

*The mineralogy of the antimony oxides and antimonates.*

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*Introduction*

**D**URING an investigation of stibiconite and cervantite (Vitaliano and Mason, 1952) we examined many specimens of antimony ochre. The commonest mineral in these specimens proved to be stibiconite, but others were found, and to establish their identity it became necessary to study the secondary products as a group. The mineralogy of these oxygenated secondary antimony minerals presents unusual problems on account of their earthy and often inhomogeneous nature. Our experience indicates that without X-ray powder photographs it is difficult to establish the true identity of much of this material. The purpose of this paper is to present the results of our investigations and to provide more adequate descriptions of some little-known species.

We would take this opportunity of expressing our appreciation to a number of persons who aided us. Professor C. Frondel of Harvard University, Dr. G. Switzer of the U.S. National Museum, Professor A. Pabst of the University of California, and Dr. H. Neumann of the Mineralogisk Museum in Oslo, made available material from the collections under their care. Dr. D. E. White of the U.S. Geological Survey provided us with a fine collection of secondary antimony minerals from Mexican deposits, which included the new mineral byströmite and material of the rare iron antimonate tripuhyite. Mr. Victor Barua obtained for us specimens of the Peruvian minerals coronguite and arequipite. Numerous spectrographic analyses were made by Mr. R. K. Leininger of the Indiana Geological Survey. Several partial and complete chemical analyses were made by Mr. M. E. Coller. To all these persons our thanks are due.

*Antimony oxides.*

Senarmontite and valentinite, polymorphs of  $\text{Sb}_2\text{O}_3$ , have been known as well-defined minerals for over a century. Senarmontite, although the stable form at ordinary temperatures, is notably rarer than valentinite.

The only senarmontite we have seen came from the type locality, Hamimat near Constantine in Algeria, whereas valentinite occurs at many localities, sometimes in pure state, but more commonly in intimate admixture with stibiconite. The abundance of valentinite contrasted to the rarity of the stable polymorph senarmontite appears to be linked with the presence of foreign ions, as suggested by Bloom (1939) from investigations of synthetic preparations. We checked this by having spectrographic analyses made of senarmontite and of valentinite; whereas the senarmontite was as pure or purer than reagent grade  $\text{Sb}_2\text{O}_3$ , showing a trace of arsenic and a slight trace of magnesium only, spectrograms of valentinite showed numerous lines of elements other than antimony.

Valentinite and senarmontite are the only anhydrous oxides of antimony found as minerals. The higher oxides of antimony occur as a hydrated phase of variable composition, which generally contains some calcium. This phase is isometric, with a structure of the pyrochlore type, and a general formula  $(\text{Sb}^{3+}, \text{Ca})_y \text{Sb}_{2-x}^{5+}(\text{O}, \text{OH}, \text{H}_2\text{O})_{6-7}$ , in which  $x$  ranges from 0 almost to 1, and  $y$  is generally about 1. Two names, stibiconite and cervantite, have been current for this phase, and since stibiconite has priority we have suggested that this name be retained and that cervantite be dropped. An additional argument for this procedure is that the name cervantite is false in significance, having been specifically applied by its author to anhydrous  $\text{Sb}_2\text{O}_4$ , which is not known to occur as a mineral.

The investigation outlined above rendered not only cervantite redundant, but a number of other mineral names also. Hydroroméite, stibianite, and volgerite were found to be identical with stibiconite; arsenostibite is arsenian stibiconite; rivotite proved to be a mixture of malachite and stibiconite; barcenite a mixture of stibiconite and cinnabar; and stibioferrite a mixture of a number of minerals, mainly bindheimite and jarosite.

The definition of stibiconite given above also includes the mineral roméite, which has long been recognized as a calcium antimonate. It is a rare mineral of rather variable composition and has the unfortunate distinction of a remarkably extensive synonymy. Practically every occurrence has been described under a distinct name, and it was not until X-ray techniques were employed that these names were recognized to belong to the same phase. Atopite, schneebergite, weslienite, mauze-liite, and lewisite are all synonyms for roméite (Machatschki, 1932), although some of them may be distinguished as varieties on account of

the presence of sodium or lead proxying for calcium, iron or titanium for antimony, manganese for either, and fluorine for oxygen and hydroxyl. All these minerals occur in metamorphosed ore-deposits, and are generally found as minute yellow or brown octahedra. Stibiconite, on the other hand, is typically the product of supergene alteration of antimony ores, generally occurs as earthy masses, and has never been found as crystals. Nevertheless, there is no essential difference between roméite and stibiconite, either in chemical composition or in crystal-structure. The question as to whether they should be recognized as distinct species we prefer to leave open until such time as some general agreement exists as to the definition of a mineral species.

