

MINERALOGY OF THE OXIDES AND CARBONATES OF BISMUTH

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ABSTRACT

The results of a survey of the mineralogy of the natural oxides and carbonates of bismuth are described. Bismutite, supposedly a hydrate, contains only non-essential water and has the composition Bi_2CO_5 . On heating, bismutite and artificial $\text{Bi}_2\text{CO}_5 \cdot n\text{H}_2\text{O}$ lose water gradually to *ca.* 290°C. where the CO_2 is lost and $\alpha\text{-Bi}_2\text{O}_3$ remains. Artificial hydrates of Bi_2CO_5 are not known. Forty-six proven localities for bismutite are cited. Bismutosphaerite and basobismutite are identical with bismutite (which name has priority). Hydrobismutite and normannite are almost certainly identical with bismutite. Waltherite, a carbonate of bismuth of unknown formula, is a distinct species. Monoclinic, with $(110) \wedge (1\bar{1}0) = 116^\circ 34' \pm 20'$; $c_0 = 5.42 \pm 0.05 \text{ \AA}$. The crystals are zoned; mostly optically negative with $2V$ about 75° and dispersion $r < v$; $Y = b = 1.91 \pm$ and $X \wedge c = 16^\circ$. The name beyerite is given to a new bismuth carbonate of unknown formula. Found at Schneeberg, Saxony, and Pala, San Diego Co., California. Beyerite is primitive tetragonal, with $a_0 = 3.78 \pm 0.01$, $c_0 = 21.77 \pm 0.05$; $a_0 : c_0 = 1 : 5.759$. Color yellow (crystals) to white or grayish-green (massive). The crystals are tiny thin plates, tabular (001) and beveled by (111). Optically negative, $\omega = 2.13 \pm 0.02$, $\epsilon = 1.99 \pm 0.02$.

It is proposed to restrict the name bismite to the alpha polymorph of Bi_2O_3 , and the first proven natural occurrence of this material is described. The new name sillenite is given to a body-centered isometric polymorph of Bi_2O_3 found as a secondary product at Durango, Mexico. Fine granular; color, green and olive drab to yellowish; isotropic; the index of refraction is above 2.42; $a_0 = 10.08$. The evidence for the existence of a definite hydrate of bismuth oxide in nature is reviewed, and a probable natural occurrence of $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is described.

X-ray powder spacing data are tabulated for bismite, bismutite, sillenite, beyerite and waltherite.

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INTRODUCTION

The mineralogy of the oxygenated secondary compounds of bismuth, especially the oxides, carbonates, and arsenates, has been a standing problem, largely by virtue of the earthy and often admixed character of the material. The primary concern of the present study has been the identity of the natural oxides and carbonates of bismuth. It became necessary during the course of the work, however, to re-examine almost all of the secondary bismuth minerals. Some of the findings of the latter survey appear in this issue of the Journal.¹

The writer wishes to express his appreciation to a number of persons who were of aid. Professor Harry Berman of Harvard University gave valued assistance throughout the investigation. Dr. E. S. Rittner of the Massachusetts Institute of Technology kindly presented samples prepared by him of the four known polymorphs of bismuth trioxide. Dr. W. F. Foshag and Mr. E. P. Henderson made available much material from the Roebing and other collections of the U. S. National Museum. Professor Paul F. Kerr of Columbia University and Dr. Fred H. Pough of the American Museum of Natural History loaned specimens from the mineral collections under their care. Type analyzed material and other specimens were obtained from the Brush collection of Yale University through the courtesy of Dr. George Switzer. Further study material was available from the collections of Harvard University and other sources. The x -ray spacing data were kindly calculated by Miss Betty Rogers. The spectrographic analyses were made through the courtesy of Mr. J. C. Rabbitt. Due to existing circumstances it seemed advisable to publish the paper even though several projected chemical analyses are not available.

BISMITE

The supposed bismuth oxide, described by Wallerius in 1753, probably was a carbonate. The material analyzed by Lampadius in 1801 and accepted by some as an oxide, definitely appears to have been a carbonate (see Table 1, Column 1). The first real evidence of the occurrence of a bismuth oxide in nature was afforded by an analysis of Suckow in 1848 (Column 2). Later, a complete analysis was reported by Carnot (1874) on material from Meymac, France (Column 3), and analyses of very impure material from Tazna, Bolivia, apparently consisting for the most part of Bi_2O_3 , were reported by Stelzner (1897). A number of additional occurrences have been mentioned but, with one exception,

¹ Frondel, C., New data on agricolite, bismoclite, koehclinite and the bismuth arsenates: *Am. Mineral.*, **28**, 536-540 (1943).

none of these are definitely proven. The orthorhombic morphology attributed to the mineral in Dana's *System* and Hintze's *Handbuch*² is based on measurements of artificial crystals of Bi_2O_3 by Nordenskiöld (1860).

