

STIBICONITE AND CERVANTITE

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ABSTRACT

The only anhydrous oxides of antimony known as minerals are senarmonite and valentinite, polymorphs of Sb_2O_3 . The higher oxides of antimony occur in nature as a single phase, crystallizing in the isometric system with a structure of the pyrochlore type. This mineral has been referred to under two names, stibiconite and cervantite; as stibiconite has priority, we recommend that the name cervantite be dropped. Stibiconite always contains water in the structure, and generally some calcium also; its range in composition can be expressed by the formula: $(\text{Sb}^{3+}, \text{Ca})_y\text{Sb}^{5+}_{2-x}(\text{O}, \text{OH}, \text{H}_2\text{O})_{6-7}$, in which y is generally near 1, and x ranges from zero towards 1. This variability in composition is reflected in the physical properties; the density varies from 3.3 to 5.5, the refractive index from 1.62 to 2.05. Volgerite, stibianite, and hydroromeite are synonymous with stibiconite; arsenostibite is arsenian stibiconite; the names stibioferrite, rivotite, and barcenite apply to mixtures of minerals.

INTRODUCTION

The standard works on mineralogy, as for example volume 1 of the seventh edition of Dana's *System of Mineralogy*, list four antimony oxide minerals senarmonite, valentinite, cervantite, and stibiconite. Senarmonite and valentinite, polymorphs of Sb_2O_3 , are well characterized both as minerals and as laboratory products. Cervantite and stibiconite are less well defined, and material described under one or other of these names is exceedingly variable. We aim to show that cervantite and stibiconite are in fact synonymous, and that the higher oxides of antimony are represented as minerals by only one phase. During the greater part of this paper however, we will refer to this phase by the non-committal term "antimony ocher" which was in fact applied to it before the names stibiconite and cervantite were introduced.

HISTORICAL SURVEY

Both stibiconite and cervantite have been used as mineral names for over a century, but the material to which these names have been applied was known to mineralogists much earlier as antimony ocher, and this term is still current in German as "Antimonocker." The name stibiconite was introduced by Beudant in 1832 (in the form "Stibiconise") as synonymous with the material called "Antimonocker"; he described it as earthy, pale yellow to whitish yellow, found in association with stibnite. Beudant quoted no analysis, but gave the formula as $\text{Sb}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, and stated that the mineral gives off water on heating. He gave no locality for it, so it is not possible to establish a type locality for stibiconite.

The name cervantite was introduced by J. D. Dana in 1850 for an

antimony ocher described by Dufrenoy (1845) from Cervantes in the Spanish province of Galicia. Dufrenoy's analysis showed no water, and agreed fairly well with the formula Sb_2O_4 . Hence the distinction between stibiconite and cervantite has been largely based on the presence or absence of water. Our experience indicates, however, that no anhydrous oxide of antimony other than Sb_2O_3 exists as a mineral.

Much pertinent information regarding the oxides of antimony is to be found in the literature of inorganic chemistry. This information is well summarized in the standard works of Mellor (1929) and Gmelin (1949). Even here, however, much confusion is apparent, and contradictory statements are not hard to find. Comprehensive investigations of the Sb-O system or the Sb-O-H₂O system have not yet been made. The two polymorphs of Sb_2O_3 corresponding to senarmontite and valentinite can readily be prepared in the laboratory; senarmontite is the stable form up to 570°, above which temperature valentinite is the stable form (although valentinite can be prepared even at room temperature). The most satisfactory data on the higher oxides of antimony have been obtained from researches carried out at the Department of Inorganic Chemistry of the University of Stockholm, and were summarized by Schrewelius (1943). Precipitates of hydrated Sb_2O_5 cannot be completely dehydrated without the loss of some oxygen, and it thus appears that anhydrous Sb_2O_5 is not a stable compound. The substance produced by heating hydrated Sb_2O_5 is generally not Sb_2O_4 , as is stated in many places, but $\text{Sb}_3\text{O}_6\text{OH}$. This substance has a structure of the pyrochlore type, and is very stable; the hydroxyl group is tenaciously held, and can be removed only by heating the substance for many days or weeks at a high temperature. Such treatment produces Sb_2O_4 , which thus appears to be the only anhydrous oxide of antimony besides Sb_2O_3 . It is orthorhombic and is isomorphous with stibiotantalite (SbTaO_4). It has not been identified as a mineral. None of the so-called cervantite, nor any other material which we have examined, shows any trace of this phase.

The work of Schrewelius and others has shown that the many ways suggested for making the higher oxides of antimony all result in more or less hydrated products with a variable Sb:O ratio. These products are either non-crystalline or have a structure of the pyrochlore type. Our experience is in agreement with these results; apart from senarmontite and valentinite the only antimony oxide mineral is a phase of variable composition with the pyrochlore structure.

METHODS OF INVESTIGATION

This investigation began with what appeared to be a simple problem of the identification of the minerals present in pseudomorphs after stib-

nite from Milton Canyon, Nevada. The evident difficulty in deciding whether cervantite or stibiconite or both were present led us to undertake the examination of similar material from other localities. We are particularly indebted to the following institutions for the loan of valuable specimens: the Mineralogical Museum of Harvard University, the U. S. National Museum, the U. S. Geological Survey (through Dr. D. E. White) and the Department of Geology of the University of California. Without such a variety of material on which to work, we would have had much greater difficulty in arriving at valid conclusions. As it was, many specimens were unsatisfactory for one or another reason. The antimony ochers are usually earthy and fine-grained, and admixture with foreign matter is general. It is always difficult and often impossible to separate homogeneous material for analysis. Even material free from foreign matter may be variable in composition, as is shown by the variation in refractive index and density of pure grains taken from different parts of the same specimen.