*Bindheimite.*

Bindheimite is the common alteration product of lead-antimony sulphides, corresponding in this respect to stibiconite, which is generally the alteration product of stibnite. Like stibiconite, too, it is generally earthy and often impure. The interpretation of published analyses is thus dubious in the absence of proof that the material was homogeneous. We did not attempt to investigate bindheimite thoroughly, since its major characteristics are comparatively well established, but our own data coupled with those in the literature indicate that argentine, cuprian, and calcian varieties exist. Analyses of bindheimite generally report some  $\text{Fe}_2\text{O}_3$ , with the remark in some cases that it represents admixed limonite.

The X-ray powder photograph of bindheimite is of the pyrochlore type, and the mineral is thus isostructural with stibiconite. A complete range in composition is presumably possible, but has not been demonstrated. The  $d$  values for the lines in a powder photograph are reported in table I. The major distinguishing features of the bindheimite pattern from that of stibiconite is the absence of a strong reflection at 5.8–6.0 and the presence of one strong line at 3.03 instead of two lines at 3.07 and 2.95.

Just as stibiconite has its own metamorphic equivalent in roméite, so has bindheimite in the mineral monimolite, described by Igelström in 1865 from Harstig manganese mine in Sweden. Monimolite is essentially a lead antimonate with some substitution of lead by other elements. The powder photograph of monimolite is the same as that of bindheimite, and the lines are rather better defined, evidently as a result of more perfect crystallinity.

The assigning of a suitable formula to bindheimite and monimolite

TABLE I. X-ray powder diffraction data for partzite, bindheimite, and stetefeldtite (Cu-K $\alpha$  radiation; intensities estimated by visual inspection).

<i>hkl</i>	Partzite.		Bindheimite.*		Stetefeldtite.	
	<i>d</i> .	Int.	<i>d</i> .	Int.	<i>d</i> .	Int.
111	5.91	90	—	—	—	—
311	3.08	70	—	—	—	—
222	2.95	100	3.03	100	3.02	100
400	2.56	50	2.62	60	2.61	70
331	2.34	10	2.41	10	—	—
511	1.96	30	—	—	—	—
440	1.81	80	1.85	80	1.85	70
531	1.73	40	—	—	—	—
622	1.54	70	1.58	80	1.58	70
444	1.48	20	1.51	30	1.51	30
711	1.43	20	—	—	—	—
731	1.33	30	—	—	—	—
800	1.28	20	1.31	20	1.31	10
662	1.17	40	1.20	40	1.20	50
840	1.14	40	1.17	40	1.17	40
844	1.04	30	1.07	40	1.07	30
666	0.987	40	1.00	40	1.00	40
880	—	—	0.925	10	—	—
10.6.2	0.867	40	0.884	50	0.884	50
884	0.854	20	0.872	40	0.872	40
12.4.0	—	—	0.827	30	—	—
10.6.6	—	—	0.798	40	—	—
12.4.4	—	—	0.788	40	—	—

\* This indexed powder photograph is similar to those previously recorded for bindheimite (ASTM cards, 1950 edition, nos. 2262, 3721, 3811); it is also similar to the ASTM card (no. 3800) for artificial lead antimonate ( $2\text{PbO}\cdot\text{Sb}_2\text{O}_5$ ); however, the ASTM card for monimolite (no. 1372) is quite different, and we believe that the material from which the powder photograph for this card was made must have been wrongly identified.

has been a matter of difficulty, due to the variability shown by chemical analyses. In the course of this research, however, two samples of analysed bindheimite and one of monimolite were obtained for study. The X-ray powder photographs gave a value of 10.47 Å. for the unit-cell dimensions in each of these samples. The analyses were then recalculated in terms of atoms or ions per unit cell. The results are set out in table II. These data indicate that bindheimite and monimolite can be formulated in a similar fashion to stibiconite, as  $\text{Pb}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$ , in which  $x$  can be zero or range toward 1, and  $y$  is variable but does not exceed 2. Total  $(\text{O},\text{OH},\text{H}_2\text{O})$  from the analyses is close to 6, but there is no apparent reason why it could not vary from six to seven. Such a formulation is in agreement with the requirements of the pyrochlore structure.

