

BISMUTOFERRITE, CHAPMANITE, AND "HYPOCHLORITE"*

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ABSTRACT

Bismutoferrite, $\text{Bi}(\text{OH})\text{Fe}_2(\text{SiO}_4)_2$ or $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ in substantial agreement with Frenzel's (1871) $\text{Bi}_2\text{Fe}_4\text{Si}_4\text{O}_{17}$, occurring as a yellow powder associated with bismuth ores at Schneeberg, Saxony, and nearby localities, gives a unique x-ray diffraction pattern and consistent chemical analyses. It is therefore to be considered a valid mineral species. The term "hypochlorite" has been used for a green mixture of bismutoferrite with quartz and chalcedony. The original analysis in 1832 was of such material; the first analysis of reasonably pure bismutoferrite was by Frenzel in 1871. A substance also termed "hypochlorite" was found at Bräunsdorf, Saxony, but it contains antimony instead of bismuth. Recognition of the composite character of "hypochlorite" and uncertainty as to whether it contained bismuth or antimony or both, with failure to accept Frenzel's work as valid, have until now left the status of bismutoferrite and "hypochlorite" dubious. Data presented here establish chapmanite (Walker, 1924) as the antimony analogue of bismutoferrite. Recognition of the proper valence states of antimony and iron (both three) in chapmanite leads to a correct interpretation of the formula from the original analysis. Bismutoferrite and chapmanite therefore form a homologous and presumably isostructural group of two valid species; the name "hypochlorite," which has been used to designate a characteristic mixture of either of these minerals dispersed in quartz or chalcedony, may well be discarded.

HISTORICAL

"Hypochlorite" was the name given by Schüler (1832) to a highly siliceous bismuth-bearing yellow-green material from Schneeberg, Saxony. Dana (1870) summarized the original account as follows: "minute crystalline, also earthy: H=6, G-2.9-3.04. Color green, streak light green, brittle, fracture even to flat conchoidal," and he cites an analysis (Table 3, A). Schüler is quoted by Frenzel (1871) as saying that "hypochlorite" occurs rarely; associated with quartz, chalcedony, bismuth, cobaltite, and arsenopyrite in veins in shale at Schneeberg; with quartz, bismuth, galena, and silver ores in mica schist at Johanngeorgenstadt; and with quartz and pyrite in mica schist at Bräunsdorf near Freiberg.

Frenzel states that Schüler's analysis was forthwith considered to be of a mixture, the question being raised by the editor of the journal that published Schüler's paper; and this view was concurred in by Dana (1868), Breithaupt (1871), and H. Fischer (1870), who pronounced it to be microscopically a mixture of three substances, namely, quartz, an opaque green substance as the most abundant constituent, and radial

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spheroidal aggregates of brown needles. (The "opaque green substance" presumably was the "hypochlorite" proper, and the brown needles possibly goethite.)

A few years after Schüler's report on (bismuth) "hypochlorite," a paper by Kersten (1844) appeared, giving an analysis of the "hypochlorite" from Bräunsdorf ("Neu Hoffnung Gottes") in which he found antimony, but no bismuth. This apparent conflict with the earlier work may well have contributed to the misgivings which became associated with these substances.

In 1871, Frenzel carefully reviewed the status of "hypochlorite" and proposed the name bismutoferrite for what he considered a valid species (correctly, in our opinion); and he clarified the ambiguous relationships of "hypochlorite" and "antimony-hypochlorite." He suggested the existence of an antimony compound "isomorphous" with bismutoferrite. The following year, in 1872, Frenzel further discussed "hypochlorite," in particular the early work of Kersten on the Bräunsdorf antimony-"hypochlorite." He cites Kersten's analysis (Table 5, H) and notes its essential agreement with his own (Table 5, I, J, K). Concerning bismutoferrite, he says that beyond doubt it must be considered as a valid mineral species. He refers again to his observations (1871) that the bismutoferrite which he analyzed (Table 3, D) contained crystals too small for precise observations, but which were apparently monoclinic.

We may observe here that our own work, almost a century later and with modern tools available, fully confirms that of Frenzel, and we agree that bismutoferrite is entitled to species rank and that the antimony-"hypochlorite" is indeed the antimony analogue of bismutoferrite dispersed in quartz or chalcedony. Further, as will be shown, the substantially pure antimony compound has been known since 1924 as chapmanite (Walker, 1924) from Ontario. Antimony-"hypochlorite" has also been found in Alaska by W. T. Schaller, U. S. Geological Survey (personal communication). Chapmanite with quartz (antimony-"hypochlorite") also occurs with sulfide ore from Velardeña, Durango, Mexico.

