Bottinoite, $Ni(H_2O)_6[Sb(OH)_6]_2$, a new mineral from the Bottino mine, Alpi Apuane, Italy

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Abstract

Bottinoite, a new nickel and antimony hydrated hydroxide mineral, occurs at the Bottino mine, Alpi Apuane, Italy. Associated minerals are ullmannite, siderite, calcite, quartz, phlogopite, pyrite, chalcopyrite, and an unidentified species containing Sb, Ni, and As. The mineral occurs as tabular or very short prismatic crystals with prominent {0001} forming roselike aggregates; crystals up to 0.4 mm and aggregates up to 2.5 mm in diameter. The mineral is light blue-green, transparent, nonfluorescent, with a vitreous luster and a very light blue streak. It is brittle, with conchoidal fracture. $VHN_{10} = 105$ kg/mm². $D_{calc} = 2.81$ g/cm³, $D_{meas} = 2.83(1)$, determined for synthetic crystals by heavy liquids. Bottinoite is uniaxial (+), nonpleochroic, with $\omega = 1.600(10)$, $\epsilon = 1.605(10)$, and very low birefringence. It is trigonal, $a = 16.026(3)$, $c = 9.795(2)$ Å, $V = 2178.6(7)$ Å³, $c/a = 0.6112$, $Z = 6$, space group choices are $P\bar{3}1m$ or, more likely, $P31m$ or $P312$. The strongest six lines in the X-ray powder diffraction pattern (d_{obs}, I_{obs}, hkl) are 4.62(100)300, 3.36(100)032, 2.34(80)332, 2.09(60)062, 1.806(70)334, 1.751(60)360. On the basis of chemical analysis, IR spectroscopy, TGA, and X-ray data, bottinoite corresponds to the synthetic compound $Ni(H_2O)_6[Sb(OH)_6]_2$. The mineral is named for the Bottino mine, which is the type locality.

Introduction

In 1987, an unusual pale blue-green mineral was collected from the Bottino mine, Alpi Apuane, Italy, by Andrea Dini of Lucca (Italy), who gave a sample to one of the authors for study. The mineral has been recognized as a new species and is named bottinoite. Its powder pattern and cell parameters closely resemble those published by Beintema (1936) for the synthetic compound $Ni(H_2O)_6[Sb(OH)_6]_2$. Chemical analyses, IR spectroscopy, and TGA have confirmed the identity of bottinoite with this synthetic compound.

Bottinoite is named for the famous Bottino di Seravezza mine, which has long been exploited for Pb, Ag, and, to a lesser extent, Zn. However, worldwide recognition of the Bottino mine and other ore veins in the area (Val di Castello, Monte Arsiccio, Canale dell'Angina, and so forth) is mainly due to the discovery of euhedral crystals of many sulfides and sulfosalts, in particular meneghinite and geocronite. Fundamental studies of the minerals from Bottino are those by Pelloux (1922) and Dessau (1935).

Both the mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names. Thus far, only three samples of bottinoite have been found in the mine, and in each case the mineral occurs as a roselike aggregate. The type specimen has

been deposited in the Mineralogical Museum at the University of Florence (no. 1747/RI).

Occurrence and Paragenesis

According to Benvenuti et al. (1989), in the Bottino district the Pb-Ag-(Zn) mineralization is hosted within the basement rocks of the Tuscan metamorphic sequence (Nucleo Metamorfico Apuano), here represented by a phyllitic member (Filladi Inferiori Formation of probable Upper Cambrian–Lower Ordovician age), which is overlain by a metavolcanic and meta-arkosic unit (Porfiroidi and Scisti Porfirici Formation of presumed Ordovician-Silurian age).

The mineral was found at Paoli's level, near Sansoni's well; it occurs on a schist matrix belonging to the volcanoclastic facies of the Porfiroidi and Scisti Porfirici Formation. Associated minerals are calcite, siderite, quartz, pyrite, chalcopyrite, and ullmannite; these minerals are crystallized on a fracture surface that is discordant with the schistosity.

Bottinoite occurs as roselike aggregates (up to 2.5 mm in diameter) of small tabular light blue-green crystals (Fig. 1) perched on ullmannite crystals. On the plates of bottinoite, very small white spherules of an unidentified species containing major amounts of Sb, Ni, As, and minor

Fig. 1. SEM photomicrograph of a roselike aggregate of tabular crystals of bottinoite associated with siderite. Scale bar equals 800 μm.