In view of the lack of optical data on analysed samples of bindheimite, the opportunity was taken to measure the refractive indices of the available samples, and the results are incorporated in table II. The refractive index of monimolite is higher than that of our highest immersion liquid, which has an index of 2.06.

TABLE II. Chemical analyses of bindheimite and monimolite, recalculated in terms of atoms per unit cell. ( $\text{Fe}_2\text{O}_3$  deducted as limonite before the recalculation of the analyses.)

	1.	2.	3.		1.	2.	3.
$\text{Sb}_2\text{O}_3$ ...	43.63	44.28	38.18	Sp. gr. ...	5.28	5.16	7.29
PbO ...	36.54	40.53	55.33	$a$ (Å.) ...	10.47	10.47	10.47
$\text{Fe}_2\text{O}_3$ ...	4.30	3.28	—	$n$ ...	1.928	1.905	> 2.06
FeO ...	—	—	5.57				
MnO ...	—	—	1.16	Sb ...	11.4	10.8	11.8
$\text{H}_2\text{O}$ ...	5.78	5.04	—	Pb ...	6.9	7.2	12.5
insol. ...	6.32	2.93	—	Fe ...	—	—	3.9
				Mn ...	—	—	0.8
	96.57	96.06	100.24	(O,OH, $\text{H}_2\text{O}$ )	47.8	44.3	46.7

1. Bindheimite, Lovelock, Nevada, U.S. Nat. Mus. 86166, E. V. Shannon, *Econ. Geol.*, 1920, vol. 15, p. 92.
2. Bindheimite, San Bernadino Co., California, U.S. Nat. Mus. 87263. E. V. Shannon, *ibid.*, p. 93.
3. Monimolite (type II), Harstig mine, Sweden. Ex Stockholms Högskolas Mineralogiska Institut. G. Flink, *Bihang K. Svenska Vet.-Akad. Handl.*, 1886, vol. 12, part 2, no. 2, p. 40.

Two other minerals which are essentially identical with bindheimite are coronguite and arequipite, both described from Peru by Raimondi (1878). Through the good offices of Mr. Victor Barua, we have received specimens of these minerals from the Raimondi collection of the Museo de la Escuela Nacional de Ingenieros de Perú, the specimens coming from the type localities and presumably identified by Raimondi himself. The coronguite gave an X-ray powder photograph identical with that of bindheimite, and in view of the 7.82%  $\text{Ag}_2\text{O}$  in the analysis it can be described as an argentian variety of this mineral. Microscopic examination of arequipite showed that it consisted of an intimate admixture of quartz and a yellow isotropic mineral of high refractive index tentatively identified as bindheimite; this was confirmed by an X-ray powder photograph, which showed strong lines of these two minerals. Arequipite is not a silicoantimonate of lead, as Raimondi supposed, but a mixture of bindheimite and quartz.

*Stetefeldtite.*

The name stetefeldtite was proposed by Riotte (1867) for material from the Empire and Philadelphia districts in south-eastern Nevada, where it was being mined at that time as a silver ore. These mining districts are centred on Belmont, a ghost town about 50 miles north-east of Tonopah. Specimens labelled 'stetefeldtite, Belmont, Nye Co., Nevada' were available for study from the collections of the Harvard Mineralogical Museum and of the U.S. National Museum.

The specimen from the U.S. National Museum (104763) showed a yellow powdery material, evidently the stetefeldtite, in a matrix of cavernous quartz. The stetefeldtite was clearly a secondary product, probably after primary sulphides. The Harvard specimen (80285) contained irregular masses of a dull black material occurring together with pyrite in vein-quartz. This black material proved to be stetefeldtite intimately admixed with chalcocite and pyrite; treatment with dilute nitric acid dissolved the sulphides and left the stetefeldtite as a yellow powder similar to the material in the specimens from the U.S. National Museum.