Nevertheless, Frenzel's contemporaries and successors were not convinced of the validity of his work, and bismutoferrite and "hypochlorite" have been consigned to the limbo of discredited species or mixtures. Thus Dana (1892) refers to Schüler's "hypochlorite" as "beyond doubt a mixture," and to Frenzel's bismutoferrite as a "supposed bismuth iron silicate." Doelter (1917) notes that bismutoferrite is a mixture, like "hypochlorite." Ramdohr (1936) lists bismutoferrite as an obsolete term for a mixture of bismuth and iron minerals, and "hypochlorite" similarly. Hey (1950) refers to "hypochlorite" as "very doubtful; probably a mixture," and lists bismutoferrite in small type, that is, not of species rank.

In 1924, Walker described an "olive-green" powdery mineral from South Lorraine, Ontario, whose composition was given as $5\text{FeO} \cdot \text{Sb}_2\text{O}_5 \cdot 5\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and which he named chapmanite. Except for ferrous instead of ferric iron and other minor variations, this formula is not greatly different from that of bismutoferrite, $2\text{Fe}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. From the extremely close similarity of the *x*-ray diffraction patterns (Table 6), the calculations of average index of refraction by Gladstone and Dale's law as given below, and critical review of the original Walker-Todd analysis of chapmanite, it will be shown that bismutoferrite is homologous (isostructural?) with chapmanite. Although chapmanite has been accepted as a recognized species, its relationships have not been known, nor has it been reported until now from any locality except the original Ontario source. Walker's formula, as will be shown, is erroneous, and because of this the relationship between bismutoferrite and chapmanite has gone unrecognized.

MATERIAL STUDIED AND ACKNOWLEDGMENTS

At the suggestion of Clifford Frondel, of Harvard University, we have restudied all available material labeled bismutoferrite, chapmanite, and "hypochlorite," (as well as stibiaferrite,¹ (Goldsmith, 1873) and jujuyite,² (Ahlfeld, 1948) both of which have been found to be unrelated to this present study). To him and to George Switzer, of the United States National Museum, and Brian Mason, of the American Museum of Natural History, New York City, all of whom supplied the specimens studied, we express thanks. Michael J. Milton studied the specimens by the *x*-ray fluorescence method (Adler and Axelrod, 1956) in the U. S. Geological Survey. Robert G. Coleman and Alfred H. Truesdell, also of the Geological Survey helped greatly in the purification of the analyzed sample of bismutoferrite, in particular by removal of microscopic particles of sulfides through the use of the Mayeda flotation cell (Kerr, 1950).

The 30 specimens labeled "hypochlorite" or bismutoferrite from the three Museum collections that were examined fall into four groups, as follows:

Group I contains more or less pure bismutoferrite, all from Saxony.

Group II contains bismutoferrite dispersed in quartz or chalcedony, that is, "bismuth hypochlorite"—all from Saxony.

Group III contains chapmanite dispersed in quartz or chalcedony:

¹ Stibiaferrite has been studied by Vitaliano and Mason (1952) and found to consist of wulfenite, bindheimite, and jarosite in quartz.

² Jujuyite also studied by Brian Mason (personal communication 1957) is tripuhyite and quartz.

that is, antimony "hypochlorite"—all from Saxony except one from Mexico and one from Hungary.

Group IV is a miscellaneous lot of mislabeled specimens mostly nontronite, only one of which is reported as from Saxony.

Others specimens from the National Museum labeled chapmanite included three more or less pure chapmanites from Ontario; and one from Alaska, termed "hydrous ferrous antimonate" (W. T. Schaller) which has been identified as essentially antimony "hypochlorite" or chapmanite dispersed in silica. Two others labeled chapmanite from Ontario from the American Museum of Natural History collections are also chapmanite from the type Ontario locality.

Group I. *Bismutoferrite*

Table 1 lists specimens identified as bismutoferrite. All of these are either soft, bright yellow and powdery, or hard and green; all tested (by x -ray fluorescence) are essentially compounds of bismuth and iron (and silica, not detectable by the x -ray spectrographic methods used), and have at most traces of antimony; eight are from Schneeberg, and one from Ullersreuth; none is from Bräunsdorf. A consistent x -ray diffraction pattern (Table 6) was obtained from the six of these so examined. Chemical analysis (Table 3, C) gave a reasonable formula, $\text{Bi}(\text{OH})\text{Fe}_2(\text{SiO}_4)_2$, in striking agreement with the older analyses (Table 3, D and E) on which Frenzel based the species bismutoferrite.

