RE-EXAMINATION OF MOSESITE*

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ABSTRACT

Mosesite is isostructural with Millon's base ($Hg_2NOH \cdot 2H_2O$) and its salts, the structure being a cubic cristobalite-type configuration of Hg_2N^+ groups. An analysis of mosesite from Huahuaxtla, Mexico, gave Hg^{++} 79.4 per cent, Hg^+ 3.6, Cl 3.3, SO_4 5.4, MoO_4 2.0, CO_3 0.8, N 2.44, and H_2O 3.2, total 100.1 per cent. The unit cell with $a = 9.524$ Å contains 8 [$Hg_2N(Cl, SO_4, MoO_4, CO_3) \cdot H_2O$]. The specific gravity is 7.72 (calc. 7.53). Cl, SO_4, MoO_4, and CO_3 are loosely held in large open channels in the structure and may be removed or introduced by anion exchange. Mosesite from El Doctor, Mexico, contains AsO_4 and very little MoO_4, but that from Terlingua, Texas, has only Cl and SO_4 as anions. X-ray d spacings are given.

INTRODUCTION

Mosesite was described as a new mineral by Canfield, Hillebrand, and Schaller (1910) from Terlingua, Brewster County, Tex. Unfortunately, very little material was available for their study, and a definitive description of mosesite was not possible at that time. An incomplete chemical analysis by Hillebrand showed the new mineral to be a mercury-nitrogen compound containing chloride, sulfate, and water. A second discovery at Fitting, Nev., described by Bird (1932), gave some additional data but still not enough to establish the chemical composition of the mineral.

In 1942 Foshag collected several specimens of a mercury mineral at Huahuaxtla, Guerrero, Mexico, which was found by comparison of the x-ray powder patterns to be identical with mosesite from Terlingua. The greater abundance of the Huahuaxtla material has made possible the definition of mosesite given in this paper.

Two specimens of mosesite were also obtained from El Doctor, Querétaro, Mexico. There was not enough material from this locality to allow more than a spectrographic analysis.

The writers wish to express their thanks to W. C. Alford, of the National Institute of Health, and Shuford Schuhmann, of the National Bureau of Standards, for their help in the chemical analysis, and to Howard Evans, of the U. S. Geological Survey, for constructing the crystal structure model of mosesite.

SUMMARY OF PREVIOUS WORK

Mosesite from Terlingua is in the form of small yellow crystals perched on crystals of calcite, nearly all spinel twins of the simple octahedron. Schaller (Canfield *et al.*, 1910) noted the octahedron as the only form. Later observations by Canfield (1913) gave the additional forms {001}, {011}, {116}, {114}, and {112}.

An incomplete chemical analysis on a 0.04-gram sample by Hillebrand gave 5 per cent of Cl and 3.5 per cent of SO_4. Spectroscopic tests by Nutting (in Canfield *et al.*, 1910) showed prominent lines and bands of mercury, nitrogen, and hydrogen, the last being ascribed to water. No further chemical work has been done on mosesite from Terlingua.

Schaller noted that mosesite is commonly anisotropic but reverts to the isotropic state when heated to about 186° C. The index of refraction was determined by Larsen (1921) to be $n = 2.065 \pm 0.01$. Other data for Terlingua mosesite are: cleavage, octahedral; fracture, uneven, brittle; hardness $= 3\frac{1}{2}$; luster, adamantine; color, lemon yellow to canary yellow, becoming light olive green on long exposure to light; streak, very pale yellow.

Mosesite was also reported by Bird (1932) from the Clock quicksilver mine in the Fitting district, northeast of Lovelock, Pershing County, Nev., where it was found with native mercury and cinnabar. Additional data given by Bird include a determination of the unit cell size to be $a = 9.55$ kX, and a partial chemical analysis, which gave in per cent Hg 83.0, Cl 5.0, SO_3 7.0, NH_3 2.2, sum 97.2.

CONSTITUTION OF MOSESITE

It had not been possible to write a satisfactory formula for mosesite because (1) the analytical data were incomplete and (2) the role of the nitrogen in the structure was not known. A new analysis of mosesite from Huahuaxtla (Table 2) did not immediately improve this situation because of the unknown role of nitrogen and because, in addition to the constituents previously found in mosesite, that from Huahuaxtla was found to contain 2.0 per cent MoO_4 and 0.8 per cent CO_3. To complicate the picture further, a spectrographic analysis of mosesite from El Doctor showed very little molybdenum but several per cent arsenic.