X-ray powder photographs of stetefeldtite are similar to those of bindheimite (table I). Stetefeldtite has the pyrochlore structure and the value of  $a$  is 10.46 Å. In view of this close resemblance to bindheimite, the identity of stetefeldtite was checked by spectrographic analysis, which showed that the major metallic elements were antimony and silver. Stetefeldtite is thus essentially a silver antimonate, which agrees with the original analysis, if it assumed that the copper, iron, and sulphur were contributed by admixed chalcocite and pyrite. If the original analysis is recalculated in terms of atoms per unit cell, using  $a$  10.46 Å. and a density of 4.6 (measured during this investigation), the result is  $\text{Ag}_{8.8}\text{Sb}_{11.4}(\text{O},\text{OH},\text{H}_2\text{O})_{50.6}$ . This can be rewritten in a similar form to that of stibiconite and bindheimite, as  $\text{Ag}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$ ;  $y$  is close to 1 in the original analysis, but can presumably vary up to a maximum of 2, while  $x$  is about 0.5 in the original analysis.

The refractive index of stetefeldtite, measured on U.S. Nat. Mus. 104763, is 1.95. Under the microscope the colour is pale yellow, and grains are isotropic.

*Partzite.*

Partzite was described by Arents (1867) as a mineral formed by the alteration of antimonial sulphide ores in the Blind Spring Hill mining district, Mono County, California. In the same year Blake (1867)

claimed that partzite was actually a mixture, and Ransome (1940), who made a careful study of the mineralogy of the ores of the Blind Spring Hill district, came to much the same conclusion. Under partzite he writes (p. 192):

'A great deal of unsuccessful effort was made to obtain some specimens of the original partzite. Several pieces of what were said to be partzite were obtained from various sources and examined, but no two were alike; and microchemical tests on what seemed to be the best material showed the presence of a large amount of copper and lead, the possibility of some iron, but little else. Tests for antimony were unsuccessful, and the presence of silver was doubtful, certainly not to the reputed extent of the richness credited to it. The polished surface of the so-called partzite showed a definite mixture of mostly oxidized minerals. The positive determination of these was not attempted because of the doubt of its representing the material originally described as partzite.'

Several specimens of partzite from the type locality were available for investigation. Foreign material, mainly quartz and limonite, were present in most specimens, but X-ray powder photographs showed that the dominant mineral in each was a phase with structure and lattice dimensions similar to those of stibiconite (table I). The colour and streak of the purest material is olive-green, but specimens are generally coated with a black tarnish. Spectrographic analyses showed variations from one specimen to another, but the dominant elements in each were copper and antimony; some iron and silver were always present, and calcium varied from a trace up to several per cent. The variability in composition is borne out by variations in density and refractive index; for the three purest specimens the following figures were obtained:

		Sp. gr.	<i>n.</i>
Harvard (83279)	...	2.98	1.61
Indiana (Z81)	...	3.50	1.70
Harvard (80284)	...	3.96	1.82

This variability is probably due largely to a varying degree of 'defectness' in the crystal lattice, since similar variations in stibiconite have been shown to be due to this cause.

If the original analysis of partzite is recalculated into atoms per unit cell, using the density (3.8) given by Arents and the figure  $10.25 \text{ \AA}$  for  $a$ , the result is  $\text{Cu}_{9.8}\text{Ag}_{1.3}\text{Pb}_{0.2}\text{Sb}_{7.6}\text{Fe}_{0.8}(\text{O},\text{OH},\text{H}_2\text{O})_{41.5}$  or, including Ag and Pb with Cu, and Fe with Sb,  $\text{Cu}_{11.3}\text{Sb}_{8.4}(\text{O},\text{OH},\text{H}_2\text{O})_{41.5}$ . Partzite can be interpreted as a hydrated copper antimonate with the pyrochlore structure and a formula similar to other minerals of this type, i.e.,  $\text{Cu}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$ , in which  $y$  has a maximum value of 2 but can be less, and  $x$  is between 0 and 1. The agreement of the analysis with this formula is not good, but the structural and other analogies of

partzite with stibiconite and other minerals of this type favour the formula adopted, and it is probable that the original analysis is somewhat in error.