Group II. *Bismuth-"hypochlorite" (Quartz and bismutoferrite)*

In Table 1, Bismutoferrite, it will be noted that Harvard 47001 is represented by three x -ray diffraction patterns, two of "hard green" material, one of "soft yellow," the former identified as quartz and more or less bismutoferrite. By x -ray fluorescence all three spindles show major bismuth and iron, and no antimony. In this specimen both types of material are present in sharply defined areas. Material of the same nature, but more easily recognized as essentially drusy quartz, is present in the five specimens listed in Table 2.

Chemical analyses substantiating the x -ray fluorescence are given in Table 3: Schüler's original analysis of "hypochlorite" (A and B) and Frenzel's (F).

Group III. *Antimony-"hypochlorite" (Quartz and chapmanite)*

So far, all the substances described have been bismuth minerals, essentially pure or admixed, with no antimony. We now come to a group of eight specimens listed in Table 4, Group III, very much alike, all char-

TABLE 1. GROUP I—BISMUTOFERRITE

Specimen	Labeled	Locality	X-ray Film	Identification	Composition (X-ray fluorescence)		Remarks
					Major	Minor	
U.S.N.M. R3998	Bismutoferrite-hypochlorite	Schneeberg	11432	Bismutoferrite	Bi, Fe	As	
U.S.N.M. C3306	Bismutoferrite	Schneeberg			Bi, Fe	As, Sb trace	
U.S.N.M. 93338	Bismutoferrite	Schneeberg			Bi, Fe	As, Sb trace	
U.S.N.M. 16698	Hypochlorite	Ullersreuth	11441, 11198	Bismutoferrite and bismutite	Bi, Fe	As trace	
U.S.N.M. R9803	Hypochlorite with bismuth	Schneeberg			Bi, Fe		Similar to others; not further studied
Harvard 46981	Hypochlorite	Schneeberg	8957	Bismutoferrite and trace of unidentified	Bi, Fe		
Harvard 46981	Hypochlorite	Schneeberg	8912	Bismutoferrite	Bi, Fe	As	Chemical analysis; soft yellow
Harvard 10880	Hypochlorite with bismuth, etc.	Schneeberg	8921	Bismutoferrite	Bi, Fe	As	This and the following are two fragments of (originally) a single specimen
Harvard 47011	Hypochlorite	Schneeberg	8919	Bismutoferrite	Bi, Fe	As	Hard Green
Harvard 47001	Hypochlorite	Schneeberg	8923	Quartz and bismutoferrite	Bi, Fe	As	Hard Green
Harvard 47001	Hypochlorite	Schneeberg	11431	Quartz and less bismutoferrite			Hard Green
Harvard 47001	Hypochlorite	Schneeberg	11430	Bismutoferrite			Soft Yellow

TABLE 2. GROUP II BISMUTOFERRITE DISPERSED IN SILICA (BISMUTH-"HYPOCHLORITE")

Specimen	Labeled	Locality	X-ray Film	Identification	Composition (X-ray fluorescence)			Remarks
					Major	Minor	None	
Harvard 47031	Hypochlorite	Gersdorf	8915, 11439	Quartz, with a little bismutoferrite	Bi, Fe	—	Sb, As	Thin section studied Locality questioned,
U.S.N.M. C3307	Hypochlorite	Schneeberg			Bi, Fe	As	Sb	Thin section studied
U.S.N.M. 12815	Hypochlorite	Ullersreuth						Thin section studied
Am. Mus. Nat. Hist. 12573	Hypochlorite	Schneeberg	11931	Quartz and bismuto- ferrite				With bismuth sulfides
Harvard 274	Hypochlorite	Schneeberg						Thin section studied

The last (Harvard 274) showed in thin section extremely minute prismatic (?) crystals in dense aggregates (Fig 1). Thin sections of Harvard 47031 and U.S.N.M. C3307 were similar.

