerals, otwayite (Nickel *et al.* 1977) and nullagineite (Nickel & Berry 1981). The occurrence of a third new mineral species at this locality emphasizes the unusual nature of the nickel mineralization there.

The nickel minerals at the Otway deposit (Lat. 21°39'S, Long. 120°06'E) occur in shears in serpentinized peridotite, and consist mainly of nodular millerite, polydymite and pecoraite in a matrix of nickel carbonates and silicates. The nickel mineralization is attributed to hydrothermal and metasomatic activity along the shears, and the primary assemblage has been subjected to some supergene alteration due to the effects of weathering.

The new mineral species *paraotwayite* has been found in two specimens. Both specimens consist largely of millerite nodules partly altered to polydymite, in a matrix of green nickeloan chrysotile. Cutting across this assemblage are veinlets of dolomite, gaspeite and, to a lesser extent, paraotwayite. The specimens containing paraotwayite were collected by Mr. Charles Otway, after whom the occurrence and the species otwayite were named. The name paraotwayite was chosen because of the mineral's close chemical and physical resemblance to otwayite, and both mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Specimens have been deposited with the Western Australian State Mineral Collection (Government Chemical Laboratories, Perth) and the Museum of Victoria, Melbourne, Australia. No additional samples are available for distribution.

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Paraotwayite occurs as masses of parallel to sub-parallel fibres up to about 0.5 mm long and 5 µm wide, some in the form of cross-fibre veinlets. The mineral is emerald-green in hand specimen, with a silky lustre, and is virtually indistinguishable from otwayite, which has a similar occurrence.

Paraotwayite is brittle, and has a hardness of VHN 223 (average of 5 determinations with a 20-g indenter; standard deviation 22). Streak is white. Density, determined by flotation in diluted Cleric solution, is 3.30 g/cm³. No cleavage or parting was observed. The mineral does not fluoresce under long- or short-wave ultraviolet light, and is not attacked by cold HCl or HNO₃.

Paraotwayite is green in transmitted light, with weak pleochroism, bluish green parallel to the fibre length, and yellowish green normal to it. The fibres have parallel extinction, and are length-slow. Indices of refraction along the principal optical directions could not be determined because of the fibrous nature of the mineral, and only maximum and minimum values could be obtained. These are 1.705 (parallel to fibre length) and 1.655 (normal to fibre length). The mineral is assumed to be optically biaxial, although the fibres are too small for interference figures; the optic axial angle ($2V$) could not be measured for the same reason.

A Gladstone-Dale calculation, based on the anhydrous composition (see below), gives a median index of refraction \bar{n} of 1.653. The measured \bar{n} is 1.688, which gives a compatibility index of 0.021, regarded as excellent (Mandarino 1979).

CHEMICAL COMPOSITION

A specimen of paraotwayite in polished section was analyzed for Ni, Mg and S using an electron-microprobe analyzer. The analysis was done by means of crystal spectrometers, using the following standards: pyrite (S), nickel metal (Ni) and MgO (Mg). Corrections were made by the MAGIC computer program (Colby 1971). Several milligrams of paraotwayite were hand-picked from the same specimen for determination of H₂O and CO₂, which was done using a CHN analyzer by the Australian Microanalytical Service. The results of the combined analyses are shown in Table 1.

The empirical formula, based on Ni + Mg = 1, and as much OH as required to maintain charge balance, is Ni_{0.99}Mg_{0.01}(OH)_{1.43}(SO₄)_{0.17}(CO₃)_{0.12}•0.37 H₂O.

The 0.37 moles H₂O may be adsorbed water, and may therefore not be essential in the ideal formula of the mineral. Recalculation of the analysis to a H₂O-free formula gives the results shown in column 3 of Table 1. Assuming partial substitution of 2(OH)⁻ by SO₄²⁻ and CO₃²⁻, the generalized anhydrous formula for paraotwayite can be written

Ni(OH)_{2-2x}(SO₄, CO₃)_{0.5x}, where x is approximately 0.6.