TABLE 1. Chemical analysis of bottinoite

	1	2	3
Sb_2O_5	52.65	52.07(0.3)	62.6(0.9)
NiO	12.16	12.04(0.2)	15.2(0.9)
H_2O	35.19	35.40(0.5)	32.9(0.9)
Total	100.00	99.51	110.7

Note: Contents in weight percent; standard deviations in parentheses. Numbers 1–3 designate the following: 1 = ideal bottinoite $Ni(H_2O)_6[Sb(OH)_6]_2$; 2 = synthetic material, AAS (Sb,Ni) and TGA (H_2O); 3 = natural material, EDS (Sb,Ni) and TGA (H_2O).

amounts of Co were also found. Bottinoite has apparently been formed by the alteration of ullmannite.

CHEMISTRY

A preliminary qualitative energy-dispersive analysis of bottinoite, utilizing Tracor equipment, showed the presence of Ni and Sb; no other element with an atomic number greater than 11 was detected. As the thermogravimetric (TGA) curve showed an easy dehydration starting at about 100 °C, energy-dispersive spectroscopy was deemed more suitable than wavelength-dispersive spectroscopy for quantitative analysis (25 kV with a sample current of 0.3 nA). The standards used were Sb_2O_4 and NiO micropellets. A total of four analyses were obtained and the average is reported in column 3 of Table 1. NiO and Sb_2O_5 prcentages are higher than those expected, probably because of the dehydration of the mineral under the electron beam. Nevertheless, the Ni/Sb atomic ratio (0.526) is close to the theoretical one. Because of the very small amount of available natural material, a complete chemical characterization was undertaken with synthetic bottinoite crystals obtained following the procedure described by Beintema (1936). Synthetic crystals (10 mg) were dissolved in 1:5 HCl; NiO and Sb_2O_5 were determined by atomic absorption spectroscopy (graphite furnace) using the multiple additions method. The H_2O content was determined by TGA on both natural and synthetic materials (see Table 1). Results suggest a slight dehydration of the natural sample. On the basis of the more reliable chemical results obtained on the synthetic crystals, the empirical formula (based on O = 18) is $Ni_{0.99}Sb_{1.98}H_{24.13}O_{18}$. The simplified formula can be written $Ni(H_2O)_6[Sb(OH)_6]_2$. IR spectroscopy gave clear indications of the presence, in both the natural and synthetic bottinoite, of H-bonded H_2O molecules and OH groups.

CRYSTALLOGRAPHY

An X-ray single-crystal study (Weissenberg camera and CAD4 diffractometer) of both natural and synthetic crystals indicated a Laue symmetry of $\bar{3}m$ with no systematic extinctions. Since $I_{hkl} = \bar{I}_{khl} \neq I_{kh\bar{l}}$, it follows that the possible space groups are $P\bar{3}1m$, $P31m$, and $P312$. A second harmonic generation of the fundamental lasing frequency (1.06 μm) has been observed at 532 nm with a Q-switched Nd-YAG laser. This observation suggests a structure without an inversion center, since the second-order nonlinear susceptibility vanishes in the electric dipole approximation for a centrosymmetric crystal. Statistical tests on the distribution of the $|E|$ values also indicated the absence of an inversion center. Therefore, the most probable space groups are $P31m$ and $P312$. As already observed by Beintema (1936), the strongest reflections are those with $l = 2n$ and $-h + k = 3n$; therefore, a first attempt at solving the structure (for both natural and synthetic crystals) was undertaken on the basis of Beintema's model (1936), but it was not successful. The presence of twinning may be the cause of these difficulties.

The X-ray powder-diffraction pattern was obtained by means of a 114.6-mm diameter Gandolfi camera using Ni-filtered Cu$K\alpha$ radiation. Data for both natural and synthetic bottinoite are given in Table 2, along with the powder data reported for the synthetic compound by Beintema (1936). A comparison of the d values and relative intensities reveals a close correspondence. Indexing was performed on the basis of single-crystal X-ray data. The unit-cell parameters of natural bottinoite [a = 16.026(3), c = 9.795(2) Å, V = 2178.6(7) Å^3, c/a = 0.6112, Z = 6] were determined by least-squares refinement using 49 reflections measured from the Gandolfi film.

