

NICKELBISCHOFITE, A NEW NICKEL CHLORIDE HYDRATE

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ABSTRACT

Nickelbischofite, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, occurs in a sulfate sublimate from Mt. Shirane, Japan, as an alteration product on drill core from the Dumont ultramafic intrusion, Quebec, and as a supergene mineral at the Oxford serpentine quarry, Llano County, Texas. The Texas material occurs as 0.1–15 mm individual crystals and powdery coatings associated with zaraitite, erythrite, annabergite and albrittonite ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). Nickelbischofite is translucent, emerald green, with refractive indices α 1.589(2), β 1.617(2), γ 1.644(2), $2V +87^\circ$. The mineral is monoclinic, space group $C2/m$ with the cell a 10.318(3), b 7.077(2), c 6.623(1) Å, β 122.37(2)°. The strongest lines in the X-ray powder pattern are 5.59(100)(001), 5.49(40)(110), 4.82(30)($\bar{1}11$), 2.924(40)($\bar{1}12$), 2.747(30)(220), 2.180(30)(400), in agreement with data for synthetic $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. G (meas.) is 1.929(5) and G (calc.) is 1.932 with $Z=2$. The name indicates that the mineral is compositionally the nickel analogue of bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

SOMMAIRE

La nickelbischofite $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ se trouve dans un sublimé à sulfates du mont Shirane (Japon); elle est aussi produit d'altération des carottes de sondage de l'intrusion ultramafique Dumont (Québec) et minéral supergène dans la carrière de serpentine d'Oxford, comté Llano (Texas). Sur les spécimens du Texas, elle se présente soit en cristaux isolés de 0.1 à 15 mm de longueur, soit en enduits pulvérulents, accompagnée de zaraitite, érythrite, annabergite et albrittonite ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). La nickelbischofite est translucide, d'un vert émeraude et d'indices de réfraction α 1.589(2), β 1.617(2), γ 1.644(2), $2V +87^\circ$; elle est monoclinique, groupe spatial $C2/m$, a 10.318(3), b 7.077(2), c 6.623(1) Å, β 122.37(2)°. Les six raies les plus intenses du cliché de poudre sont les suivantes (intensité et symbole entre parenthèses): 5.59(100)(001), 5.49(40)(110), 4.82(30)($\bar{1}11$), 2.924(40)($\bar{1}12$), 2.747(30)(220), 2.180(30)(400); elles concordent avec les données du $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ synthétique. D (mes.) 1.929(5), (calc.) 1.932, $Z=2$. Le nom indique que le minéral est l'analogue nickelifère de la bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, comme composition chimique.

INTRODUCTION

The first indications that the compound $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ occurs in nature were obtained by Shima (1957) in his study of sulfate-rich sublimates from Mt. Shirane, Gumma Prefecture, Japan. Based on X-ray patterns and the presence of nickel and chlorine in a green sublimate, Shima concluded that the material was mainly alunogen with about 3% admixed $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. No additional data could be obtained from the Japanese material. Nickel chloride hexahydrate was noted subsequently by Jambor (1975) on drill core from the Dumont ultramafic body near Amos, Québec. The Dumont drill core, although stored in a dry warehouse when examined in 1974, nevertheless was undergoing *in situ* disintegration, accompanied in most cases by growth of abundant coalingite. A few pieces of the core contained green chlorides that also had formed during storage. A green deliquescent spot on one of the cores was identified by X-ray powder patterns as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; subsequent energy-dispersive analysis of the X-ray mount confirmed that nickel and chlorine are its non-aqueous constituents.

In 1977, the first author examined the products from a supergene alteration halo found the previous year at the Oxford serpentine quarry, Llano County, Texas. Associated with erythrite, annabergite, zaraitite and albrittonite were several small green crystals and coatings subsequently shown to be $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The data reported below pertain to the Texas material.

The name nickelbischofite indicates that the new mineral is compositionally the nickel analogue of bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, but the two are not isostructural. The new name and the mineral have been approved by the Commission on new Minerals and Mineral Names, IMA. The Texas material has been deposited in the U.S. National Museum of Natural History (Smithsonian Institution; No. 144189). The Québec material is in the National Mineral Collection, Ottawa (NMC 17980).

OCCURRENCE

In the Oxford serpentine quarry, nickelbischofite occurs in a narrow oxidized zone above a small veinlet containing cobaltite, linnaeite, siegenite and nickeline. Associated with the nickelbischofite are erythrite, annabergite, zaraitite and albrittonite. Mode of occurrence and formation of the nickel chloride seem to be identical to those of the cobalt analogue, albrittonite (Crook & Marcotty 1978).