CRYSTALLOGRAPHY

Single-crystal X-ray studies could not be carried out because single crystals of a sufficiently large size could not be isolated. Electron-diffraction studies gave a two-dimensional orthogonal lattice of dimensions 3.0 and 13.6 Å; the third dimension could not be determined. However, the two parameters enabled a fibre-rotation pattern to be partly indexed, and those indexed lines were used to calculate and refine the unit-cell parameters on the basis of a monoclinic unit-cell with a 7.89(1), b 2.96(1), c 13.63(3) Å, β 91.1(2)°. The b repeat distance is parallel to the fibre length. The unit-cell volume is 318 Å³. Assuming Z to be equal to 6, the calculated density is 3.520

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR PARAOOTWAYITE

hkl	d_{calc}	d_{obs}	I	hkl	d_{calc}	d_{obs}	I
100	7.888	7.95	2	008	1.703		
002	6.814	6.81	10	306	1.702	1.698	<1
102	5.108	5.083	8	404	1.692		
200	3.943	3.944	<1	314	1.692		
103	3.904			108	1.658	1.656	1
201	3.808	3.859	5	017	1.626		
201	3.769	3.775	<1	411	1.626	1.621	<1
004	3.407	3.390	2	117	1.588		
		3.305	<1	315	1.583	1.585	2
104	3.106			501	1.564	1.567	1
203	3.007	3.052	<1	502	1.543	1.544	1
010	2.959			413	1.535	1.536	<1
203	2.950	2.946	4	406	1.503	1.508	<1
110	2.771	2.780	<1	021	1.471		
300	2.629	2.627	<1	414	1.469	1.469	1
301	2.572	2.578	2	122	1.423		
112	2.560	2.543	<1	209	1.423	1.425	<1
		2.508	<1	506	1.308		
303	2.257	2.259	1	601	1.306	1.306	<1
212	2.244			224	1.286		
014	2.234	2.239	8	602	1.286		
106	2.194	2.208	<1	125	1.285	1.285	<1
304	2.062	2.060	<1	321	1.285		
015	2.005	2.011	1	506	1.284		
400	1.972	1.973	3	603	1.269		
312	1.896	1.895	<1	322	1.269	1.267	<1
402	1.884	1.892	<1	219	1.269		
305	1.874	1.868	1	417	1.265		
313	1.813	1.814	<1	603	1.256	1.253	<1

CuK α radiation, 1.54178 Å. 57.3 mm Debye-Scherrer camera. Cell parameters: a 7.89(1), b 2.96(1), c 13.63(3) Å, 91.1(2)°.

TABLE 1. CHEMICAL COMPOSITION OF PARAOOTWAYITE

	Recalculated to anhydrous formula		Mol. Props.	
NiO	66.25 wt.%	69.63 wt.%	Ni	0.993
MgO	0.24	0.25	Mg	0.007
SO ₃	11.80	12.72	SO ₄	0.165
CO ₂	4.67	5.35	CO ₃	0.119
H ₂ O	17.42	12.05	OH	1.432
	100.38	100.00		

TABLE 3. CHEMICAL FORMULA AND CRYSTALLOGRAPHIC PARAMETERS FOR SOME RELATED NICKEL HYDROXIDES AND HYDROXY-CARBONATES

Name	Chemical Formula	Cryst.	a	b	c	β	Ref.
Paraotwayite	Ni(OH) _{1.43} (SO ₄ ,CO ₃) _{0.28}	mon.	7.89	2.96	13.63	91.1	1
Otwayite	Ni ₂ (OH) ₂ CO ₃ •H ₂ O	orth.	10.18	27.4	3.22		2
Nullaginite	Ni ₂ (OH) ₂ CO ₃	mon.	9.24	12.00	3.09	90.48	3
Theophrastite	Ni(OH) ₂	hex.	3.13		4.60		4
Jamborite	Ni(OH) ₂ (OH,S,H ₂ O)	hex	3.07		23.3		5

Refs.: 1) This paper; 2) Nickel et al. (1977); 3) Nickel & Berry (1981); 4) Marcopoulos & Economou (1981); 5) Morandi & Dalrio (1973).

Units: a , b , c in Angstrom units, β in degrees.

g/cm^3 , which is substantially greater than the measured density of $3.30 \text{ g}/\text{cm}^3$. The discrepancy is probably due to the presence of adsorbed water.