TABLE 1. ANALYSES OF NATURAL Bi_2O_3 (?)

	Bi_2O_3	As_2O_3	Sb_2O_3	Fe_2O_3	CO_2	H_2O	Rem.	Total
1.	86.3			5.2	4.1	3.4		99.0
2.	96.5	1.5		2.0				100.0
3.	96.7	0.13	0.22		0.68	0.95	1.06	99.74

1. *Lampadius* (1801). 2. *Suckow* (1848). *Ullersreuth, Germany*. 3. *Carnot* (1874). *Meymac, France*. Rem. is PbO 0.55, FeO 0.16, SO_3 0.15, HCl 0.20. $S.G. = 9.22$.

Artificial Bi_2O_3 is known through the work of Sillén (1938, 1941) and of Rittner (1942) to exist in four polymorphous modifications: (1) A monoclinic, low-temperature form, $\alpha\text{-Bi}_2\text{O}_3$, which corresponds to the supposed orthorhombic artificial crystals measured by Nordenskiöld. (2) A body-centered cubic form with $a_0 = 10.08$, which apparently requires for its existence a definite impurity content of Si, Al or Fe. (3) A simple-cubic form with $a_0 = 5.525$, and (4) a tetragonal phase with $a_0 = 10.93$, $c_0 = 5.62$ and space group $C4_2b$. Only one of the previously suspected natural occurrences of Bi_2O_3 can be identified as a particular polymorph. This material comprises microscopic crystals described by Rogers (1910) from Rincon, San Diego Co., California, which appear from his data to be $\alpha\text{-Bi}_2\text{O}_3$.

In furtherance of this problem the writer examined 26 specimens from 15 localities, labelled bismite, available from various collections. Unfortunately, none of these proved to consist of Bi_2O_3 ; most were Bi_2CO_3 and the remainder were identified variously as bismuth arsenates and other materials. Later, an authentic natural occurrence of Bi_2O_3 came to hand among a small suite of bismuth minerals from Bolivia. This specimen, from the neighborhood of Colavi, consisted of a large water-worn cobble of native bismuth which was thickly incrustated by a coherent, fine-grained, grayish-green alteration product. The latter substance proved on x -ray powder study to be $\alpha\text{-Bi}_2\text{O}_3$. Confirmatory chemical tests also were made. The x -ray spacing data are given in Table 2 and the pattern is shown in Fig. 1. Optically, the mineral is biaxial with high dispersion and indices above 2.42. Hardness = $4\frac{1}{2}$. The specific gravity, determined on the microbalance on a coarse powder, is 8.64.

² See Hintze, C., *Handbuch der Mineralogie*, Leipzig, 1, [2A], 1246 (1915).

TABLE 2. X-RAY POWDER SPACING DATA FOR BISMITE, SILLENITE, BISMUTITE, BEYERITE AND WALTHERITE

Copper radiation; filtered

Bismite		Sillénite		Bismutite		Beyerite		Waltherite	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
10	3.232	1	4.195	7	6.903	1	5.431	1	5.892
1	2.746	1	3.744	7	3.708	1	3.708	2	5.670
9	2.676	2	3.600	3	3.402	6	3.632	1	5.412
2	2.537	10	3.216	10	2.943	6	3.354	1	5.100
2	2.423	1	3.035	8	2.724	10	2.851	1	4.901
1	2.247	7	2.939	1	2.527	9	2.721	0.5	4.094
1	2.166	8	2.730	4	2.276	2	2.636	1	3.951
1	2.121	1	2.544	1	2.225	1	2.598	2	3.442
1	2.043	2	2.410	8	2.134	1	2.403	2	3.359
7.5	1.951	2	2.274	7	1.936	5	2.178	7	3.240
3	1.909	3	2.171	2	1.857	5	2.148	10	3.108
3	1.873	1	2.140	9	1.745	5	1.913	8	3.035
1	1.760	1	2.099	4	1.715	4	1.892	8	2.722
7.5	1.740	1	2.077	3	1.681	1	1.865	2	2.590
5	1.722	2	2.022	9	1.616	8	1.755	2	2.490
8	1.670	3	1.997	5	1.473	7	1.688	7	2.410
8	1.640	2	1.928	6	1.413	2	1.594	1	2.317
1	1.572	2	1.859	5	1.366	6	1.575	1	2.236
5	1.557	1	1.766	1	1.336	2	1.551	7	2.184
4	1.499	9	1.743	5	1.284	8	1.530	3	2.119
3	1.482	4	1.695	1	1.268	1	1.483	3	2.060
3	1.457	6	1.651	4	1.237	2	1.428	6	2.005
1	1.433	4	1.618	6	1.222	5	1.359	1	1.976
3	1.406	1	1.574	1	1.202	1	1.340	4	1.930
1	1.390	1	1.536	3	1.172	1	1.326	5	1.897
1	1.377	6	1.499	3	1.148	4	1.286	5	1.854
2	1.361	1	1.471	5	1.140	1	1.255	5	1.804
6	1.342	2	1.440	3	1.116	1	1.242	6	1.769
2	1.325	1	1.413	6	1.077	5	1.211	1	1.722
6	1.315	2	1.384	1	1.069	1	1.198	7	1.693
1	1.302	1	1.360	1	1.052	4	1.188	1	1.661
1	1.286	2	1.293	5	1.044	2	1.137	1	1.642
4	1.271	1	1.269	2	1.016	5	1.102	1	1.630
1	1.263	1	1.253	5	0.982	3	1.094	1	1.602
3	1.231	5	1.216	2	0.967	1	1.063	1	1.559
1	1.213	5	1.198	1	0.940	3	1.047	3	1.525
3	1.204	5	1.182	4	0.918	1	1.038	3	1.500
2	1.191	2	1.152	3	0.911	4	1.017	6	1.473
7	1.167	2	1.123	3	0.898	1	1.006	1	1.438
1	1.157	2	1.111	1	0.889	4	0.998	1	1.395
1	1.149	2	1.098	4	0.876	1	0.951	5	1.367
1	1.135	3	1.072	3	0.864	1	0.948	1	1.348
7	1.121	1	1.051	4	0.846	2	0.925	5	1.329
4	1.110	5	1.028	2	0.838	2	0.916	4	1.302
3	1.104	1	1.016	2	0.834	1	0.908	1	1.229
3	1.088	1	1.008			5	0.896	1	1.171
2	1.081	1	0.998			1	0.887	1	1.161
1	1.074	1	0.988			4	0.882	1	1.123
4	1.069	1	0.980			1	0.874	1	1.109
4	1.055	2	0.969			2	0.856	1	1.069
3	1.036	1	0.954			3	0.848	1	1.061