Just at the time the writers were puzzling over the mosesite analysis, Lipscomb (1951) described the structure of Millon's base ($Hg_2NOH \cdot 2H_2O$) and its salts as being a cubic cristobalite-type configuration of Hg_2N^+ groups. The identity of the x-ray powder diffraction data of Millon's base with that of mosesite made it apparent that the two materials have the same structure, and the interpretation of the mosesite analysis became a simple matter.

The d spacings for Millon's base, as published by Lipscomb, and for mosesite are compared in Table 1. The agreement in d spacings is very good. The agreement in intensities is not as good, especially in the low angle region. However, Lipscomb has pointed out (private communication) that the (111) intensity would be decreased by the presence of heavier ions in the interstices of the Hg_2N^+ framework, and that his estimated intensities in the low angle region are somewhat in error, owing to rising background on his films. Also, our intensities have not been corrected for absorption in the sample, which would make the inner ones relatively weaker.

TABLE 1. COMPARATIVE X-RAY DIFFRACTION DATA FOR MOSESITE
AND MILLON'S BASE

Mosesite Huahuaxtla (U.S.N.M. 105159) $a=9.524\pm0.002$Å Cu/Ni=1.542Å		$Hg_2NOH \cdot 2H_2O$ (Lipscomb, 1951) $a=9.58$Å		hkl
I	d (A)	I	d (A)	
4	5.44	237	5.52	111
8	2.86	65	2.88	311
10	2.74	131	2.76	222
5	2.38	48	2.40	400
6	2.18	43	2.20	331
5	1.83	24	1.84	511, 333
7	1.68	41	1.69	440
6	1.61	36	1.62	531
1	1.45	8	1.46	533
7	1.44	42	1.44	622
2	1.38	11	1.38	444
3	1.33	15	1.34	711, 551
5	1.24	17	1.25	731, 553

Lipscomb determined the structure of $Hg_2NOH \cdot 2H_2O$ to consist of a three-dimensional framework of Hg_2N^+ groups in an idealized cristobalite-type of arrangement. The mercury atoms form linear sp bonds, while the nitrogen forms tetrahedral sp^3 bonds, in a face-centered cubic lattice with $a=9.58$ Å ±0.01. The Hg-N bond distance is 2.07 Å. The space group is F $\bar{4}$ 3 m. The mercury atoms are placed at 1/8, 1/8, 1/8; 1/8, $\bar{1}/8, \bar{1}/8$; $\bar{1}/8$, 1/8, $\bar{1}/8$; and $\bar{1}/8, \bar{1}/8$, 1/8 plus the face-centered permutation, and the nitrogen atoms are placed in the diamond arrangement at 0, 0, 0 and 1/4, 1/4, 1/4 plus the face-centered permutation. A model of the structure constructed by H. T. Evans, Jr., of the Geological Survey is shown in Figures 1 and 2.
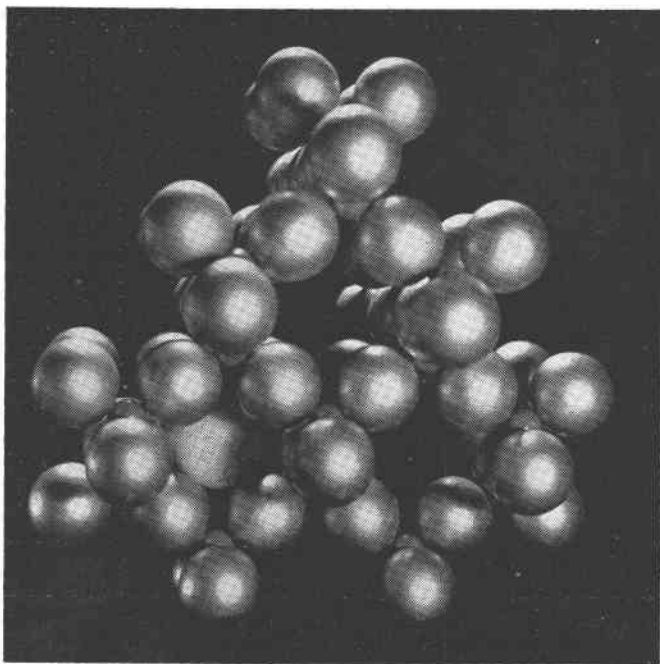
FIG. 1. View along [110] direction showing channels in structure of mosesite. The small nitrogen atoms are located at the centers of tetrahedra formed by large mercury atoms. A chloride ion is present in the lower left channel. Model by H. T. Evans, Jr. Photograph by J. A. Denson.