Refractive indices were measured in white light by the immersion method; for indices greater than 1.81 P-S-CH₂I₂ liquids, standardized by the prism method, were used. Densities were determined on carefully selected grains by means of the Berman balance, carbon tetrachloride being used as the displacement liquid. X-ray powder photographs (Cu radiation, Ni filter) were made of material from all specimens, using 114.6 mm. diameter cameras. Spectrographic analyses were made of most specimens. We are indebted to the Indiana Geological Survey and to its spectrographer, Mr. R. K. Leininger, for the great amount of valuable data thereby obtained. Some specimens were selected for complete analyses, which were carried out by Mr. M. E. Coller, to whom we would express our appreciation for his careful work on a difficult problem. The differential thermal analyses were made on a standard type of apparatus.

CHEMICAL COMPOSITION

The first step in the investigation was the determination of refractive index and density and the taking of x-ray powder photographs of all the samples of antimony ocher available to us. The powder photographs all gave a similar pattern of lines, indicating that we were dealing with a single phase, but the variation in density and refractive index from one specimen to another showed that this phase must be exceedingly variable in composition. To obtain a picture of the variation in the composition chemical analyses for total antimony and H₂O (minus and plus 105°) were made on all reasonably pure specimens. The resulting data are given in Table 1.

TABLE 1. DATA ON SPECIMENS OF ANTIMONY OCHER

No.	Sb ¹	H ₂ O—	H ₂ O+	<i>n</i>	<i>D</i>	<i>a</i> ₀ ²	Valentinite	³
1	76.9	0.92	1.63	2.047	5.27		20-25%	<i>c</i>
2	75.4	1.27	3.15	1.865	5.12		15-20%	<i>c</i>
3	74.8	1.58	2.75	2.046	5.32		15-20%	<i>c</i>
4	73.8	0.61	1.98	1.993	5.54		10-15%	<i>c</i>
5	72.2	1.78	3.48	1.790	4.58		10-15%	<i>b</i>
6	69.4	3.28	5.08	1.785	4.52		10-15%	<i>b</i>
7	68.7	0.61	3.11	1.929	4.96		10-15%	<i>b</i>
8	68.2	0.72	3.10	1.735	4.68		10-15%	<i>a</i>
9	67.4	0.66	4.13	1.775	4.82		5-10%	<i>a</i>
10	67.4	1.17	4.82	1.795	4.70		5-10%	<i>b</i>
11	67.2	0.30	2.84	1.915	5.16		present?	<i>b</i>
12	66.4	0.34	3.00	1.762	5.00	10.266 Å	present?	<i>a</i>
13	65.5	0.36	3.27	1.908	4.89		5-10%	<i>b</i>
14	65.4	0.85	3.54	1.807	4.96		5-10%	<i>a</i>
15	65.4	0.14	2.85	1.795	4.76	10.275 Å	—	<i>a</i>
16	63.4	0.28	3.04	1.822	4.88		present?	<i>a</i>
17	63.4	1.78	4.61	1.775	4.23		—	<i>b</i>
18	62.9	0.77	3.67	1.728	4.43	10.264 Å	—	<i>a</i>
19	61.8	1.08	4.24	1.741	4.56	10.264 Å	present?	<i>a</i>
20	61.0	0.93	4.71	1.713	4.16		—	<i>b</i>
21	60.4	2.32	5.20	1.755	4.10	10.282 Å	—	<i>a</i>
22	59.4	1.28	5.68	1.748	4.06		—	<i>b</i>
23	56.7	0.96	5.65	1.743	4.01		—	<i>a</i>
24	56.3	1.77	5.83	1.698	3.74	10.261 Å	—	<i>a</i>
25	56.0	0.70	4.51	1.702	4.80		—	<i>a</i>
26	56.0	1.66	5.60	1.705	3.89	10.257 Å	—	<i>a</i>
27	55.8	1.51	8.68	1.705	3.72		—	<i>b</i>
28	53.7	0.72	4.99	1.731	3.96	10.269 Å	—	<i>a</i>
29	53.3	4.42	8.82	1.64	3.32		—	<i>b</i>
30	53.3	2.64	8.73	1.638	3.32		—	<i>b</i>
31	52.9	1.16	6.29	1.717	4.16	10.255 Å	—	<i>a</i>
32	52.7	3.57	9.20	1.698	3.73		—	<i>a</i>
33	52.6	0.71	4.77	1.765	4.18	10.262 Å	—	<i>a</i>

¹ Mean of two analyses; the difference between the figures given in this table and those for the same specimens in Table 2 is because the figures in this table are calculated on "dried at 105°" basis, those in table 2 on "as received" basis.

² ± 0.005 Å.

³ Quality of x-ray powder photograph: *a*=back reflections clear and sharp; *b*=back reflections diffuse; *c*=no back reflections.

KEY TO TABLES 1, 2 AND 3

1. Borneo. Harvard 95976.
2. Lugo, Spain (probably from Cervantes area).
3. Esmeralda County, Nevada. Harvard 80282.

(Continued on next page)

4. Yucunani Mine, Tejocotes, Oaxaca, Mexico.
5. $3\frac{1}{4}$ km. N.W. of Ateca, Zaragoza, Spain.
6. Mexico.
7. Mexico.
8. Sonora(?), Mexico. Harvard 96084.
9. Constantine, Algeria. Harvard 83283. Labelled volgerite.
10. Sonora, Mexico. Harvard 97270.
11. Argentina Mine, El Antimonio, Sonora, Mexico.
12. Ojuela Mine, Mapimi, Durango, Mexico.
13. Argentina Mine, El Antimonio, Sonora, Mexico.
14. Empire district, Nevada. Harvard 83277.
15. China. Harvard 88887.
16. El Antimonio, Sonora, Mexico.
17. Mexico.
18. Palotes district, Durango, Mexico.
19. No locality. Univ. of California collection. Specimen is no. 4 of Larsen, *Geol. Surv. Bull.* 697, p. 136, (1921).
20. Sud Chichas, Bolivia.
21. Poggio Fuoco, Manciano, Italy (labelled hydrromeite).
22. Oaxaca, Mexico.
23. Pachecho, Zacatecas, Mexico.
24. El Antimonio, Sonora, Mexico.
25. El Antimonio, Sonora, Mexico.
26. El Antimonio, Sonora, Mexico.
27. Poggio Fuoco, Manciano, Italy (labelled hydrromeite).
28. Mexico.
29. Near San Jose Mines, Wadley, San Luis Potosi, Mexico.
30. Milton Canyon, Nevada.
31. Mexico.
32. Shia Ying Shan, near Shinkwan, North Kwangtung, China.
33. Near Taxco, Guerrero, Mexico.