Note: With the exception of bismutite, spacings smaller than the last value given have been omitted from the Table.

Luster sub-resinous to sub-adamantine. Color grayish-green, with a grayish streak; artificial α - Bi_2O_3 is bright yellow in color. According to Sillén (1941) artificial α - Bi_2O_3 is monoclinic, pseudo-orthorhombic, with $a_0 = 5.83$, $b_0 = 8.14$, $c_0 = 7.48$; $\beta = 67^\circ 4'$; contains Bi_8O_{12} in the unit cell; space group $P2_1/c$. The name bismite, originally proposed by J. D. Dana in the 5th (1868) edition of the *System*, may be restricted to α - Bi_2O_3 . An isometric modification of Bi_2O_3 also occurs in nature and is described beyond as a new species, sillenite.

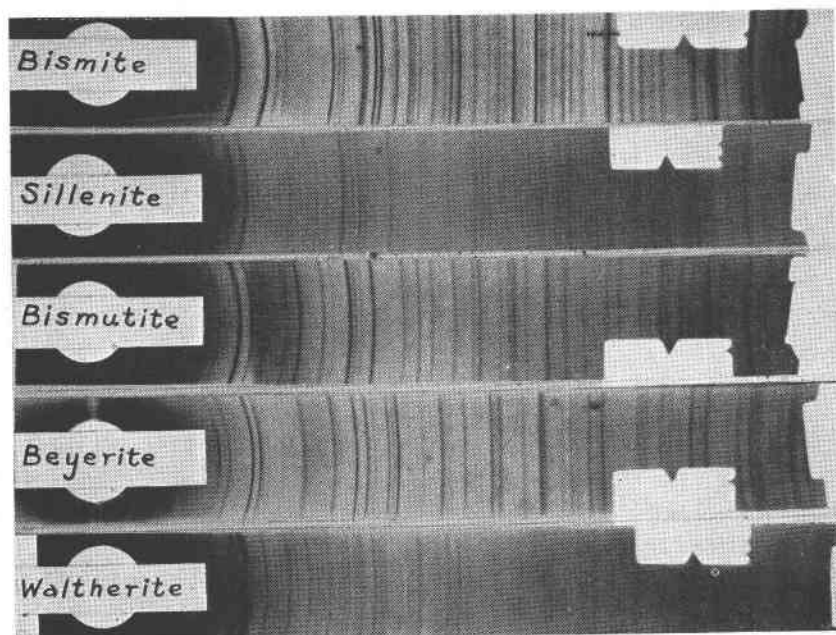


FIG. 1. X-ray powder patterns of bismite, sillenite, bismutite, beyerite and waltherite. Cu radiation.