TABLE 3. CHEMICAL ANALYSES "HYPOCHLORITE" (BISMUTH) AND BISMUTOFERRITE

	A	B	C	D	E	F	G
Bi ₂ O ₃	13.02	13.08	42.5	43.26	42.83	4.76	44.65
Al ₂ O ₃	14.65	14.65	.3	—	—	—	—
SiO ₂	50.24	50.34	23.9	23.08	24.05	88.45	23.02
FeO	—	—	1.8	—	—	—	—
Fe ₂ O ₃	10.54	10.54	29.3	33.33	33.12	6.00	30.60
Sb ₂ O ₃	—	—	—	—	—	—	—
P ₂ O ₅	9.62	9.62	—	—	—	—	—
As ₂ O ₃	—	—	.08	—	—	—	—
H ₂ O ⁺	—	—	1.8	—	—	—	1.73
SO ₃ MgO MnO	trace	—	—	—	—	—	—
Sp. gr.	98.07	98.23	99.7 >3.3	99.67 4.47	100.00	99.21	100.00

- A. "Hypochlorite," Schneeberg, G. Schüler, analyst (Schüler, 1832), as cited in Dana, 3rd Ed. (Dana, 1870).
- B. "Hypochlorite," Schneeberg, G. Schüler, analyst (Schüler, 1832), as cited by Frenzel (Frenzel, 1871).
- C. Bismutoferrite, Schneeberg, Blanche Ingram, U. S. Geol. Survey, analyst, 1956, Harvard 46981.
- D. Bismutoferrite, Schneeberg, A. Frenzel, analyst (Frenzel, 1871).
- E. Bismutoferrite, Schneeberg, A. Frenzel, analyst (Frenzel, 1872).
- F. Bismuth-"hypochlorite" (quartz and bismutoferrite), A. Frenzel, analyst (Frenzel, 1871).
- G. Bismutoferrite, theoretical, Bi(OH)Fe₂(SiO₄)₂.

acterized by antimony and containing no bismuth. They contain a mineral dispersed in quartz or chalcedony, with an *x*-ray diffraction pattern almost identical with that of bismutoferrite. This mineral is chapmanite, discussed below.

It will be observed that Harvard 46972 is labeled as from Schneeberg; three other Harvard specimens, apparently very similar to it, are ascribed to Bräunsdorf. Schneeberg is the probable source of all the bismuth minerals in question, and Bräunsdorf, of the antimony minerals. The original label of this particular specimen has been lost (C. Frondel, personal communication, 1956) and the present label may well be erroneous. Our questioning of the Schneeberg locality for Harvard 46972 and suggestion that it too should be Bräunsdorf, is borne out by Frenzel's statement (1871, page 361) that no bismuth minerals occur at Bräunsdorf.

The first four specimens are similar in appearance; hard, dull olive-green, massive, with small holes; they form part of quartz veins, with pyrite and associated minerals, between the green mineral and the vein

TABLE 4—GROUP III—ANTIMONY-"HYPOCHLORITE" (QUARTZ AND CHAPMANITE)

Specimen	Labeled	Locality	X-ray Film	Identification	Composition (X-ray Fluorescence)			Remarks
					Major	Minor	None	
U.S.N.M. R4024	Hypochlorite	Bräunsdorf			Sb, Fe	As	Bi	This is very similar to H46972 Locality should be Bräunsdorf?
Harvard 46972	Hypochlorite	Schneeberg (error)	8913	Quartz and a little chapmanite	Sb, Fe	As	Bi, As	
Harvard 10881	Hypochlorite	Bräunsdorf	8914	Quartz and a little chapmanite	Sb, Fe	As	Bi	
Harvard 105310	Antimony-Hypochlorite	Bräunsdorf	8917, 11440	Quartz and a little chapmanite	Sb	As	Bi	
Harvard 47021	Hypochlorite	Hungary	8916, 11438	Quartz and a little chapmanite, nontronite	Fe		As, Sb, Bi	Collected by J. B. Mer-tie, Jr., examined by W. T. Schaller
U.S.N.M. 105722	Hydrous ferrous antimonate	Venesela Mt., Alaska	11747	Quartz and chapmanite				
Am. Mus. Nat. Hist., N.Y.C. No number	Unlabeled	Velardeña, Durango, México	11914	Quartz and chapmanite	Fe, Sb		Bi	Soft yellow and hard green
Am. Mus. Nat. Hist., N.Y.C. 12574	Hypochlorite	Freiberg, Saxony	11915	Quartz and chapmanite				

TABLE 5. ANALYSES OF "ANTIMONY-HYPOCHLORITE" (QUARTZ AND CHAPMANITE) AND CHAPMANITE

	H	I	J	K	L	M
Sb ₂ O ₃	3.01	5.0	5.56	7.3	—	33.6
Sb ₂ O ₅	—	—	—	—	31.65	—
SiO ₂	88.50	86.0	86.40	78.0	28.28	27.6
FeO	—	—	—	—	33.91	—
Fe ₂ O ₃	5.01	7.8	8.04	11.4	—	36.8
P ₂ O ₅	2.03	trace	trace	—	—	—
H ₂ O	1.00	—	—	1.0	3.46	2.1
NiO	—	—	—	—	.36	—
CoO	—	—	—	—	.03	—
Cu	—	—	—	—	.17	—
Bi	—	—	—	—	.20	—
As	—	—	—	—	1.28	—
Al ₂ O ₃	—	—	—	—	.28	—
	99.55	98.8	100.00	97.7	99.62	100.1