Significant features of these results are the variability in total antimony, from 50% to nearly 80%, and the universal presence of combined water, its amount ranging from 1.63 to 9.20%. Significant too is the presence of valentinite as an impurity in all specimens containing more than about 67% of total antimony. This valentinite was revealed by extra lines on the powder photographs. It was seldom detected optically, and is evidently present in extremely small grains. Unfortunately the strong lines of valentinite coincide either with those of the major phase or with strong lines of quartz, which is often present as an impurity. As a result it is difficult to detect less than 10% of valentinite by means of powder photographs, so some samples labelled homogeneous may also contain this mineral.

Spectrographic analyses were also made of each of the specimens enumerated in Table 1. Besides antimony in major amounts, the spectrograms showed that calcium was omnipresent, ranging up to about 10% or more; silicon (ubiquitous as admixed quartz) occurred in amounts up

to about 1% or a little more; minor amounts (<1%) of Fe, Al, and Mg were present in most specimens; and occasional traces of Ag, Mn, Pb, Na, and Ti were observed.

The data showed that the antimony ochers with which we were working were essentially hydrated antimony oxides with a variable calcium content. From a consideration of the results of these initial investigations, some specimens were selected for complete chemical analysis. A major problem was the determination of the relative amounts of trivalent and quinivalent antimony. The antimony ochers are remarkably insoluble in all the common reagents, and our experience is that they can only be dissolved in the presence of a reducing agent, which of course immediately alters the relative amounts of the two forms of antimony. We did not find a suitable reducing agent insensitive to air, so abandoned methods based on solution. The procedure finally adopted was to determine the oxygen as water removed when the antimony ocher was heated at 850° in a stream of purified hydrogen. The water given off included of course the water content of the mineral and had to be corrected for this; the remainder represented the oxygen combined with antimony plus that combined as Fe₂O₃. We are not entirely satisfied with the reliability of the procedure for samples with a high water content, since the correction involved is then considerable. Total antimony was determined by dissolving a sample in concentrated HCl containing KI as a reducing agent, under refluxing conditions in an Erlenmeyer flask. The antimony was precipitated with H₂S, and the precipitate filtered off and digested in a Kjeldahl flask with concentrated H₂SO₄ and Na₂SO₄. Upon complete solution the antimony was reduced with Na₂SO₃ and the reduced antimony then titrated with standard KMnO₄ at 5° C. A separate sample was used for the determination of SiO₂, Fe₂O₃, Al₂O₃, CaO, and MgO. The sample was dissolved as above and the insoluble residue filtered off; this residue was examined microscopically and proved to be quartz in all samples and is therefore reported as SiO₂. Antimony was removed by precipitation with H₂S. The iron and aluminum were then precipitated with NH₄OH. The iron was determined colorimetrically and the Al₂O₃ value obtained by difference. The calcium was determined as oxalate and the magnesium as phosphate. The Penfield method was used to determine H₂O+. Duplicate analyses were run on all samples. The results of these chemical analyses are given in Table 2.

When the analyses in Table 2 are recalculated to atoms or ions per unit cell (as recommended by Hey, 1939), using a value of 10.27 Å for a_0 and the measured density for each sample (the analyses and densities of samples 4 and 9 being corrected for an estimated admixture of 10% valentinite) the figures in Table 3 are obtained. These figures have now

TABLE 2. ANALYSES OF STIBICONITE. ANALYST, M. E. COLLER

	4	9	16	18	23	24	29	30
Sb	73.4	67.0	63.4	62.5	56.2	55.3	51.0	51.9
O	21.3	20.4	20.9	19.6	18.6	17.0	16.3	16.9
CaO	1.79	5.77	9.63	8.56	13.5	13.1	13.9	11.9
H ₂ O—	0.61	0.66	0.28	0.77	0.96	1.77	4.42	2.64
H ₂ O+	1.98	4.13	3.04	3.67	5.65	5.83	8.82	8.73
SiO ₂	1.03	1.51	0.76	3.65	2.81	6.41	5.20	7.19
Al ₂ O ₃	0.05	0.08	0.99	0.07	0.23	0.94	0.11	0.33
Fe ₂ O ₃	0.10	0.04	0.17	0.06	0.50	0.07	0.60	0.99
MgO	0.05	0.49	0.28	0.05	0.24	0.40	0.09	0.32
Total	100.3	100.1	99.5	99.6 ²	99.7 ¹	100.8	100.4	100.9

¹ Includes Na₂O, 1.02%.² Includes CO₂, 0.69%.

to be interpreted in terms of the pyrochlore structure.