SILLENITE (New Species)

The body-centered cubic modification of Bi_2O_3 , described by Sillén (1938), was identified in specimens from Durango, Mexico. The mineral occurs as fine-grained granular masses intimately admixed with bismutite. In part the mineral forms waxy masses which closely resemble the bismutite itself. The color is olive-drab to olive-green, gray-green and green; also yellowish-green and yellow. Isotropic. The index of refraction is above 2.42. The color in transmitted light is a rich golden-brown to yellow in thick grains. Sufficient material was hand-picked for x-ray powder study and for spectrographic examinations. The spectro-

graph revealed only Bi in large amount together with traces of Si, Al, Cu, Fe, Ca and other elements. Excellent powder photographs were obtained which corresponded in every respect to the powder data of Sillén and to the pattern of a sample of artificial body-centered Bi_2O_3 prepared by Dr. E. S. Rittner. The x -ray powder spacing data are given in Table 2. Artificial body-centered Bi_2O_3 has $a_0 = 10.08$. The structure has been analyzed by Sillén (1938), who also discusses the rôle played by small amounts of Al and Fe present in artificial material. The calculated specific gravity for the cell contents $\text{Bi}_{24}\text{O}_{36}$ is 8.80. The name sillenite is proposed for the species after Dr. Lars Gunnar Sillén of Stockholm, who has contributed much to the knowledge of the polymorphs of Bi_2O_3 .

BISMUTH HYDROXIDE

A number of artificial hydrates of Bi_2O_3 have been reported, but the dehydration and x -ray study of Hüttig, Tsuji and Steiner (1931) of the system $\text{H}_2\text{O}-\text{Bi}_2\text{O}_3$ indicates that only the compound $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = \text{Bi}(\text{OH})_3$ exists. Their data, however, suggest that their compound is not the trihydrate but a dihydrate, and this view is accepted by Weiser (1935). No evidence was found by Hüttig, et al., or by Carfield and Woodward (1924) of the existence of $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O} = \text{BiO}(\text{OH})$. This compound might be the end member of the isomorphous series between bismoclite, BiOCl , and daubreite, $\text{BiO}(\text{OH}, \text{Cl})$.

The existence in nature of a bismuth hydroxide, or hydrated oxide, was first indicated by the work of Schaller (1911) on the bismuth ochers from San Diego Co., California. An analysis by Schaller of material from the Stewart mine conforms fairly well with the formula $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, after the deduction of 26 per cent of hydrous impurities. Nevertheless doubt must be attached to this evidence because of the extremely small size of the analyzed sample (95 mg.), and of the uncertain assumptions made as to the nature of the impurities. An x -ray and dehydration study of this substance would be desirable, but no further material can be had. The occurrence in nature of a bismuth hydroxide also has been mentioned by Nenadkevich (1917) and Mountain (1935) but details are lacking.

In the course of the present work, a further occurrence of a substance possibly identical with $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was noticed. This material comprised creamy-white to yellow-layered, earthy crusts formed by the alteration of bismite ($\alpha\text{-Bi}_2\text{O}_3$) from Colavi, Bolivia. Chemical tests indicated the substance to contain only Bi_2O_3 and H_2O . A water determination gave 9.2 per cent H_2O , which compares to the 10.4 per cent H_2O contained in $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. However, no evidence is available to indicate

whether the water is essential or not. The dehydrated material gave the x -ray pattern of α - Bi_2O_3 . The fresh material gave an extremely faint and diffuse pattern which differed from those of the four polymorphs of Bi_2O_3 . The pattern could not be identified with the x -ray pattern of the compound $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, as represented by Hüttig, Tsuji and Steiner (1931). The x -ray data of these authors are given in such form, however, as to preclude any exact comparison. Artificial $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was prepared according to the procedure described by Hüttig, et al., but unfortunately this preparation did not give an x -ray pattern. Efforts to develop a pattern from both the natural and the artificial substances by heating resulted only in the gradual appearance of the pattern of α - Bi_2O_3 . Optically, the natural material was very fine grained, seemingly isotropic, and of high index. The present data is not sufficient to establish the substance as a definite species.

BISMUTOSPHAERITE

Bismutosphaerite was first formally described and named by Weisbach in 1877. The mineral occurred as fibrous crusts with a spheroidal surface (to which the name alludes) at Neustädtel, near Schneeberg, Saxony. The same mineral had earlier been recognized by Beyer in 1805 and by Breithaupt in 1817. Weisbach examined the original specimens kept in Werner's collection. The analysis cited by Weisbach in the original description and later analyses³ of material referred to this species all conform closely to the formula Bi_2CO_5 . The original analyzed specimens of the material from Mexico, analyzed by Winkler (cited by Weisbach (1882)), and of material from Willimantic and Portland, Connecticut, analyzed by Wells (1887), were available for examination, together with seven non-type specimens of the fibrous, spheroidal mineral from Schneeberg. X -ray powder diffraction study proved the identity of this material with analyzed artificial Bi_2CO_5 and with bismutite. It is shown beyond that the mineral bismutite, which has been thought to be a definite hydrate, actually contains only non-essential water and is identical in all respects with artificial anhydrous Bi_2CO_5 , and with bismutosphaerite. The name bismutite, proposed by Breithaupt in 1841, has priority.