Bottinoite crystals appear tabular, with cross-section dimensions up to 0.4 mm. Figure 2 shows a SEM image of isolated synthetic crystals: the observed forms are {0001} (dominant) and {10$\bar{1}$0}.

Relationships to other structures

The lattice of bottinoite can be described as a superlattice (54×) of brucite and brucite-like compounds. Applying the transformation matrix [−⅓, −⅔, 0; ⅔, ⅓, 0; 0, 0, ½] to the direct lattice vectors of bottinoite ($\mathbf{a}^b$, $\mathbf{c}^b$), the vectors $\mathbf{a}'$ and $\mathbf{c}'$ are obtained, with $\mathbf{a}' \perp \mathbf{a}^b$ and $\mathbf{c}' \parallel \mathbf{c}^b$

TABLE 2. Powder X-ray diffraction data for bottinoite

h	k	l	d_{calc}	1		2		3	
				d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0
0	0	1	9.795	—	—	9.74	5	—	—
1	1	0	8.013	7.96	10	8.00	5	—	—
1	1	1	6.202	6.18	20	6.18	2	—	—
0	0	2	4.898	4.88	50	4.88	50	4.91	40
3	0	0	4.626	4.62	100	4.62	100	4.65	80
3	0	1	4.183	4.20	25	4.18	10	4.19	20
1	1	2	4.179	4.17				—	—
2	2	0	4.007	4.01	10	4.00	2	—	—
0	2	2	4.001					—	—
2	2	1	3.708	—	—	3.70	2	—	—
1	2	2	3.580	3.58	15	3.58	2	—	—
0	3	2	3.363	3.36	100	3.36	70	3.37	70
1	4	0	3.029						
1	3	2	3.026	3.02	15	3.04	5	—	—
1	1	3	3.024						
1	4	1	2.894	2.89	10	2.88	5	—	—
3	3	0	2.671	2.67	30	2.67	15	2.67	40
0	3	3	2.668					—	—
3	3	1	2.577	2.58	40	2.58	20	2.58	40
1	4	2	2.576					—	—
3	3	2	2.345	2.34	80	2.35	30	2.36	100*
0	6	0	2.313	2.31	30	2.31	20	2.31	40
2	5	0	2.222						
1	5	2	2.222	2.22	15	2.22	2	—	—
1	2	4	2.219						
0	3	4	2.164	2.16	50	2.16	15	2.17	40
0	6	2	2.092	2.09	60	2.09	20	2.09	50
3	3	3	2.067	2.07	25	2.07	5	—	—
1	3	4	2.066					—	—
2	5	2	2.024	2.02	10	2.02	5	—	—
0	4	4	2.001	1.996	10	—	—	—	—
1	6	2	1.943	1.938	15	—	—	—	—
2	3	4	1.941					—	—
1	4	4	1.904	1.902	10	1.902	2	—	—
0	5	4	1.836	1.834	10	1.836	2	—	—
3	3	4	1.805	1.806	70	1.804	15	1.807	40
2	6	2	1.791	1.789	5	—	—	—	—
2	4	4	1.790					—	—
3	6	0	1.749	1.751	60	1.750	20	1.752	40
3	6	1	1.721	1.721	15	1.722	5	1.725	20
1	7	2	1.721						
0	6	4	1.682	1.682	40	1.686	10	1.684	40
3	6	2	1.647	1.648	50	1.648	20	1.650	50
1	6	4	1.601	1.600	15	1.599	5	—	—
0	9	0	1.542	1.543	40	1.539	10	1.543	40
3	0	6	1.540						
2	2	6	1.512	1.512	15			—	—
2	8	1	1.497	1.498	15			—	—
0	4	6	1.477	1.477	5			—	—
0	9	2	1.471	1.474	25			1.473	30
1	4	6	1.437	1.438	20			—	—
3	6	4	1.423	1.425	25			1.424	30
3	3	6	1.393	1.393	20			—	—
6	6	0	1.336	1.335	20			1.338	30
0	6	6	1.334					—	—
6	6	2	1.289	—	—			1.291	30
3	9	0	1.283	1.282	15			1.286	30
3	9	2	1.241	1.243	15			1.243	30
0	9	5	1.212	1.211	15				
1	1	8	1.210						
2	9	4	1.194	1.194	15				
3	6	6	1.193						

Note: Numbers 1–3 indicate the following: 1 = natural bottinoite crystals (Gandolfi camera with a diameter of 114.6 mm, Ni-filtered Cu$K\alpha$ radiation); 2 = synthetic bottinoite (Philips diffractometer, Fe-filtered Co$K\alpha$ radiation); 3 = Powder data for Ni(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ after Beintema (1936) (Debye-Scherrer camera with an effective radius of $R = 5.742_5$ cm, CuK radiation, Ag as internal standard); d_{obs} calculated from the original θ values using Cu$K\alpha = 1.54178$ Å.
* Reflection overlapped with the 111 Ag diffraction line.