The pyrochlore structure belongs in the space group *Fd3m*, which has two distinct sets of 16-fold lattice positions, one set of 48-fold positions, and one set of 8-fold positions. In the type substance pyrochlore,

TABLE 3. ANALYSES OF STIBICONITE, RECALCULATED IN ATOMS PER UNIT CELL

	4	9	16	18	23	24	29	30
Sb ⁵⁺	17.5	15.8	17.1	13.9	12.7	10.1	9.5	10.0
Sb ³⁺	4.2	1.3	—	1.8	—	2.1	0.6	0.3
Ca	1.3	3.6	5.6	4.2	7.1 ¹	6.2	6.0	5.1
O, OH, H ₂ O	55.9	53.2	54.0	48.0	47.7	43.3	42.3	42.4

¹ Includes Na, 0.5.

whose ideal formula is Ca₂Nb₂O₆F, there are eight formula groups in the unit cell (i.e. Ca₁₆Nb₁₆O₄₈F₈), and the atoms are distributed as follows:

16 Ca in 16 (*d*)
 16 Nb in 16 (*c*)
 48 O in 48 (*f*)
 8 F in 8 (*b*)

Many substances crystallize in this structure, and it has been shown that the 16 (*d*) positions may be occupied by Ca, Na, Sb³⁺, Pb, Ag, K and many other elements with an ionic radius of about 1Å or greater; the 16 (*c*) positions may be occupied by Nb, Ta, Sb⁵⁺, Al, Ti and other elements with an ionic radius of 0.5Å to 0.8Å; the 48 (*f*) and the 8 (*b*) positions may be occupied by oxygen, hydroxyl, and fluoride ions, or water molecules. Pabst (1939) has given a useful summary of the characteristics of the pyrochlore structure and emphasizes the occurrence of

defect lattices among substances of this type. He cites examples illustrating that both the 8 (*b*) and 16 (*d*) positions can be partly or wholly unoccupied. The figures in Table 3 show that this situation is usual in antimony ochre; the 16 (*d*) positions are only partially occupied by Sb^{3+} , Ca, and (in no. 23) Na, and the 8 (*b*) positions are completely occupied only in no. 4. In addition the 16 (*c*) positions, occupied by Sb^{5+} , are also not entirely filled in some specimens (18, 23, 24, 29, 30). It is believed that the slight excess of Sb^{5+} above 16 atoms per unit cell shown by the analyses of no. 4 and no. 16 is apparent rather than real, being due to error in the oxygen determination, which is the least precise of the analytical data. Similarly, the deficiency in (O, OH, H_2O) below 48 in nos. 24, 29, 30 is not believed to reflect empty lattice points in the 48 (*f*) positions, but to be due to part of the considerable amount of $\text{H}_2\text{O}(-)$ in these specimens being constitutional. The role of water in the antimony ochres, whether present as adsorbed water, as water molecules occupying lattice positions, or as hydroxyl ions, is difficult to evaluate; probably all three forms are present in greater or less quantity in most specimens.

The structural and chemical data thus indicate that analyses of homogeneous material of antimony ochre should be interpreted in terms of the following formula: $(\text{Sb}^{3+}, \text{Ca})_y\text{Sb}_{2-x}(\text{O}, \text{OH}, \text{H}_2\text{O})_{6-7}$. From the nature of the pyrochlore structure it is conceivable that *y*, i.e. total (Ca, Sb^{3+}), might rise as high as 2 in the general formula. In the analyzed stibiconites, however, this total does not exceed 1 and is usually less. The value of *x* can be zero, or can range towards 1.

At first glance, it is remarkable that the variability in cell content is not accompanied by changes in the size of the unit cell. Our measurements show that most specimens have a value for a_0 between 10.26 Å and 10.27 Å. Admittedly only a few samples gave powder photographs with sharp back-reflection lines from which accurate lattice dimensions could be calculated, but the less legible photographs showed a close correspondence with the measured ones. However, as Pabst points out, the pyrochlore structure is characterized by the presence of a large amount of oxygen. On account of the large size of the oxygen anion the volume of the unit cell is determined almost entirely by the anions alone, and as a first approximation the structure may be regarded as consisting of a rigid framework of oxygen, in the interstices of which the cations are situated.

PHYSICAL PROPERTIES

As may be expected from the variability in chemical composition, the physical properties also vary greatly. The density ranges from about 3.3 up to a maximum of about 5.5 (when allowance is made for the approxi-

mate content of valentinite present in the densest specimens). A marked correlation exists between density and hardness. Specimens of high density are quite hard and generally cannot be scratched with a knife blade; the maximum hardness is about the same as that of quartz. With decreasing density the hardness falls off rapidly, and although the hardness of the more earthy specimens cannot be readily evaluated, it appears to be from 3 to 4 on Mohs scale. The usual color of most specimens of antimony ocher is chalky white to pale yellow, but orange, brown, gray, and black are not uncommon. The depth of color shows a distinct correlation with the amount of iron in the specimen, and brown or black colors often signify the presence of admixed tripuhyite (iron antimonate). In material from El Antimonio gray colors generally indicated admixed bystromite (magnesium antimonate).

In the literature the statement sometimes appears that cervantite is found as acicular orthorhombic crystals. Many specimens of this type were seen, but in every case the crystals were clearly pseudomorphs after stibnite. Under the microscope, all the material proved to be exceedingly fine-grained, with no trace of crystal outlines. Mr. T. B. Rhinehammer of the Chemistry Department of this university kindly examined some of our material under the electron microscope. He reports that even under the highest magnifications most of the material appeared to be structureless aggregates; a few grains, however, showed square cross-sections. X-ray powder photographs of antimony ochers sometimes have broadened and diffuse lines, indicating that the crystal size is very small; this is especially the case with the more hydrated specimens.

OPTICAL PROPERTIES

The optical study of all the specimens was done in immersion oils. In general the mineral grains vary from highly turbid to translucent. Occasionally some clear glassy isotropic grains were found intermixed with the turbid grains. The refractive index of the clear grains was similar to that of the more turbid material in all cases.

Most of the material examined has irregular fracture. A few notable exceptions are the platy material with vicinal faces in no. 27 from Poggio Fuoco, Italy, and fibrous material in specimens from the Argentina Mine, El Antimonio, Sonora, Mexico, and in no. 4 from the Yucunani Mine, Oaxaca, Mexico.

Impurities consisted of original antimony minerals, chiefly incompletely replaced valentinite and stibnite; quartz in a number of specimens, and gypsum (?) in specimen no. 1, from Borneo. Iron oxide is the most common impurity and occurs in many of the specimens examined.