At the Dumont ultramafic body near Amos, Québec, nickelbischofite was found as a 2 mm green spot that formed on the surface of stored drill core. Associated minerals also of secondary origin are coalingite, paratacamite, and an as yet unnamed nickel chloride thought to be $\text{Ni}_{10}\text{Cl}_7(\text{OH})_{13}\cdot 8\text{H}_2\text{O}$. Paratacamite is by far the most abundant of the chlorides; it is present on surfaces of both whole and split cores.

PHYSICAL PROPERTIES

Nickelbischofite occurs on serpentine as powdery coatings and as aggregates of poorly formed monoclinic crystals. Individual crystals are 0.1 to 15 mm long and commonly show the principal forms $\{100\}$, $\{110\}$ and $\{011\}$. Crystal morphology is identical to that of albrittonite (Crook & Marcotty 1978). Nickelbischofite is emerald green, translucent, has a vitreous lustre, and is brittle, with subconchoidal to conchoidal fracture and perfect (001) cleavage. The hardness is about $1\frac{1}{2}$ and the streak is very pale green to white. The mineral is deliquescent and readily soluble in water.

Nickelbischofite is biaxial (+), with measured $2V = 87^\circ$; refractive indices for NaD are α 1.589(2), β 1.617(2), γ 1.644(2), in agreement with indices reported by Swanson *et al.* (1974) for synthetic $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$: α 1.590, β 1.620, γ 1.648. The mineral is weakly pleochroic, with α pale green, β pale green to green, γ green ($\alpha > \beta > \gamma$). Optic orientation is $b = Y$, $X\wedge c = +8^\circ$.

Specific gravity was measured in toluene on a Berman balance by repeated measurements of a single-crystal group weighing 18 mg: $G(\text{meas.})$ is 1.929(5), $G(\text{calc.})$ is 1.932 with $Z = 2$. Neither natural nor synthetic material fluoresces under ultraviolet light.

X-RAY CRYSTALLOGRAPHY

Weissenberg and precession photographs and least-squares refinement of the X-ray powder data (Table 1) using $\text{CuK}\alpha$ radiation gave a

TABLE 1. POWDER X-RAY DATA FOR NICKELBISCHOFITE FROM TEXAS

I_{est}	d_{meas}	d_{calc}	hkl	I_{est}	d_{meas}	d_{calc}	hkl
100	5.59	5.59	001	5	2.193	2.194	022
40	5.49	5.49	110			2.190	221
15	4.96	4.96	201	30	2.180	2.179	400
30	4.82	4.82	$\bar{1}11$	10	2.055	2.057	311
10	4.36	4.36	200	10	2.030	2.030	422
10	3.540	3.539	020	5	1.980	1.981	$\bar{1}13$
5	3.390	3.389	111	10	1.970	1.971	512
5	3.290	3.286	202	5	1.930	1.930	202
5	3.091	3.093	311	5	1.920	1.920	511
10	2.990	2.990	021	15	1.901	1.901	$\bar{1}32$
40	2.924	2.923	$\bar{1}12$	5	1.862	1.862	223
10	2.800	2.797	002	10	1.856	1.855	420
30	2.747	2.747	220	10	1.695	1.695	222
5	2.728	2.727	312	5	1.685	1.687	041
20	2.686	2.687	310	5	1.685	1.687	041
10	2.541	2.542	401	5	1.610	1.610	314
20	2.406	2.408	222			1.608	113
5	2.220	2.220	$\bar{1}31$	10	1.605	1.605	333
5	2.210	2.209	112			1.605	204

Indexed with a 10.318, b 7.077, c 6.623Å, β 122.37°, $C2/m$.

8.783(2), b 7.077(2), c 6.623(2)Å, β 97.19(2)°, in excellent agreement with data for synthetic $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (a 8.787, b 7.076, c 6.625Å, β 97.20°; JCPDS No. 25-1044). These data are for space group $I2/m$. However, the present writers have retained the early morphological setting, also adopted in the structural refinements by Mizuno (1961) and Kleinberg (1969), in which the perfect cleavage in nickelbischofite is (001), the space group is $C2/m$, and a 10.318(3), b 7.077(2), c 6.623(1)Å, β 122.37(2)°. The X-ray axial ratio is $a:b:c$ 1.468:1:0.936; the morphological ratio is $a:b:c$ 1.468:0.943, β 122.5° (Groth 1906).