Lipscomb points out that the Hg_2N^+ three-dimensional network contains large channels in which it is presumed that the negative ions and water molecules are more or less randomly situated in such a way as to satisfy the electrostatic valency. He further found that the base and its salts give substantially the same powder photographs, that is, the powder photographs of the following compounds are essentially identical: $Hg_2NOH \cdot 2H_2O$, $Hg_2NCl \cdot H_2O$, Hg_2NCl, $Hg_2NBr \cdot H_2O$, Hg_2NI, Hg_2NNO_3 and Hg_2NClO_4. The scattering powers of all atoms except mercury are relatively so small that their positions can only be inferred. Probably the amounts of water are not really definite but merely enter into the structure in inexact proportions. The unit cell of Millon's base contains eight $Hg_2NOH \cdot 2H_2O$ units.

INTERPRETATION OF MOSESITE ANALYSIS

The chemical analysis has been calculated on the basis of a formula of the type $Hg_2NCl \cdot H_2O$, with a unit cell containing eight of these formula units, as shown by Lipscomb's structural studies.
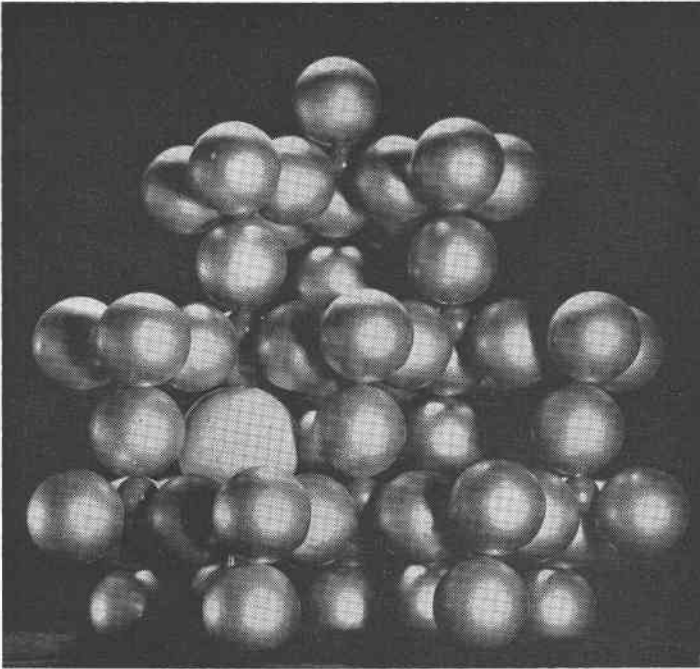
Fɪɢ. 2. View along [112] direction in the mosesite structure, showing edge view of sheets parallel to (111). The cleavage of the mineral is parallel to these sheets. The chloride ion is in the same position as in Figure 1.

The sample analyzed contained 3.6 per cent of Hg^+ which has been combined with the 79.4 per cent of Hg^{++}. Theoretically all of the mercury should be in the mercuric state. The reason for the reduction of part of it to the lower valence state is not known. The possibility that Hg^+ is present as calomel is briefly discussed in the footnote to Table 2.

The molecular ratios are given in column 2 of Table 2. The ratios for Cl, SO_4, MoO_4, and CO_3 are combined. These ratios divided by the factor required by a formula of the type $Hg_2NCl \cdot H_2O$ are given in column 3. As stated above, the value for total mercury varies considerably from that required by theory. Values for the other constituents are in better agreement.

In column 4 of Table 2 the individual values for the ratios of Cl, SO_4, MoO_4, and CO_3 are reduced to approximate whole numbers. This gives the relative proportion (average) of these four constituents per unit of structure. In column 5 the unit cell content is listed assuming $8[Hg_2NCl \cdot H_2O]$ as shown by Lipscomb. The unit cell content of Cl, SO_4, MoO_4, and CO_3 respectively is adjusted to match as closely as possible the