Under the microscope the color ranges from white (as in the Milton Canyon and Broken Hills specimens), through yellow (massive material, Siena, Italy), yellow-brown (Losacio, Spain), to dark brown (Piedra Azul Mine, El Antimonio, Mexico). Although mainly isotropic, many of the fragments, especially where turbid, show pinpoints or aggregates of doubly refracting material in a thin band around the edge of the grains.

The refractive index of the specimens examined ranged from 1.621 to 2.047. The majority of the specimens were homogeneous. Some gave a single refractive index value, while others exhibited a range of index of refraction. In no. 31 (Mexico) the refractive index ranged from 1.701 to 1.725 with a few grains slightly higher than 1.725. In no. 18 (Paletos district, Durango, Mexico), the refractive index of the majority of the grains is 1.728 with a few grains ranging from 1.710 to 1.740. Generally no relationship between n and other physical properties was apparent where a range of refractive index was found. No. 23 (Pachecho, Zacatecas, Mexico) was an exception. This was a white ocher with a yellow tinge. As the refractive index decreased the yellow tinge became stronger. In some heterogeneous specimens, composed of turbid and clear fragments, there is little or no variation in n between the different component parts, e.g. specimen no. 1 (Borneo) microcrystalline phase $n=2.045$, acicular phase $n=2.047$. A sample of heterogeneous material, which gave a considerable difference in the n of the separate fractions, was no. 29 (Wadley, San Luis Potosi, Mexico); fraction *A*, $n=1.621$ and fraction *B*, n slightly less than 1.649.

Qualitatively the refractive index (and density) shows a direct relationship to the antimony content and an inverse relationship to the water content. These relations are not linear, however, evidently because of the complex variability of the chemical composition coupled with a greater or less degree of defectness in the structure. Hence it is not possible to establish the chemical composition of a particular specimen from a measurement of refractive index or density.

DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analyses were made on all specimens for which complete chemical analyses were available. The thermal equipment and techniques used in determining the behavior of the antimony ochers are essentially similar to those described by Kerr, Kulp and Hamilton (pp. 7-11). The major difference is that but one sample can be determined during each furnace run. Preliminary runs at ordinary sensitivity yielded curves with small indistinguishable exothermic peaks and no visible endothermic peaks. All samples were then rerun with the D.C.

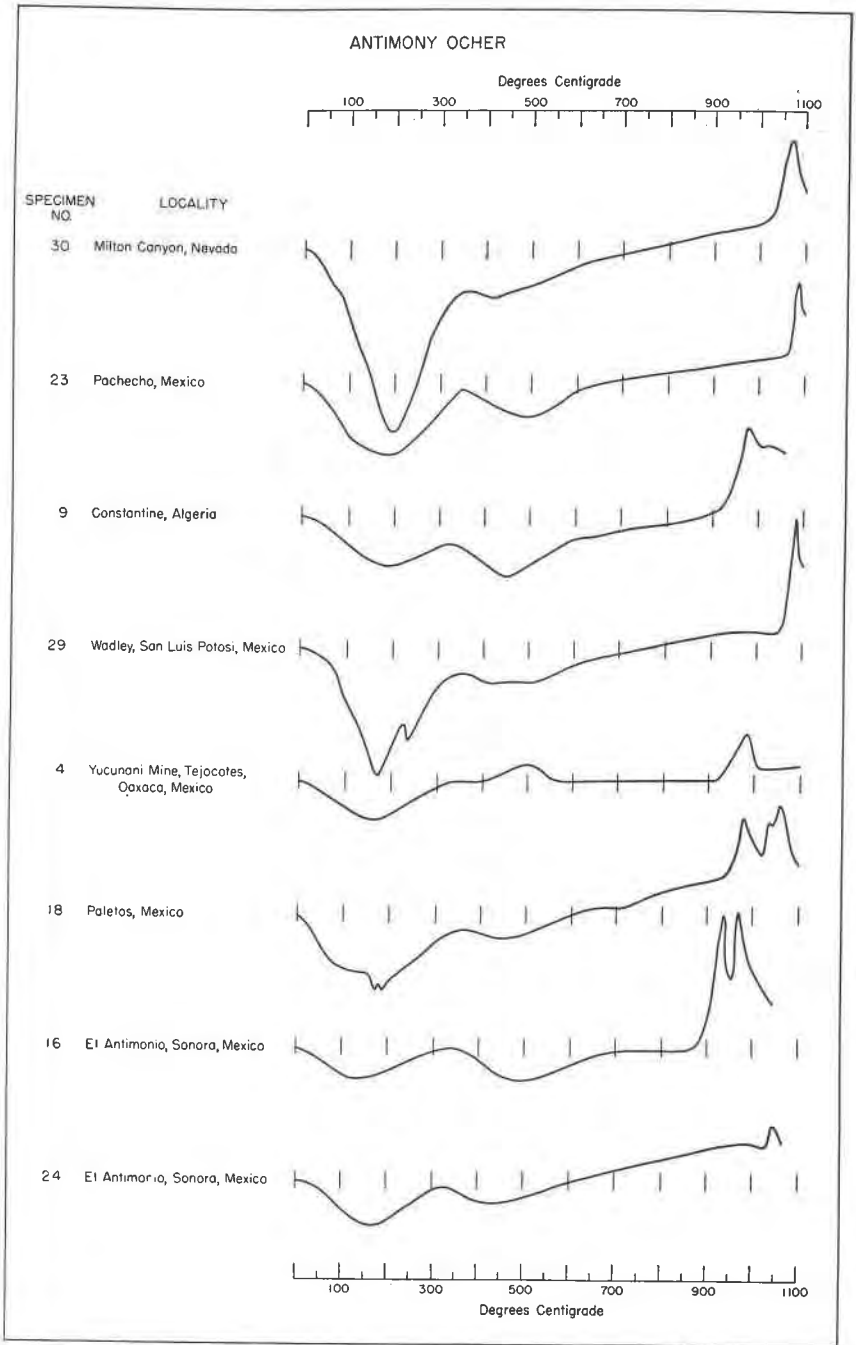


FIG. 1

microvolt pre-amplifier in the circuit between the furnace and the recorder. The specimens were all run at a pre-amplifier scale of 50, the lowest possible magnification obtainable with the pre-amplifier in the circuit.