*Byströmite.*

We have recently (1952) described byströmite, a magnesium antimonate from El Antimonio, Sonora, Mexico. An interesting feature is that this is the first antimonate with the trirutile structure to be recognized as a mineral, although synthetic antimonates of this type have been known for some years. We have since found that the iron antimonates tripuhyite and flajolotite also have this structure. It is not unlikely that other antimonate minerals of this structure type will be found, since studies on synthetic compounds have shown that metals with ionic radii between 0.6 Å. and 0.9 Å. form antimonates of this kind.

*Tripuhyite.*

Iron antimonates have been known as minerals for many years; tripuhyite was named by Hussak and Prior in 1897, flajolotite by Lacroix in 1910. Nothing has been known as to their crystallography, since tripuhyite was found as fragments in alluvial deposits, and flajolotite occurs only as fine-grained earthy masses. The discovery of byströmite provided the clue for the elucidation of tripuhyite and flajolotite; comparison of X-ray powder photographs of the three minerals showed that all had similar structures. It has also resulted in the finding of another locality for tripuhyite; while examining antimony ore from El Antimonio, Sonora, Mexico, we found some specimens of a dark brown to black substance which proved to be that mineral. It is present in specimens from the Palo Verde and Argentina mines, and the mineral is probably not uncommon at El Antimonio. We have since recognized by means of powder photographs that the brown or black colour of some stibiconites is generally due to the presence of admixed tripuhyite; such admixture has been recognized in material from near Taxco, Guerrero, Mexico, and from Losacio in Spain.

The tripuhyite from El Antimonio is always very fine-grained, and shows no trace of crystal form or cleavage. The colour is dark brown or black, the streak dark brown with a greenish tinge. The hardness is about 7. The density of the analysed material, determined by a modification of the Penfield method (Mason, 1944), is 3.99, which when corrected for the presence of 36 % quartz gives a density of 5.6 for the tripuhyite.

Specimens of tripuhyite from El Antimonio are so nearly opaque, even in the thinnest grains, that it has not been possible to measure the refractive indices. In part at least this opacity is due to minute inclusions. The same is true for material of flajolotite from Algeria. For optical data we can therefore do no more than quote from E. S. Larsen's report (1921) on tripuhyite from the type locality in Brazil: 'Greenish-yellow grains. Optically +, 2V small,  $\rho < v$  (very strong);  $\alpha = 2.19 \pm 0.01$ ,  $\beta = 2.20 \pm 0.01$ ;  $\gamma = 2.33 \pm 0.01$ .' Evidently the tripuhyite from Brazil is anomalously biaxial.

TABLE III. X-ray powder diffraction data for tripuhyite. (Cu- $K\alpha$  radiation; intensities estimated by visual inspection.)

<i>hkl.</i>	<i>d</i> (Å.).	Int.	<i>hkl.</i>	<i>d</i> (Å.).	Int.	<i>hkl.</i>	<i>d</i> (Å.).	Int.
101	4.23	20	116	1.39	20	406	0.921	10
110	3.28	100	303	1.38	30	219	0.914	20
103	2.56	90	206	1.28	10	510	0.908	10
200	2.32	40	323	1.19	20	336	0.888	10
113	2.24	20	400	1.16	10	503	0.885	20
210	2.08	10	226	1.12	20	426	0.857	20
202			330	1.09	10	309	0.849	10
213	1.72	90	316	1.06	20	523	0.827	30
220	1.64	50	413	1.05	20	329	0.797	10
006	1.52	30	420	1.03	10	516	0.782	20
310	1.47	40	109	0.993	10			

Table III gives the data for the X-ray powder photograph of tripuhyite. The lines are indexed on the basis of a tetragonal unit cell, with dimensions  $a$  4.63,  $c$  9.14 Å. On this basis the structure is of the trirutile type, and tripuhyite is isostructural with byströmite and tapiolite ( $\text{FeTa}_2\text{O}_6$ ). The identification of the structure as of the trirutile type rests on the very weak (101) reflection; otherwise the powder photograph could be completely indexed on a cell of the simple rutile type, with a value for  $c$  one-third that given above.