H. "Antimony-hypochlorite," Bräunsdorf, Kersten, analyst (1844) (SO₃, MgO, MnO, trace).

I. "Antimony-hypochlorite," Bräunsdorf, A. Frenzel, analyst (1871).

J. "Antimony-hypochlorite," Bräunsdorf, A. Frenzel, analyst (1871).

K. "Antimony-hypochlorite," Bräunsdorf, A. Frenzel, analyst (1871).

L. Chapmanite, Ontario, E. W. Todd, analyst (Walker 1924).

M. Chapmanite, theoretical, Sb(OH)Fe₂(SiO₄)₂.

quartz. Microscopically, the color is seen best with the condenser in, under high magnification. The needles are too small for optical study; their abundance agrees with what would be expected if Kersten's analysis (Table 5, H) is of a mixture with quartz. The fifth specimen in Table 4 is mostly nontronite, containing a little antimony "hypochlorite."

A somewhat nondescript material (U.S.N.M. 105722) collected by J. B. Mertie, of the U. S. Geological Survey, in 1938, from Venesela Mountain, Alaska (Lat. 60°41' N Long. 155°43' W) containing iron, antimony, and water, was found by *x*-ray to be essentially the same as the Bräunsdorf "antimony hypochlorite," that is, chapmanite, dispersed in quartz.

Analyses of the material—"antimony hypochlorite," actually, chapmanite dispersed in quartz or chalcedony—are given in Table 5. Also, in this table, are given the original analysis of the Ontario chapmanite (Walker, 1924); and the true composition inferred from its relationship to bismutoferrite. It will be observed that the two analyses are not greatly different. *X*-ray data are given in Table 6 for bismutoferrite and chapmanite.

GLADSTONE AND DALE'S LAW APPLIED TO BISMUTOFERRITE
AND CHAPMANITE

Howard Jaffe (1956) has recently called attention to the usefulness of Gladstone and Dale's law (Larsen and Berman, 1934) in checking the validity of proposed compositions of minerals where the refractive indices and density are known with reasonable certainty. Although, because of minute grain size, precise optical determinations on bismutoferrite are difficult, it is possible to use what data are available, and to obtain, on one hand, corroboration of the formula proposed by us for bismutoferrite and chapmanite, and, on the other hand, strong indication of the untenability of Walker's formula for chapmanite.

Available data are:

For bismutoferrite

- (a) indices of refraction $\alpha=1.93$, $\beta=1.97$, $\gamma=2.01$ (determined by us)
- (b) density 4.47 (Frenzel, 1871)
- (c) proposed formula $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
- (d) specific refractive energies of above oxides, as given by Larsen and Berman (1934) except for Fe_2O_3 , as given by Jaffe (1956).

For chapmanite

- (a) indices of refraction $\alpha=1.85$, $\gamma=1.96$ (Walker, 1924)
- (b) density 3.58 (Walker, 1924)
- (c) proposed formula $\text{Sb}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
Walker's formula $\text{Sb}_2\text{O}_6 \cdot 5\text{FeO} \cdot 5\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (d) Specific refractive energies of above oxides with alternate values for Sb_2O_3 0.209 and 0.232 and for Sb_2O_6 0.152 and 0.222 (Larsen and Berman, 1934).

Calculation using this data gives

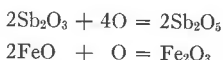
	Density	Indices of Refraction Observed			Average Observed	Average Calculated	
Bismuto- ferrite	4.47	$\alpha=1.93$	$\beta=1.97$	$\gamma=2.01$	1.97	1.96	
Chapmanite (Correct formula)	3.58	$\alpha=1.85$		$\gamma=1.96$	1.905	1.86,	1.89
Chapmanite (Walker's formula)	3.58	$\alpha=1.85$		$\gamma=1.96$	1.905	1.673,	1.752

Evidently, the agreement of observed average index of refraction with the calculated index for bismutoferrite is excellent; for chapmanite (our formula) good; but for chapmanite, using Walker's formula, very poor. In summary, application of Gladstone and Dale's law supports the

formula $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ for bismutoferrite, and $\text{Sb}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ for chapmanite.