The resulting thermal curves (Fig. 1) show a change in composition and structure resulting in almost all instances when the specimens were heated to 1100° C. The curves for all the specimens are similar in the lower temperature ranges. A large endothermic peak representing dehydration occurs in samples nos. 30, 23, 29 and 18; and a somewhat smaller one in samples 4, 9, 16, and 24. The temperature at which the peak occurs varies slightly in each sample, but does not go above 200° C. The cause of the double peak in 29 and 18 is unknown. All the samples except no. 4 show an exothermic dome between 425° C. and 490° C. This is probably the result of a slight rearrangement of the crystal lattice. It was noted that all the thermal curves except no. 4 from the Yucunani Mine, Mexico, showed a very gradual return to the zero line after the peak representing the expulsion of H₂O. It was suspected that this might indicate gradual rather than rapid loss of H₂O in the antimony ocher. This was verified by making heat loss determinations on several specimens. These were heated up to 850° C., with weight determinations at regular intervals. Weight loss continued up to 750° C., at which temperature the last of the water had evidently been expelled. Finally, a strong exothermic peak occurs above 925° C. in all of the samples. This represents a change of phase. X-ray powder photographs were made on all the samples tested in the thermal apparatus. Comparison of the patterns before and after thermal analysis demonstrated the inversion to CaSb₂O₆ (hexagonal) at the exothermic peak temperature in all samples except no. 4. Sample 9 had, in addition to the CaSb₂O₆ lines on the powder photograph, a few weak lines which possibly could be attributed to unchanged stibiconite. Sample 4 remained essentially unchanged. A rerun of sample 29 to 950° C., a temperature just below the exothermic peak for this sample, showed that no change of phase had occurred as yet. On this basis it is believed that the phase change in all the specimens occurs at the exothermic peak temperature.

X-RAY DATA

The measurements of a powder photograph of a sample of pure stibiconite are reproduced in Table 4. This photograph was selected for measurement because of the purity of the sample and the sharpness of the lines. In many powder photographs of stibiconite the α_1 and α_2 lines of the back reflections are not resolved, and when the lines become very diffuse many of the weaker ones no longer appear and the strong reflections at 3.09 and 2.96 may almost coalesce. Although not the strongest

line, the innermost reflection at 5.9 is useful for characterizing stibiconite, since it is extremely weak or absent in other antimony minerals with the pyrochlore structure, such as bindheimite. The strong reflection at 3.09 practically coincides with the strongest line for valentinite (3.13), which makes it difficult to recognize admixture when this mineral is present in amounts less than 10%. The best clue is a change in the relative intensities of the second and third lines in the stibiconite pattern; if the second line becomes equal to, or greater in intensity than the third, admixed valentinite is probably present.

TABLE 4. X-RAY POWDER DIFFRACTION DATA FOR STIBICONITE (Cu-K α RADIATION; INTENSITIES ESTIMATED BY VISUAL INSPECTION)

d	I	hkl	d	I	hkl
5.93	90	111	1.15	40	840
3.09	70	311	1.13	10	{753
2.96	100	222	1.08	10	911
2.57	40	400	1.05	20	931
2.36	10	331	.987	20	844
1.98	30	{511	.908	10	{666
1.81	80	333	.897	10	10.22
1.74	30	440	.868	30	880
1.57	20	533	.855	20	955, 971, 11.31
1.55	60	622	.847	10	10.62
1.48	30	444	.824	10	{884
1.44	30	{711	.811	20	12.00
1.34	30	551	.785	10	777
1.28	20	731	.783	20	{11.51
1.18	40	553	.774	20	975
		800			11.53
		662			{12.40
					993, 11.55, 11.71, 13.11
					10.66
					12.44

The powder photograph of stibiconite indexed in Table 4 is essentially identical with or similar to powder photographs of a number of antimony compounds indexed in the card file of x-ray diffraction data published by the A.S.T.M. (American Society for Testing Materials). For the convenience of those using this card file, the relevant cards are enumerated in Table 5. We believe that in effect all these cards index the same phase, the discrepancies between different cards being due partly to differences in technique (camera radius, radiation used, etc.), and partly

to the nature of the material from which the powder photographs were made (poor crystallinity, admixture of foreign material). The photograph indexed in Table 4 was selected as the best of many taken during the course of this investigation, and the material from which it was made was carefully checked for homogeneity. We therefore believed that the data in Table 4 are the most reliable yet published for stibiconite and artificial antimony oxides with the pyrochlore structure.

TABLE 5. CARDS CORRESPONDING TO STIBICONITE IN THE A.S.T.M.
FILE OF X-RAY DIFFRACTION DATA

Description	No. in 1950 ed.	Three strongest lines		
Antimony pentoxide	0363	6.0	3.10	2.97
Stibiconite	2364	2.92	1.80	1.53
Stibiconite	2480	2.88	1.42	1.79
Lewisite	3723	1.81	1.55	2.96
Romeite	3724	1.81	1.54	1.18
Stibiconite	3726	1.81	1.54	1.03
Hydroromeite	3725	1.80	1.54	1.17
Antimony tetroxide	3810	1.55	2.96	1.18
Antimony pentoxide hydrate, $Sb_2O_5 \cdot 3H_2O$	3815	1.55	1.81	1.18
Calcium antimony oxide, $2CaO \cdot Sb_2O_5$	3822	1.55	1.05	1.82
Antimony pentoxide	3831	1.54	1.81	1.17
Antimony pentoxide hydrate, $Sb_2O_5 \cdot H_2O$	3832	1.54	1.81	1.14
Hydroromeite	3833	1.54	1.79	1.15

STIBICONITE OR CERVANTITE?