The analysis of tripuhyite in table IV was carried out in the following way. A weighed sample was dissolved in concentrated HCl to which KI had been added as a reducing agent, the solution diluted slightly, and the undissolved material filtered off and ignited. The ignited residue was examined microscopically and found to be quartz grains with numerous inclusions of tripuhyite. The antimony was precipitated from the filtrate by  $\text{H}_2\text{S}$ .  $\text{NH}_4\text{OH}$  was then added to the solution to precipitate Fe, Al, and Ti. Iron was determined by titration with  $\text{KMnO}_4$ , Ti estimated colorimetrically, and the  $\text{Al}_2\text{O}_3$  computed by difference. Calcium was tested for but not found; magnesium was precipitated as phosphate. Antimony was determined on a separate sample dissolved

TABLE IV. Chemical analysis of tripuhyite from El Antimonio, Sonora, Mexico.

		1.			2.
Sb	...	34.3	Sb <sub>2</sub> O <sub>5</sub>	...	70.3
Fe	...	10.71	Fe <sub>2</sub> O <sub>3</sub>	...	23.6
O	...	16.8			—
TiO <sub>2</sub>	...	1.34			2.1
Al <sub>2</sub> O <sub>3</sub>	...	1.48			2.3
CaO	...	nt. fd.			—
MgO	...	0.14			0.2
H <sub>2</sub> O+	...	0.98			1.5
HO <sub>2</sub> -	...	0.34			—
insol.*	...	36.0			—
		102.09			100.0

1. Analysis of mixture of tripuhyite and quartz.

2. Same, recalculated to 100 after deducting quartz, with Sb as Sb<sub>2</sub>O<sub>5</sub> and Fe as Fe<sub>2</sub>O<sub>3</sub>.

\* Quartz with tripuhyite inclusions.

as before; the antimony was precipitated as the sulphide, and the precipitate redissolved by digestion with concentrated H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> in a Kjeldahl flask. The solution thus obtained was reduced with Na<sub>2</sub>SO<sub>3</sub> and the antimony titrated with standard KMnO<sub>4</sub> solution at 5° C. Combined water was determined by the Penfield method. Reducible oxygen was determined by igniting the mineral in a stream of purified hydrogen at 850° C. and absorbing and weighing the water thus formed. Allowance was made for the water content of the mineral. The reducible oxygen exceeds slightly the amount required for trivalent iron and quinquivalent antimony, and this excess is probably due in part to the oxygen equivalent to titanium. However, most of the discrepancy probably results from incomplete solution giving low values for iron and antimony compared with complete breakdown of the material on ignition in a stream of hydrogen. This factor is responsible also for the high summation of the analysis as a whole.

In table V the analysis of the tripuhyite from El Antimonio is compared with the original analyses of tripuhyite from Brazil and flajolotite from Algeria. The analyses are recalculated into atoms per unit cell, using the cell dimensions given above and the measured densities. Structural considerations predict that the ideal unit-cell content should be Fe<sub>3</sub>Sb<sub>3</sub>O<sub>12</sub>, and experience with other antimony oxide minerals suggests the possibility of defect lattices. The results set out in table V support these ideas, except for the analysis of the original tripuhyite from Brazil, for which oxygen appears deficient. However, if the iron

TABLE V. Chemical analyses of tripuhyite and flajolotite, recalculated in terms of atoms per unit cell.

	1.	2.	3.		1.	2.	3.
Sb <sub>2</sub> O <sub>5</sub> ...	66.68	70.3	63.5	Sb. ...	2.9	2.8	2.2
Fe <sub>2</sub> O <sub>3</sub> ...	—	23.6	31.4	Fe ...	2.7	1.9	2.3
FeO ...	27.70	nt. fd.	—	Ti ...	0.1	0.2	—
TiO <sub>2</sub> ...	0.86	2.1	—	Al ...	0.2	0.3	—
Al <sub>2</sub> O <sub>3</sub> ...	1.40	2.3	—	Mg ...	—	0.03	—
MgO ...	—	0.2	—	Ca ...	0.1	—	—
CaO ...	0.82	nt. fd.	—	(O,OH,H <sub>2</sub> O) ...	10.6	11.9	11.8
H <sub>2</sub> O ...	—	1.5	5.1				
	98.81	100.0	100.0				
Sp. gr. ...	5.8	5.6	5.1*				

\* Determined on a specimen from the U.S. National Museum (94635).