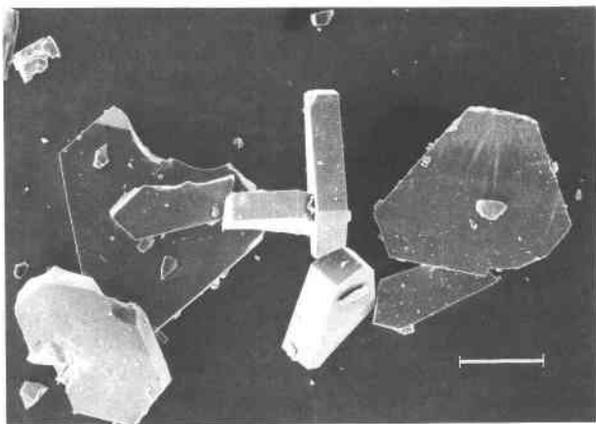Fig. 2. SEM photomicrograph of crystals of synthetic $Ni(H_2O)_6[Sb(OH)_6]_2$. Scale bar equals 100 μm.

and $a = 3.084$ and $c = 4.897$ Å. These values are close to those of brucite $Mg(OH)_2$ ($a = 3.147$, $c = 4.769$ Å, as quoted in PDF card 7-239) and theophrastite $Ni(OH)_2$ ($a = 3.131$, $c = 4.608$ Å, according to Marcopoulos and Economou, 1981). Brucite and theophrastite crystallize in space group $P\overline{3}m1$ and therefore have the mirror planes perpendicular to the edges of the unit cell. Since a_1' and a_2' are perpendicular to a_1^b and a_2^b, respectively, the positions of the symmetry elements are the same in bottinoite and in the brucite-like structures. Therefore, the structure of bottinoite may be expected to be similar to that of brucite. However, the cations in bottinoite would occupy only one-sixth of the octahedral positions, since the ratio of the number of cations to the number of anions in bottinoite is 1:6 instead of 1:2, as in brucite.

PHYSICAL AND OPTICAL PROPERTIES

Tabular crystals of bottinoite are transparent and pale blue-green with a vitreous luster and a very light blue streak; they are nonfluorescent and brittle, and they possess a conchoidal fracture. A density of 2.83(1) g/cm^3 was measured by heavy liquids for synthetic crystals; the determination for the natural material was unsuccessful because of the scarcity and the small size of the crystals. The calculated density for the ideal formula is 2.81 g/cm^3. The microindentation hardness with a 10-g load (VHN_{10}) is 105 kg/mm^2 (range 94–110), corresponding to a Mohs hardness of approximately 3.

Crystals appear to be nonpleochroic, uniaxial with very low birefringence and are optically positive. The indices of refraction, measured in white light using the immersion method, are $\omega = 1.600(10)$, $\epsilon = 1.605(10)$ (natural); $\omega = 1.610(10)$, $\epsilon = 1.615(10)$ (synthetic).

The mean index of refraction calculated from the Gladstone-Dale relationship, using the ideal formula and the constants given by Mandarino (1976), is 1.623. The compatibility indices (Mandarino, 1981) are 0.039 and 0.023 for natural and synthetic material, respectively.

Infrared spectra of natural and synthetic samples mixed with KBr are identical. The spectra show a broad peak at 3450 cm^{-1} caused by OH stretching and a sharp one at 1650 cm^{-1} caused by H-O-H bending of the H_2O molecules. At 1030, 1070, 1100, and 1150 cm^{-1}, there are four peaks caused by Sb-O-H bending (Siebert, 1953); a broad band, probably due to the presence of H bonding, is present at approximately 2200 cm^{-1}. At 600, 620, and 730 cm^{-1}, three strong peaks due to Sb-O stretching (Siebert, 1953) are also present. The Ni-O absorption peaks are masked by the KBr absorption peaks.

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