BISMUTITE

The name bismutite was given by Breithaupt in 1841 to a bismuth mineral from Ullersreuth, Voightland, Germany. Qualitative chemical and blowpipe tests by Plattner, cited in the original description, indicated that the substance was a carbonate of bismuth containing small

³ Listed by Hintze, C., *Handbuch der Mineralogie*, Leipzig, 1, [3A], 3403 (1929).

amounts of iron and copper as impurities, together with an extremely small amount of water. The water was ascribed by Breithaupt to admixed hydrous impurities. Schneeberg, Johanngeorgenstadt, and Aue, in Saxony, were cited as additional localities. The later usage of the name has been very indefinite in lack of characterizing crystallographic, chemical and physical data. In practice, the name appears to have been applied arbitrarily to bismuth carbonates that contained an apparently significant amount of water. Material with little or no water has been ascribed to bismutosphaerite. The conception that bismutite is hydrated dates from the first quantitative analysis, made by Rammelsberg (1849) on material from North Carolina, but this definitely is not the sense of the original description. The available analyses⁴ are loosely grouped about the ratio $\text{Bi}_2\text{O}_3:\text{CO}_2=1:1$. Ordinarily from 1 to 3.5 per cent of water is present. A few analyses correspond to the formula $\text{Bi}_2\text{CO}_5 \cdot \text{H}_2\text{O}$, which requires 3.31 weight per cent H_2O , but this must be regarded in light of the findings to be described below, to be due only to chance. Many of the analyses were made on impure material.

Material from 46 different localities, comprising about 70 specimens variously labeled bismutite or bismuth ocher, were available for examination. Several specimens from analyzed localities were represented. Suites of secondary bismuth ores from deposits near Hillside, Arizona, and near Tularosa, New Mexico, also were studied. These specimens without exception gave an x -ray powder diffraction pattern which was completely identical with that of artificial Bi_2CO_5 and of bismutosphaerite (Bi_2CO_5). The original specimens of Breithaupt's bismutite were not available, but three of the four original localities were represented. Dehydration data for two artificial preparations of $\text{Bi}_2\text{CO}_5 \cdot n\text{H}_2\text{O}$ and for two natural bismutites are given in Fig. 2. The water is lost continuously up to about 290°C ., where the CO_2 is lost abruptly and $\alpha\text{-Bi}_2\text{O}_3$ remains.⁵ The available evidence indicates that bismutite has the composition Bi_2CO_5 , and is not a hydrate but contains only non-essential water. The relatively large content of adsorbed and capillary water is not surprising in view of the fine-grained, earthy, or gel-like character and often metacolloidal origin of the mineral. A list of the localities for bismutite, proven by x -ray study, is given in Table 3. The x -ray powder data are given in Table 2 and Fig. 1. Bismutite is the only common carbonate of bismuth. The others—beyerite, bokspitite and waltherite—are extremely rare.

⁴ Listed by Hintze, C., *Handbuch der Mineralogie*, Leipzig, 1, [3A], 3406 (1929).

⁵ The ignition product in these and similar experiments was identified by its x -ray pattern as $\alpha\text{-Bi}_2\text{O}_3$, but the writer has been informed by Dr. E. S. Rittner that the tetragonal modification of Bi_2O_3 sometimes is formed.

TABLE 3. PROVEN LOCALITIES FOR BISMUTITE

United States

Anderson Apache mine, Hachita, New Mexico.
 Casher's Valley, Jackson Co., North Carolina.
 Gaston Co., North Carolina.
 The Granites, near Bagdad copper mine, 30 miles west of Hiliside, Yavapai Co., Arizona.
 Mostly pseudomorphous after bismuthinite.
 Salida, Chaffee Co., Colorado.
 Las Animas, La Plata Co. (?), Colorado. After bismuthinite.
 Telluride, San Miguel Co., Colorado.
 Maricopa Co., Arizona.
 Lillian mine, Leadville, Colorado. Alteration of bismuth sulfosalts.
 Petaca, New Mexico. In pegmatite.
 Mohave Co., Arizona.
 Eagle Station, Sierra Co., New Mexico.
 Grand View claim, San Andreas Mtns., west of Tularosa, New Mexico.
 Pioneer claim, San Andreas Mtns., New Mexico.
 30 miles west of Tularosa, New Mexico.
 Mammoth mine, Tintic, Utah.
 Hales Quarry, Portland, Connecticut. In pegmatite after bismuthinite.
 Willimantic, Connecticut.