1. Tripuhyite, Tripuhy, Brazil. Total includes SiO<sub>2</sub> 1.35. (Hussak and Prior, 1897.)

2. Tripuhyite, El Antimonio, Sonora, Mexico. (New analysis.)

3. Tripuhyite (Flajolotite), Hammam N'baïl, Algeria. Analysis by — Flajolot (quoted by A. Lacroix, 1910).

in the Brazilian tripuhyite is assumed to be trivalent, the unit-cell content will be (Fe,Ti,Al,Ca)<sub>3.1</sub>Sb<sub>2.9</sub>O<sub>11.9</sub>, close to the ideal formula. Actually, in Prior's original analysis the iron was assumed to be in the ferrous state, but no proof of this was given, and when calculated on this basis the analysis agrees reasonably well with the formula Fe<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> (2FeO.Sb<sub>2</sub>O<sub>5</sub>). However, a formula of this type is improbable for a substance with the trirutile structure; it should be either FeSb<sub>2</sub>O<sub>6</sub> (FeO.Sb<sub>2</sub>O<sub>5</sub>) or Fe<sub>2</sub>Sb<sub>2</sub>O<sub>8</sub> (Fe<sub>2</sub>O<sub>3</sub>.Sb<sub>2</sub>O<sub>5</sub>), or some variant of these. The recalculation of Prior's analysis on the assumption of the iron being in the ferric state shows good agreement with the latter formula. Supporting evidence for this assumption is provided by the dimensions of the unit cell; the unit cell of tripuhyite is smaller than that of byströmite, whereas if tripuhyite were a ferrous antimonate one would expect the unit cell to be larger, since the ferrous ion is larger than the magnesium ion. The ferric ion being smaller than the magnesium ion allows for the observed diminution in the volume of the unit cell.

On these grounds, therefore, it seems that Prior's assumption that in tripuhyite the iron is in the ferrous state is not justified, and that tripuhyite should be formulated Fe<sub>2</sub>O<sub>3</sub>.Sb<sub>2</sub>O<sub>5</sub> (FeSbO<sub>4</sub>) rather than Fe<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>. However, on this basis there is no significant difference between tripuhyite and flajolotite. They have the same structure, as shown by X-ray powder photographs, and essentially the same chemical composition. The analysis of flajolotite shows the presence of water in

the mineral, which represents hydroxyl groups replacing oxygen in the structure and thereby balancing a deficiency in cations.

We therefore believe that the ideal formula of tripuhyite is  $\text{FeSbO}_4$  and that a deficiency in cations is possible (such as we have demonstrated for byströmite), so that actual analyses may correspond to a formula of the type  $\text{Fe}_{1-y}\text{Sb}_{1-x}(\text{O},\text{OH})_4$ , the  $x$  and  $y$  indicating possible 'defectness' in the lattice. When tripuhyite is defined in this way it includes flajolotite, and since tripuhyite has priority, the name flajolotite should be relegated to the synonymy.

#### Summary.

The mineralogy of the antimony oxides and antimonates is summarized in table VI. Apart from the polymorphs of  $\text{Sb}_2\text{O}_3$ , senarmontite

TABLE VI. Mineralogy of the antimony oxides and antimonates.

Senarmontite	...	$\text{Sb}_2\text{O}_3$	Cubic
Valentinite	...	$\text{Sb}_2\text{O}_3$	Orthorhombic
Stibiconite	...	$(\text{Sb}^{3+},\text{Ca})_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$	Cubic
Bindheimite	...	$\text{Pb}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$	"
Stetefeldtite	...	$\text{Ag}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$	"
Partzite	...	$\text{Cu}_y\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_{6-7}$	"
Tripuhyite	...	$\text{Fe}_{1-y}\text{Sb}_{1-x}(\text{O},\text{OH})_4$	Tetragonal
Byströmite	...	$\text{Mg}_{1-y}\text{Sb}_{2-x}(\text{O},\text{OH})_6$	"

and valentinite, they fall into two structural groups, a cubic group with the pyrochlore structure and a tetragonal group with the trirutile structure. When the antimony is associated with large cations the pyrochlore structure is stable; with smaller cations the trirutile structure is the stable form. Defect lattices are usual in these minerals, resulting in great variability of chemical composition and in physical and optical properties within the individual species.

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