THE COMPOSITION OF CHAPMANITE

Still other reasons exist for rejecting E. W. Todd's (Walker, 1924) analysis of chapmanite and Walker's formula based upon it. Michael Fleischer has pointed out (oral communication) that the formula derived from Todd's analysis is open to serious question. Walker says that "the state of oxidation of the iron was determined by dissolving the mineral in hydrofluoric acid and titrating with potassic permanganate." Todd and Walker assumed that ferrous iron was thereby oxidized to ferric. In our opinion, what actually happened was that antimonous oxide was oxidized to antimonic. Indeed, titration of antimonous salts with permanganate is a standard analytical method for the determination of antimony (Scott, 1939). Considering the two oxidation reactions,



it is evident that the amount of oxygen (or the equivalent permanganate) necessary to oxidize four moles of FeO is equal to that necessary to oxidize one mole of Sb_2O_3 . Todd, therefore, mistook the oxidation of a mole of Sb_2O_3 for the oxidation of a substantially equivalent amount (actually, five moles) of FeO. He was, of course, familiar with this standard analytical procedure for the quantitative analysis of antimony, and it is therefore clear that he wrongly assumed that the antimony in the mineral was unaffected by permanganate, that is, it was in the pentavalent state, Sb_2O_5 . Hence, his formula is erroneous with respect to valence states of both iron and antimony.

Walker further notes that "at 270° the mineral lost its green color and became pale brownish, due, apparently, to a change in the state of oxidation which would result in an increase of weight." We do not regard this color change as necessarily indicating oxidation of ferrous iron; it could reflect decomposition of the silicate mineral, with release of ferric oxide as such. Many ferric silicates are green, not yellow or brown.

Unlike Sb_2O_3 , Bi_2O_3 is not oxidized by permanganate. Titration of FeO in bismutoferrite by permanganate as in Mrs. Ingram's analysis is therefore a valid procedure; and it may be noted that she found the iron present to be almost wholly ferric iron.

Finally, the remarkable similarity of the x-ray diffraction patterns of bismutoferrite and chapmanite is further weighty evidence for their formulas being homologous. We therefore reject Walker's formula for chapmanite and accept chapmanite as $\text{Sb}(\text{OH})\text{Fe}_2(\text{SiO}_4)_2$ or $\text{Sb}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, homologous or isostructural with bismutoferrite $\text{Bi}(\text{OH})\text{Fe}_2(\text{SiO}_4)_2$ or $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$.

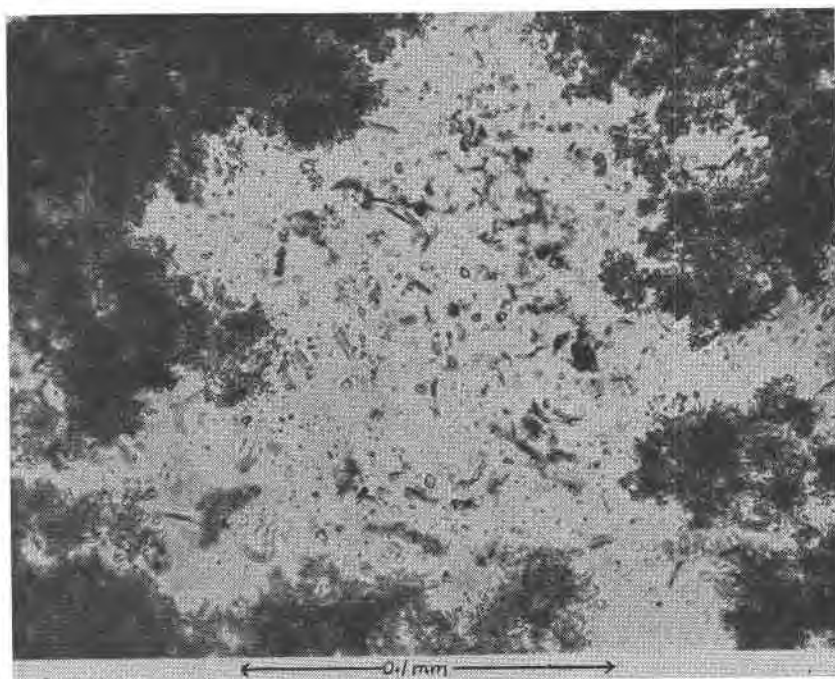


FIG. 1. Thin section of "hypochlorite (bismutoferrite in quartz), Schneeberg, Saxony. Harvard 274. Shows typical aspect of "hypochlorite" (the same for both bismuth and antimony types). At the edges of the dense aggregates of bismutoferrite, extremely small, poorly developed single crystals are discernible. Ordinary light.