South America and Mexico

El Casse, Durango, Mexico. Alteration of native bismuth.
 El Carmen mine, Durango, Mexico. In part after native bismuth.
 Unspecified locality in Durango, Mexico.
 Guanajuato, Mexico. After an unidentified tetragonal mineral.
 San Luis Potosi, Mexico.
 Sao Jose de Bryamba, Minas Geraes, Brazil.
 Itabira de Matto Grosso, Brazil. After bismuthinite.
 Huarancaca, Peru.
 Pueblo Viejo, Esmoraca, Bolivia. After bismuthinite.
 Carmen mine, Huanya, Potosi, Bolivia. After native bismuth.
 Santa Vela Cruz, near Pongo, Bolivia.
 San Baldomero mine, Sorata, Bolivia. After bismuthinite.
 Tazna, Bolivia. Specimens from several different places in this district; mostly an alteration of bismuthinite.
 Isca-Isca, Bolivia. Alteration of native bismuth.
 La Reforma, Chorolque, Bolivia. Alteration of bismuthinite.
 Espiritu Santo, Chorolque, Bolivia. After bismuthinite.

Other Localities

Kingsgate, New South Wales.
 Ukalunda, Queensland.
 Schorl Mtn., Transbaikalia, Russia. After bismuthinite(?)
 Beresov, Urals, Russia. After aikinite (?)
 Ampangabe, Madagascar.
 Meymac, France.

Restormel mine, Cornwall, England. Another specimen from an unspecified locality in Cornwall.

Tavistock, Devonshire, England.

Aue, Saxony. After bismuthinite.

Joachimsthal, Bohemia.

Ullersreuth, Voightland, Germany. After bismuthinite.

Schneeberg, Saxony. A suite of 11 specimens from various mines in this district.

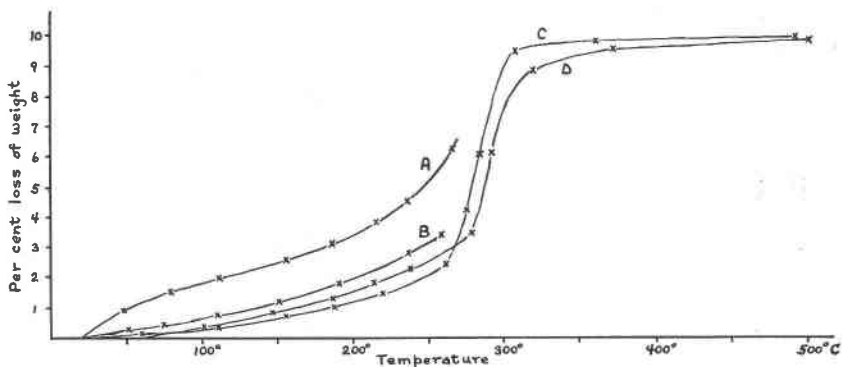


FIG. 2. Dehydration data for $\text{Bi}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$. A. Artificial $\text{Bi}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$. Precipitated by conc. ammonium carbonate at 13°C . Air dried at room temperature. B. Natural bismutite. Semivitreous material from Eagle Station, New Mexico. Contains 3.8 per cent H_2O . C. Artificial " $\text{Bi}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ " of Lefort (1848). Air dried at room temperature. D. Natural bismutite. Earthy, straw colored. Tazna, Bolivia. All determinations made by heating to constant weight.

Physical Properties of Bismutite. Distinct crystals of bismutite have not been found. The mineral occurs as pulverulent to dense and hard earthy masses, as opaline crusts, and as radially fibrous crusts or spheroidal aggregates; rarely as lamellar, pearly, aggregates. Bismutite often possesses a prismatic or other pseudomorphous structure. The hardness ranges up to $3\frac{1}{2}$ in material tested by the writer, but values up to $5\frac{1}{2}$ have been cited. The specific gravity is quite variable. The values given in the literature range for the most part between 6.8 and 7.67. The writer obtained the following values for the specific gravity, using a micro-balance:

6.61 (Meymac, France)	6.95 (Petaca, N. M.)
6.74 (San Andreas Mtns., N. M.)	7.24 (Willimantic, Conn.)
6.77 (Hillside, N. M.)	7.33 (Mohave Co., Arizona)

The color of the mineral is variously straw- to brownish-yellow and citron-yellow (the most common colors), brown, green, white, greenish-gray, gray; rarely bluish-green or blue. The blue tint was found in several instances to be caused by included malachite, and in one instance to mixite. Sometimes deep gray to black in color, especially in the interior

portions of pseudomorphs after bismuthinite. Under the microscope, bismutite ordinarily appears as indistinctly polarizing cryptocrystalline grains. The mean index is quite variable and ranges from below 2.12 to above 2.30. The birefringence appears to be moderately large and is estimated by Larsen (1921) at about 0.05. Fibrous material usually has parallel extinction and positive elongation. There appears to be a good cleavage, with an optic axis perpendicular thereto.