Nickelbischofite is isostructural with its cobalt analogue, albrittonite. Cell dimensions for the latter as given in Crook & Marcotty (1978) refer to the $I2/m$ setting, and crystal forms shown (1978, p. 411) are for an untwinned individual and twinned crystals in the $C2/m$ setting adopted here. The perfect cleavage in both albrittonite and nickelbischofite is (001); in the $I2/m$ setting, the cleavage is ($\bar{1}01$).

CHEMICAL ANALYSES

Electron microprobe analyses of nickelbischofite are given in Table 2. The analyses were

TABLE 2. ANALYSES OF NICKELBISCHOFITE, LLANO COUNTY, TEXAS

wt. %	anal. 1	anal. 2	$\text{NiCl}_2\cdot 6\text{H}_2\text{O}$
Ni	24.2	23.0	24.70
Cu	0.15	0.21	-
Fe	0.04	0.06	-
Co	0.5	1.4	-
Cr	0.1	0.1	-
Cl	30.0	30.1	29.83
H_2O^*	45.6	45.7	45.47
Total	100.59	100.57	100.00

* H_2O obtained from total weight loss on ignition, minus Cl obtained from the microprobe analyses.

conducted at 150 nA specimen current and 12 kV excitation voltage using Co metal, chrome spinel, halite and analyzed Cu-Ni-Fe alloy as standards. Water was obtained by weight loss on ignition minus the microprobe-determined chlorine content. Corrections were made with the EMPADR VII program of Rucklidge & Gasparrini (1969). Tests for fluorine were negative.

DISCUSSION

Although the Québec and Texas occurrences of nickelbischofite differ, both may represent similar geochemical environments. The Dumont intrusion in Québec is a huge, low-grade nickel prospect; most of its recoverable nickel is present as pentlandite, awaruite and minor heazlewoodite. Serpentine in the intrusion contains appreciable amounts of chlorine (up to slightly more than 0.9%: Rucklidge 1972, Rucklidge & Patterson 1977). The presence of nickel and chlorine in the serpentinites, the *in situ* disintegration of some of the drill core, and the growth of secondary minerals on the cores suggest that some components of the host rocks are unstable under atmospheric conditions and have provided the elements to form nickelbischofite.

Analyses of the Oxford, Texas serpentine show that it also contains chlorine. The element is usually present in only trace amounts (0.01%), but values up to 0.10% Cl have been obtained. Both the nickel and chlorine in nickelbischofite seem to have been derived by supergene alteration of primary and secondary minerals (nickeline, siegenite, annabergite, zaratite) by chlorine-rich ground waters. The deliquescence and extreme solubility of nickelbischofite lead to the repeated dissolution and crystallization of the mineral to form small single crystals and a halo of powdery coatings.

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REFERENCES

- CROOK, W.W., III & MARCOTTY, L.-A. (1978): Albritetonite, a new cobalt chloride hydrate from Oxford, Llano County, Texas. *Amer. Mineral.* 63, 410-412.
- GROTH, P. (1906): *Chemische Kristallographie* 1. Wilhelm Engelmann, Leipzig.
- JAMBOR, J.L. (1975): Secondary minerals in an ultramafic intrusion, Amos area, Quebec. *Geol. Surv. Can. Pap.* 75-1A, 261-263.
- KLEINBERG, R. (1969): Crystal structure of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature and 4.2°K by neutron diffraction. *J. Chem. Phys.* 50, 4690-4696.
- MIZUNO, J. (1961): The crystal structure of nickel chloride hexahydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. *J. Phys. Soc. Japan* 16, 1574-1580.
- RUCKLIDGE, J.C. (1972): Chlorine in partially serpentinized dunite. *Econ. Geol.* 67, 38-40.
- & GASPARRINI, E.L. (1969): Electron microprobe analytical data reduction: EMPADR VII. *Dep. Geol. Univ. Toronto*.
- & PATTERSON, G.C. (1977): The role of chlorine in serpentinization. *Contr. Mineral. Petrology* 65, 39-44.
- SHIMA, M. (1957): A new sublimate containing nickel found in a fumarole of an active volcano. *J. Sci. Res. Inst.* 51, 11-14.
- SWANSON, H.E., MCMURDIE, H.F., MORRIS, M.C., EVANS, E.H. & PARETZKIN, B. (1974): Standard X-ray diffraction powder patterns. *Nat. Bur. Stand. Mon.* 25, Sect. 11, 42.

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