X-RAY DATA

Except for the several specimens which were identified as nontronite and other extraneous species, *x*-ray powder patterns of the specimens labeled "bismutoferrite" and "hypochlorite", and chapmanite included one distinctive pattern. The pattern varied slightly from sample to sample, as is not unusual for a mineral species. However, when *x*-ray spectroscopy showed a mutual exclusion of bismuth and antimony, the most obvious variation, that in the relative *d*-spacings of a medium intensity triplet around 2.59\AA , was re-examined; the triplet $2.66\text{-}2.59\text{-}2.53\text{\AA}$ is characteristic for the bismuth mineral and the triplet $2.67\text{-}2.59\text{-}2.54\text{\AA}$ is characteristic for the antimony mineral. Other variations in spacing conform so there are actually two slightly different patterns, those of bismutoferrite and chapmanite. Intensity relationship differences between the two patterns in Table 6 result at least in large part from preferred orientation in bismutoferrite. Lines obviously strengthened in some patterns by preferred orientation are marked by a plus sign and those weakened are marked by a minus sign.

TABLE 6. X-RAY POWDER DIFFRACTION PATTERNS OF BISMUTOFERRITE AND CHAPMANITE

$$\lambda = 1.5406 \text{ \AA} \text{ (Cu/Ni)}$$

$$r = 114.6 \text{ mm.}$$

Bismutoferrite HMM 46981 Film No. 8912 Max. <i>d</i> -spacing cutoff 14.73		Chapmanite U.S.N.M. 94866 Film No. 11748 Max. <i>d</i> -spacing cutoff 13.59		Bismutoferrite HMM 46981 Film No. 8912 Max. <i>d</i> -spacing cutoff 14.73		Chapmanite U.S.N.M. 94866 Film No. 11748 Max. <i>d</i> -spacing cutoff 13.59	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
7.63	100—	7.63	100—	1.471	3	1.471	5
4.52	6—			1.456	2		
4.47	6	4.44	3	1.451	1		
4.18	18+	4.17	25	1.435	4	1.443	5
3.87	100—	3.88	90—	1.394	1b	1.397	5
3.79	2	3.80	5	1.370	4	1.373	12
3.58	35+	3.58	100	1.360	1		
3.18	50+	3.19	90	1.329	1		
2.90	70—	2.90	70	1.299}	1	1.296	9
2.66	12+	2.67	25	1.291}	1		
2.59	35+	2.59	70	1.282	<1	1.281	3
2.53	25—	2.54	35	1.257-1.252	1	1.256	5
2.383	10	2.380	18			1.241	2
		2.344	9	1.224	1	1.228	3
		2.287	3	1.215	1	1.221	5
		2.243	18	1.203	2	1.204	5
2.251	9			1.184	1		
2.225	3			1.176	<1		
2.201	9—	2.217	18	1.169	1	1.167	3
2.162	15—	2.156	18	1.161	<1		
2.086	5	2.085	18	1.143	1	1.142	2
2.040	9	2.044	18	1.124	1	1.124	6
2.011	1			1.106	<1	1.109	3
1.976	<1			1.093	1		
1.935	12—	1.941	15	1.080	1b		
1.907	9	1.910	18	1.067	<1		
1.891	6—			1.049	1		
1.863	3	1.873	5	1.037	<1	1.016	2
1.835	3	1.838	6	.9830	2	.9826	5
1.785	1	1.785	9	.9736	<1		
1.744	3			.9418	<1b		
1.719	12	1.725	22	.9286	<1b	.9259	2
1.694	4	1.698	9	.9188	<1		
1.683	6—	1.683	12	.9096	<1		
1.659	2	1.659	3	.9045	1		
1.637}	9	1.634	12	.8967	<1b	.8978	1
1.628}	3	1.613	12	.8872	<1		
1.608	9	1.605	12	.8770	1		
1.592	4	1.590	12				
1.570	1	1.570	5			.8755	1
1.542	1b	1.544	6			.8659	2
1.516	4	1.523	5			.8285	1
1.504	12	1.501	25			.7964	1

b=broad line.

}=band with peaks.

+=strengthened by preferred orientation.

—=weakened by preferred orientation.