Artificial Hydrous Bismuth Carbonate. Two artificial carbonates of bismuth have been reported: the anhydrous compound Bi_2CO_5 , and a hydrate $\text{Bi}_2\text{CO}_5 \cdot \text{H}_2\text{O}$. The synthesis of the latter compound, reported by Lefort (1848), was duplicated and the substance was found on *x*-ray and dehydration study (Fig. 2) to be only Bi_2CO_5 with adsorbed and capillary water. The precipitates obtained by adding solutions of alkali, or ammonium carbonates, or of alkali bicarbonates to bismuth nitrate solutions, together with commercial, C.P., preparations of bismuth sub-carbonate or basic-carbonate, all proved on *x*-ray study to be identical with anhydrous Bi_2CO_5 . The air-dried precipitates ordinarily contain up to several per cent of loosely held water. The freshly prepared carbonate often gives a rather diffuse and faint *x*-ray pattern, which becomes sharp after ageing in the mother-liquid, or after slight heating. The particle size and water content of the material is noticeably influenced by the concentration of the reagents and especially by the temperature. The dehydration curve of an air-dried sample of a highly voluminous and hydrous precipitate obtained with ammonium carbonate at 13° is shown in Fig. 2.

HYDROBISMUTITE

This name was given by Nenadkevich (1917) to a supposed hydrated bismuth carbonate, $\text{Bi}_2\text{CO}_5 \cdot 2\text{--}3\text{H}_2\text{O}$, from Transbaikalia, Russia. Specimens were not available for study. The material was thought to differ from bismutite in containing more water. It is practically certain that this substance is merely bismutite containing a relatively large amount of non-essential water.

BASOBISMUTITE

The above name was given by Nenadkevich (1917) to a supposed hydrated bismuth carbonate, $\text{Bi}_4\text{CO}_8 \cdot \text{H}_2\text{O}$, found as gray, earthy masses on Schorl Mtn., Transbaikalia, Russia. Analysis gave: Bi_2O_3 94.49, CO_2 4.07, H_2O 1.43, Cl 0.12; total 100.11. A type specimen obtained by the U. S. National Museum by exchange was available for study. *X*-ray study proved the mineral to be identical with bismutite. Optically, the material was very fine-grained and impure.

NORMANNITE

A name that was given in a manuscript by Weisbach in 1877 to an ill-characterized brownish bismuth carbonate, supposedly $\text{Bi}_6\text{CO}_{11}$, found in spheroidal aggregates at Neustädtel, near Schneeberg, Saxony (see Tetzner and Edelmann (1926)). It seems likely that this material is

identical with that from the same locality described under the name bismutite by Weisbach in 1880, inasmuch as the analysis there cited yields the formula $\text{Bi}_6\text{CO}_{11} \cdot \text{H}_2\text{O}$. In any case, this substance, as remarked by Schairer (1930), presumably is identical with Bi_2CO_5 , bismutite.

BOKSPUTITE

The name boksputite was given by Mountain (1935) to a carbonate of lead and bismuth, $\text{Bi}_2\text{Pb}_6\text{C}_3\text{O}_{15}$, from Boksput, in Gordonia, Cape Province, South Africa. The mineral occurs as fine-grained, yellow masses. Hardness $3\frac{1}{2}$; specific gravity 7.29. The material has a slightly pearly luster apparently due to a cleavage or a scaly habit. X-ray powder photographs are stated to be distinctive, but no spacing data are given. Specimens of this apparently distinct species could not be obtained for examination. Genth (1892) cited analyses of a bismuth carbonate from Colorado which show 4.6-5.0 per cent PbO , but the lead clearly appears to be due to admixture.

BEYERITE (New Species)

The new species here described was first found as pulverulent earthy masses and drusy crystals on specimens from Schneeberg, Saxony, and was later recognized in massive earthy form on a specimen from Pala, San Diego Co., California. The material from Schneeberg comprised sparkling rectangular plates up to 0.5 mm. in size scattered over chalcidonic quartz and bismutite. The tetragonal crystals are extremely thin plates flattened on (001), and are commonly grouped into subparallel aggregates or rosettes. The plates are bounded laterally by two equivalent line faces from which accurate measurements could not be obtained. The measured ρ values varied between $81^\circ 55'$ and $79^\circ 25'$ with an average value of $81^\circ 32'$; this value corresponds to the value $81^\circ 17'$ for (111) in the x-ray structural cell. A crystal drawing is shown in Fig. 3. The mineral ordinarily is in the form of distinct crystals, but sometimes forms soft, white, microcrystalline masses. One specimen exhibited compact earthy pseudomorphs of yellow beyerite after embedded cubic crystals of smaltite (?). Entirely satisfactory Weissenberg and rotation x-ray data could not be obtained due to the markedly imperfect character of the crystals. Approximate cell dimensions were obtained from rotation films taken about [001], [100] and [101], and these were refined by Weissenberg 0-layer measurements, as follows:

$$a_0 = 3.78 \pm 0.01 \quad c_0 = 21.77 \pm 0.05; \quad a_0 : c_0 = 1 : 5.759$$

The following data also were obtained: symmetry, tetragonal centrosymmetrical, D_{4h} ; space lattice type, primitive; 00 l present only when $l = 2n$. Cu radiation was employed.