The data presented in this paper indicate that the naturally occurring antimony oxides comprise three minerals: senarmontite, valentinite, and a third compound which we have referred to as antimony ocher. The latter compound is variable in composition and includes both stibiconite and cervantite. Which of these names should be adopted for this mineral? Since the name stibiconite (1832) antedates cervantite (1850) we suggest that the rule of priority is applicable and that stibiconite be adopted and cervantite relegated to the synonymy. Additional grounds for this procedure are that the name cervantite is false in significance. It was expressly applied by its author to the anhydrous compound Sb_2O_4 , and all our analyses of antimony ocher show constitutional water. We believe that the few analyses of cervantite in the literature which show no water are unreliable, and that anhydrous Sb_2O_4 does not occur as a mineral.

We would therefore provide the following definition for stibiconite: an isometric mineral with the pyrochlore structure and the general formula $(Sb^{3+}, Ca)_y Sb_{2-x} (O, OH, H_2O)_{6-7}$. The only objection to this definition is that it is perhaps too wide, since it can include the mineral

romeite, whose formula may be written $\text{Ca}_{14}\text{Sb}_2(\text{O}, \text{OH})_{6-7}$. If mode of occurrence were sufficient grounds for the naming of different minerals both names could be retained, since stibiconite is always found as a supergene alteration product whereas romeite is a mineral of metamorphosed ore deposits. The question is one which we prefer to leave to individual choice until such time as a clear formulation of what constitutes a mineral species has been generally accepted.

SYNONYMY

A number of names have appeared in the literature for antimony oxide minerals supposedly distinct from senarmontite, valentinite, and stibiconite. We have endeavored to obtain authentic specimens for as many of these as possible, in order to compare them with our own material, and to establish whether or not they are valid species. The results are enumerated in the following section.

Hydroromeite. The name hydroromeite was introduced by Natta and Baccaredda (1933), who applied it to specimens of "antimony ocher" from Higuera and Villafranca in Spain. Their analyses are comparable with those of stibiconite presented in this paper and the material had the pyrochlore structure with $a = 10.25 \text{ \AA}$. Natta and Baccaredda expressed the analyses in the formulas $\text{CaO} \cdot \text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ and $3\text{CaO} \cdot 2\text{Sb}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$, which are special cases of the general formula for stibiconite suggested in the preceding section. Under these circumstances we suggest that the name hydroromeite be dropped in favor of stibiconite.

Volgerite. The name volgerite was applied by Dana (1854) to an analyzed antimony ocher from Constantine in Algeria. The analysis is similar to those of stibiconite. A specimen labelled "Volgerite, Constantine, Algeria" (Harvard 83283) proved to consist of stibiconite with some admixed valentinite (no. 9, Table 1).

Arsenostibite (arsenstibite). Arsenstibite was introduced as a mineral name by Adam (1869) for a hydrous oxide of antimony and arsenic, with the Sb:As ratio about 3:1. The only other oxide of antimony and arsenic mentioned in the literature is that from Varuträsk, Sweden, described by Quensel (1937). The analysis of this material resembled that of arsenstibite, and Quensel revived this name for it, modifying it to arsenostibite for the sake of euphony. Professor Quensel kindly supplied us with a small portion of the type material from Varuträsk. It gave the characteristic x -ray powder photograph of the pyrochlore type, and arsenostibite is evidently structurally identical with stibiconite. Arsenostibite is a stibiconite with about one-quarter of the antimony replaced by arsenic, and in accordance with the nomenclature adopted in the seventh edition of "Dana's System of Mineralogy" it may be considered a variety of this mineral and referred to as arsenian stibiconite.

Stibianite. Stibianite was described by Goldsmith (1878) as an alteration product of stibnite from Victoria, Australia. Goldsmith's material is preserved in the museum of the Academy of Natural Sciences of Philadelphia, which kindly supplied a specimen (no. 2032) marked "Stibianite (type)" for examination. It proved to be stibiconite admixed with quartz.

Stibioferrite. Stibioferrite (the name was changed to stibioferrite by Dana) was also described by Goldsmith (1873). Two specimens were available for study, one from the museum of the Academy of Natural Sciences of Philadelphia (no. 18562, from the Vaux Collection, labelled "Stibioferrite from California, E. D. Brown, 1918"), the other from the U. S. National Museum (no. R1769, labelled "Stibioferrite, Santa Clara County, California"). The curator of the mineral collection of the Philadelphia Academy of Natural Sciences informs us that the specimen supplied is the only one of stibioferrite in the collection, and its history is unknown. This specimen agrees with Goldsmith's description, showing small yellow crystals in yellow to brownish-yellow earthy material, the whole being enclosed in a matrix of vein quartz. It is a gross mixture; the small yellow crystals are wulfenite, the yellow to brownish-yellow material is bindheimite admixed with jarosite. The specimen from the U. S. National Museum consisted of similar brownish-yellow material in a quartz matrix without the yellow crystals. The brownish-yellow material on this specimen consisted entirely of jarosite; traces of antimony were detected spectrographically. It must be concluded that stibioferrite is not a valid species.