The X-ray powder-diffraction pattern is shown in Table 2. The strongest line of the pattern (6.81 \AA) is very close to the strongest line of the otwayite pattern (6.84 \AA) (Nickel *et al.* 1977), owing to the fact that the b dimension of otwayite is almost exactly twice the c dimension of paraotwayite (Table 3).

DISCUSSION

The fractional mole of $\text{SO}_4 + \text{CO}_3$ in the generalized formula $\text{Ni}(\text{OH})_{2-x}(\text{SO}_4, \text{CO}_3)_{0.5x}$ raises a question as to whether these components are essential. If x is taken as 0, the formula becomes $\text{Ni}(\text{OH})_2$, but it is not known whether such a composition could maintain the paraotwayite structure. A mineral of $\text{Ni}(\text{OH})_2$ composition is known as theophrastrite, but its X-ray-diffraction pattern and other properties (Marcopoulos & Economou 1981) are quite distinct from those of paraotwayite. The unit-cell parameters of paraotwayite and other nickel hydroxide minerals are listed in Table 3 for comparison. The only common feature among these parameters is a dimension approximating 3 \AA , which is also common to minerals of the brucite, pyroaurite and carboydite groups (Nickel & Wildman 1981); this length represents the distance that separates octahedral cation sites in a hexagonal close-packed lattice of oxygen atoms. Until the crystal structures of paraotwayite and the other minerals listed in Table 3 are determined, the structural interrelationships among them must remain obscure.

The paragenetic relationship between paraotwayite and otwayite is unclear. Both occur as cross-fibre veinlets that cut across a nickel-rich assemblage consisting largely of millerite, polydymite and nickeloan chrysotile, and are therefore relatively late in the paragenetic sequence. However, otwayite and paraotwayite have not been observed together, and it was therefore not possible to determine whether or not they had crystallized contemporaneously. Some hydrothermal experiments were conducted in an attempt to study the stability relations of the two minerals, but had to be abandoned because neither

of the two minerals could be synthesized using the relatively unsophisticated experimental apparatus available to us. An understanding of the stability relations of these minerals will have to await a more systematic study of the system $\text{NiCO}_3\text{-NiSO}_4\text{-H}_2\text{O}$.

ACKNOWLEDGEMENTS

We appreciate the kindness of Mr. Charles Otway in providing the mineral specimens for study. We also acknowledge the assistance of Dr. A.W.S. Johnson of the Crystallography Centre of the University of Western Australia, who obtained the electron-diffraction patterns, and of Mr. A.B. Fletcher of our Division, who made the density determination.

REFERENCES

- COLBY, J.W. (1971): MAGIC IV - a new improved version of MAGIC. *Proc. 6th Nat. Conf. Electron Probe Anal. (Pittsburgh)*.
- MANDARINO, J.A. (1979): The Gladstone-Dale relationship. III. Some general applications. *Can. Mineral.* **17**, 71-76.
- MARCOPOULOS, T. & ECONOMOU, M. (1981): Theophrastrite, $\text{Ni}(\text{OH})_2$, a new mineral from northern Greece. *Amer. Mineral.* **66**, 1020-1021.
- MORANDI, N. & DALRIO, G. (1973): Jamborite, a new nickel hydroxide mineral from the northern Apennines, Italy. *Amer. Mineral.* **58**, 835-839.
- NICKEL, E.H. & BERRY, L.G. (1981): The new mineral nullagineite and additional data on the related minerals rosasite and glaukosphaerite. *Can. Mineral.* **19**, 315-324.
- _____, HALLBERG, J.A. & HALLIGAN, R. (1979): Unusual nickel mineralisation at Nullagine, Western Australia. *J. Geol. Soc. Aust.* **26**, 61-71.
- _____, ROBINSON, B.W., DAVIS, C.E.S. & MACDONALD, R.D. (1977): Otwayite, a new nickel mineral from Western Australia. *Amer. Mineral.* **62**, 999-1002.
- _____ & WILDMAN, J.E. (1981): Hydrohonessite - a new hydrated Ni-Fe hydroxy-sulphate mineral; its relationship to honessite, carboydite, and minerals of the pyroaurite group. *Mineral. Mag.* **44**, 333-337.

Received June 20, 1986, revised manuscript accepted October 22, 1986.