The observed specific gravity, measured by the microbalance on massive material from California, is 6.56. The x -ray powder spacing data are given in Table 2 and the pattern shown in Fig. 1. No cleavage was observed. The hardness is 3 or less. Color, bright yellow to lemon-yellow (crystals) and, in massive material, yellowish-white to white (Schneeberg) or grayish-green to gray (California). Streak white. Luster vitreous. Optically, uniaxial negative (-). The indices were determined in phosphorus-methylene iodide and sulfur-selenium melts as: $\omega = 2.13 \pm 0.02$, $\epsilon = 1.99 \pm 0.02$. Some crystals have an anomalous biaxial character with very small $2V$. Not pleochroic. The indices ($\omega = 2.13$, $\epsilon = 1.94$) given by Larsen (1921) for platy yellow crystals labeled bismutosphaerite from Schneeberg, doubtless refer to this species. Beyerite occurs at the Stewart mine, Pala, California, as compact masses of a greenish-gray color embedded in massive quartz. Here the mineral appears to be an alteration product of a primary bismuth mineral in the pegmatite.



FIG. 3

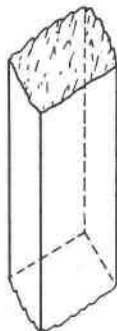


FIG. 4

A spectrographic examination of a small, handpicked sample of the crystals from Schneeberg revealed the presence of Bi and a lesser amount of Ca together with traces of Si, Al, Mn, Pb, Mg, Cd and Cu. The mineral effervesces briskly in dilute HCl. An unnamed mineral from Schneeberg very briefly described by Arzruni and Thaddéeff in 1899 is almost certainly identical with beyerite. The mean of two partial analyses by Thaddéeff on very small samples, after deducting quartz 8.33 and Fe_2O_3 1.50 per cent, is Bi_2O_3 90.0, CaO 3.5, CO_2 4.6, H_2O 1.0; total 100.0. Beyerite appears to be a carbonate of bismuth and calcium, but a definite formula must await a new analysis. A possibly similar mineral from Argentina was analyzed by Bodenbender (1899).

The name beyerite is proposed for this well-defined new species after Adolph Beyer (1743-1805), a mining engineer and mineralogist of Schneeberg, Saxony, who in 1805 recognized the occurrence of a bismuth carbonate in nature. Beyer's mineral was later shown by Weisbach (1877) to be bismutite, Bi_2CO_3 .

WALTHERITE

This little known mineral was briefly described in 1857 by Vogl as a bismuth carbonate found in thin prismatic crystals associated with torbernite, at Joachimsthal, Bohemia. The color was described as siskin-green to clove-brown, and the luster as vitreous. On the basis of a qualitative examination by Lindacker (cited by Vogl) the mineral was believed to contain Bi_2O_3 , CO_2 , H_2O , and silica. Later, Bertrand (1881) examined specimens of waltherite and recognized two apparently distinct minerals: (1) A brown mineral with a prism angle of 116° and cleavages parallel to $\{110\}$, $\{010\}$ and $\{001\}$. Optically positive, with $X=c$, $Y=b$ and $Z=a$. (2) A green mineral not as easily cleavable as the first, optically negative, with the acute bisectrix, instead of the obtuse bisectrix, perpendicular to the best cleavage.

Several non-type specimens labeled waltherite from Joachimsthal were available for study. These exhibited a few tiny, imperfect, crystals of a brownish prismatic mineral which reacted qualitatively for Bi and CO_2 . The x -ray powder pattern and optical constants of this mineral are distinct from those of the other bismuth minerals, and there appears to be no question but that waltherite is a distinct species. The x -ray spacing data are given in Table 2 and the pattern shown in Fig. 1. The color of the mineral ranges from dark olive-drab to brownish-green, and often passes inwardly into a yellowish-green. The apical portions of some crystals are deep brown. The luster is sub-resinous to vitreous. Hardness about 4. The specific gravity was determined by means of the microbalance on 17 mg. of coarse powder as 5.32—a value which seems low in view of the composition of the mineral. The crystals are doubly terminated and are monoclinic in appearance, as shown in Fig. 4. The terminal form is too rough to measure and only an approximate value, $116^\circ 34' \pm 20'$ could be obtained for the prism. An x -ray rotation photograph taken with Cu radiation gave the $[001]$ period as $5.42 \pm 0.05 \text{ \AA}$. Crushed crystals yield both brown and green grains with rather unlike optical properties. The brownish material is biaxial negative with $2V$ about 75° and has strong birefringence. $Y=b=1.91 \pm$ and $X \wedge c = 16^\circ$; dispersion $r < v$. Weakly pleochroic in brown with absorption $X=Y < Z$. Most of the greenish material has higher indices and stronger birefringence. A few grains had $2V$ up to 90° and others were optically positive with dispersion $r > v$. The x -ray powder patterns of the green and brown materials are identical.

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