Rivotite. Rivotite was described by Ducloux in 1874 as a massive yellowish-green mineral disseminated through a yellowish white limestone on the west side of the Sierra del Cadi, province of Lerida, Spain. The following analysis was given: Sb_2O_5 42.00, Ag_2O 1.18, CuO 39.50, CO_2 21.00; total 103.88. Several specimens of rivotite from the type locality were available for study, all of which tallied closely with the description of Ducloux. X-ray powder photographs of all three were similar, and were found to correspond to malachite, with a few weak and diffuse lines of stibiconite. Dilute HCl dissolved the malachite and left a reddish colored residue which gave the stibiconite pattern alone. Under the microscope a few particles could be recognized as malachite but most grains consisted of submicroscopic aggregates, were turbid to opaque due to inclusions, and no diagnostic data could be obtained from them. To confirm our diagnosis of rivotite as a mixture of malachite and stibiconite we had a partial analysis made, with the following results: SiO_2 3.64, Al_2O_3 0.90, Fe_2O_3 5.86, CaO 1.74, Sb_2O_5 14.4, CuO 47.6, Ag_2O 1.03, CO_2 13.6, $H_2O(-)$ 1.29, $H_2O(+)$ 7.43. The proportions of CuO , CO_2 , and $H_2O(+)$ in this analysis correspond closely with those required for malachite. The original analysis quoted by Ducloux is evidently

erroneous. Rivotite is a mixture and the name can therefore be deleted.

Barcenite: Barcenite was described by Mallet (1878) as an antimonate of mercury occurring as pseudomorphs after livingstonite from Huitzuco, Guerrero, Mexico. Apparently no further data on this mineral has been published since Mallet's original description. A sample of barcenite, agreeing in all respects with Mallet's description, was obtained from the U. S. National Museum (no. 94243). Spectrographic analysis showed that the major metallic constituents were antimony, mercury, and calcium, in agreement with the published analysis. X-ray powder photographs gave a strong pattern of stibiconite accompanied by a weaker pattern of cinnabar. It is therefore concluded that barcenite is not a homogeneous mineral but an intimate mixture of stibiconite and cinnabar.

OCCURRENCE

Stibiconite typically occurs as an alteration product of stibnite, and is often clearly pseudomorphous after this mineral. The lead antimony sulfides, such as bournonite and jamesonite, generally alter to bindheimite rather than stibiconite. Stibiconite is an important ore of antimony, especially in China and Mexico. Indeed, a major part of the antimony produced in North America comes from Mexican stibiconite. Many of the Mexican deposits consist entirely of this mineral, and the derivation from stibnite is not obvious. In the El Antimonio district of Sonora, one of the larger producers of antimony ore, the stibiconite occurs as irregular masses in quartz veins, and no stibnite has ever been found in most of the mines (White and Guiza, 1949). However, it is probable that stibnite was the primary mineral.

An interesting feature is the common occurrence of valentinite intimately intermixed with stibiconite. This valentinite is often undetectable microscopically, and can only be recognized in x-ray powder photographs. On this account we are dubious as to whether the analyses of stibiconite and cervantite in the literature can be interpreted as representing homogeneous material. Our experience indicates that intimate admixture of stibiconite and valentinite is as common as pure stibiconite. It is intriguing that the common form of Sb_2O_3 as a mineral is valentinite, not senarmontite, which is the stable form at ordinary temperatures. The only senarmontite which we have seen is from the type locality at Hamimat near Constantine in Algeria; none of the specimens of antimony ore which we examined contained this mineral, although many contained valentinite. Bloom (1939) showed that the formation of valentinite is favored by the presence of foreign ions, and this is confirmed by our data. Spectrographic analyses of senarmontite from Hamimat showed that it was as pure or purer than reagent grade Sb_2O_3 ; apart from anti-

mony it contained a trace of arsenic and a slight trace of magnesium. Spectrograms of valentinite, however, always had numerous lines of elements other than antimony.

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REFERENCES

- ADAM, M. (1869), Tableau minéralogique (no. 347).
- BEUDANT, F. S. (1832), *Traite elementaire de minéralogie*, 2nd edition, vol. 2, p. 616.
- BLOOM, M. C. (1939), The mechanism of the genesis of polymorphous forms: *Am. Mineral.*, **24**, 281-292.
- DANA, J. D. (1850), *The System of Mineralogy*, 3rd edition.
- DANA, J. D. (1854), *The System of Mineralogy*, 4th edition.
- DUCLoux, X. (1874), Note sur une nouvelle espèce minérale de la province de Lerida: *Comptes rendus*, **78**, 1471-1473.
- DUFRENOY, A. (1845), *Traite de minéralogie*, vol. 2.
- GMELIN, L. (1949), *Handbuch der anorganischen Chemie*, 8th edition, vol. 18.
- GOLDSMITH, E. (1873), Stibiaferrite, a new mineral from Santa Clara County, California: *Proc. Acad. Nat. Sci. Philadelphia*, 366-370.
- GOLDSMITH, E. (1878), Stibianite, a new mineral: *Proc. Acad. Nat. Sci. Philadelphia*, 154-155.
- HEY, M. H. (1939), On the presentation of chemical analyses of minerals: *Mineral. Mag.*, **25**, 402-412.
- KERR, P. F., KULP, J. L., AND HAMILTON, P. K. (1949), Differential thermal analyses of reference clay mineral specimens: Preliminary Report No. 3, *Am. Petrol. Inst. Project* **49**.
- MALLET, J. W. (1878), On barcenite, a new antimonate, from Huitzucó, Mexico: *Am. J. Sci.*, **16**, 306-309.
- MELLOR, J. W. (1929), *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. 9.
- NATTA, G., AND BACCAREDDA, M. (1933), Tetrossido di antimonio e antimoniate: *Zeits. Krist.*, **85**, 271-296.
- PABST, A. (1939), Formula and structure of ralstonite: *Am. Mineral.*, **24**, 566-576.
- QUENSEL, P. (1937), Minerals of the Varuträsk pegmatite III. Arsenostibite, a hydrous oxidation product of allemonite: *Geol. Fören. Stockholm Förh.*, **59**, 145-149.
- SCHREWELIUS, N. (1943), Studier över antimonat, hydroxoantimonat och fluoantimonat: Dissertation, University of Stockholm.
- WHITE, D. E., AND GUIZA, R. (1949), Antimony deposits of El Antimonio district, Sonora, Mexico: *U. S. Geol. Surv., Bull.* **962-B**.

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