TABLE 7. GROUP IV—MISCELLANEOUS SPECIMENS LABELED (ERRONEOUSLY) "HYPOCHLORITE" OR "BISMUTOFERRITE"

Specimen	Labeled	Locality	X-ray Film	Identification	Composition (X-ray Fluorescence)			Remarks
					Major	Minor	None	
Harvard 46971	"Hypochlorite"	Goritz, Reuss.	8918	Nontronite				
Harvard 46991	"Hypochlorite"	Haar, near Passau, Bavaria	8920	Nontronite and tremolite (?)				
Harvard (No number)	"Hypochlorite"	(No locality)	8922	Nontronite	Fe	Sb	Bi(?)	
U.S.N.M. R4025	"Hypochlorite"	Schneeberg	11433	Mostly talc, also white pyroxene, graphite, etc.				Clear glassy green
Am. Mus. Nat. Hist. 12576	"Hypochlorite"	Schneeberg	11933	Copper sulfate in opaline silica on magnetite				Pb and Bi by chemical test. Waxy yellow.
Am. Mus. Nat. Hist. 26395	"Bismutoferrite"	Schneeberg	11916	Bindheimite				No Bi or Sb, much Fe.
Am. Mus. Nat. Hist. 12575	"Hypochlorite"	Schneeberg	11932	Nontronite				

The patterns of the two minerals are remarkably similar and the pair may be classed with such pairs as scheelite-powellite and magnesite-siderite in which one element completely substitutes for another with very little change in the x-ray patterns.

Group IV. *Miscellaneous substances termed "Hypochlorite" or "Bismutoferrite"*

In all three Museum collections were found specimens labeled "hypochlorite" which proved to be something different. These are listed in Table 7. Apparently nontronite is easily mistaken for "hypochlorite" which it superficially resembles.

BIBLIOGRAPHY

- ADLER, I., AND AXELROD, J. M., 1956, Application of X-ray fluorescence spectroscopy to analytical problems: *Norelco Reporter*, v. 3, 65-68.
- AHLFELD, F., 1948, An unusual antimony deposit in Argentina, *Econ. Geol.*, 43, 598-602.
- BREITHAAPT, A., 1871, "Oral communication", cited by Frenzel.
- DANA, E. S., 1892, System of Mineralogy, 6th ed., p. 562, J. Wiley & Sons Inc., New York.
- DANA, J. D., 1870, System of Mineralogy, 3rd ed., p. 392, J. Wiley & Sons Inc., New York.
- DOELTER, C., 1917, Handbuch der Mineralchemie, Band 2, Abt. 2, p. 164, Steinkopff, Dresden.
- FISCHER, H., 1870, Critische, mikroskopisch-mineralogische Studien: *Berichte der Naturf. Gesellsch., Freiburg*, Band 5, Hft. 2, pp. 1-64.
- FRENZEL, A., 1871, Hypochlorit: *Journal Prakt. Chemie*, (N.F. 4) 353-362.
- FRENZEL, A., 1872, Letter to Prof. H. G. Beinitz: *Neues Jahrb für Mineral.*, 514-517.
- GOLDSMITH, E., 1873, *Proc. Acad. Philadelphia*, 366.
- HEY, M. H., 1950, Chemical Index of Minerals, pp. 102, 199. British Museum, London.
- JAFFE, H. W., 1956, Application of the rule of Gladstone and Dale to minerals, *Am. Mineral.*, 41, 757-777.
- KERR, P. F., Mineralogical studies of uraninite and uraninite-bearing deposits: AEC Interim Technical Report, July 1, 1948, to June 30, 1950, p. 12.
- KERSTEN, C. M., 1844, Ueber die chemische Zusammensetzung einiger sächsischer Mineralien und Gebirgsarten: *Berg. und Hütten. Zeitung*, 3, 59.
- LARSEN, ESPER S., AND BERMAN, HARRY, 1934, Microscopic determination of the non-opaque minerals. *U. S. Geological Survey Bulletin* 848.
- RAMDOHR, P., 1936, Klockmann's Lehrbuch der Mineralogie, Enke Verlag, Stuttgart, pp. 601, 603.
- SCHÜLER, 1832, Sogenannter Grüneisenerde von Schneeberg, Hypochlorit: *Jour. für Chemie und Physik*, 66, p. 41.
- SCOTT, W. W., 1939, Standard methods of chemical analysis, p. 76, D. Van Nostrand & Co., New York.
- VITALIANO, C. J., AND MASON, BRIAN, 1952, Stibiconite and cervantite: *Am. Mineral.*, 37, 982-999.
- WALKER, T. L., 1924, Chapmanite, a new mineral from South Lorraine, Ontario, *Univ. of Toronto Studies, Geol. Ser.* 17, p. 5.

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