TABLE 2. ANALYSIS AND UNIT CELL CONTENT* OF MOSESITE FROM HUAHUAXTLA

	1	2	3		4	5	6	7
Hg^{+2}	79.4 ⎫ 83.0	0.414	2.20	2		16	+32	85.6
Hg^{+1}	3.6 ⎭							
Cl	3.3	0.093 ⎫			~ 3	3	− 3	
SO_4	5.4	0.056 ⎟ 0.175	0.93	1	$\sim 1\frac{1}{2}$	$1\frac{1}{2}$	− 3	7.6
MoO_4	2.0	0.013 ⎟			$\sim \frac{1}{2}$	$\frac{1}{2}$	− 1	
CO_3	0.8	0.013 ⎭			$\sim \frac{1}{2}$	$\frac{1}{2}$	− 1	
N	2.4	0.174	0.93	1		8	−24	3.0
H_2O	3.2	0.178	0.95	1		8		3.8
	100.1						0	100.0

* If the univalent mercury were assumed to be present as HgCl and the ratios in column 3 recomputed, the figures would be 2.04 for Hg, 0.89 for the anions, and 0.97 and 0.99 for N and H_2O, respectively. Because calomel was not definitely recognized as an impurity in the mosesite, this assumption was not adopted in interpreting the analysis.

1. Huahuaxtla. U.S.N.M. 105159. J. J. Fahey, analyst. N determined by W. C. Alford, National Institute of Health.
2. Atomic and molecular proportions.
3. Ratios for $Hg_2N(Cl, SO_4, MoO_4, CO_3) \cdot H_2O$.
4. Approximate ratios of Cl, SO_4, MoO_4, and CO_3 only.
5. Number of atoms per unit cell. Unit cell contains $8[Hg_2N(Cl, SO_4, MoO_4, CO_3) \cdot H_2O]$.
6. Electrical charges associated with each type of atom or radical. The substitution SO_4, MoO_4, or CO_3 for Cl is made on the basis of one SO_4, MoO_4, or CO_3 for two Cl.
7. Theoretical composition of $Hg_2NCl \cdot H_2O$.

amounts indicated by the analysis. The electrical charges are shown in column 6. Substitutions of SO_4, MoO_4, and CO_3 for Cl are figured on the basis of one SO_4, MoO_4, or CO_3 for Cl. The theoretical composition for $Hg_2NCl \cdot H_2O$ is given in column 7.

The ease with which salts of the Millon's base type can exchange anions has been pointed out by Srinath, Lipscomb, and Sneed (1951), who found that pure solid Hg_2NNO_3 was easily converted to Hg_2NCl $\cdot H_2O$, $Hg_2NBr \cdot H_2O$, Hg_2NI, or $Hg_2NOH \cdot 2H_2O$ by treatment, respectively, with 10 to 20 per cent aqueous solutions of KCl, KBr, KI, or KOH, which treatment displaced substantial quantities of nitrate ion in each case. The large open channels that are present in the structure are analogous to similar channels in zeolites. However, the continuous framework of Millon's base has a net positive charge rather than the net negative charge of zeolites so that anion rather than cation exchange occurs.

For mosesite, assuming a unit cell content of 16 Hg, 3 Cl, $1\frac{1}{2}$ SO_4, $\frac{1}{2}$ CO_3, $\frac{1}{2}$ MoO_4, 16 H, 8 O, and 8 N and a unit cell volume of 847.77 Å³, the calculated density is 7.53. This compares favorably with the measured density of 7.72 (determined on the analyzed sample from Hua-

huaxtla). The octahedral cleavage of the mineral follows the (111) planes of NHg_4 tetrahedra.

ANALYTICAL PROCEDURE

The chemical analysis of Huahuaxtla mosesite was made by Fahey on a carefully purified sample, weighing slightly less than one gram, after the specific gravity had been determined by use of a fused silica Adams-Johnston pycnometer. Total Hg and Cl were determined on the same sample. The univalent Hg was precipitated and weighed as HgCl. Sulfate was determined as $BaSO_4$ and the MoO_4 was computed from the MoO_3 obtained by igniting the sulfide. Total H_2O was determined by the Penfield method, using sodium tungstate as a flux. Nitrogen was determined by W. C. Alford, of the National Institute of Health, on a 20-mg. sample using the microkjeldahl procedure. Carbon dioxide was determined by a method previously described (Fahey, 1945), after having been identified as CO_2 by Shuford Schuhmann of the National Bureau of Standards, using the mass spectrograph.

CHEMICAL PROPERTIES

Mosesite is decomposed by HCl, leaving an insoluble residue of HgCl. The solution contains divalent Hg but no NH_3 as stated by Hillebrand (Canfield *et al.*, 1910). Carbon dioxide is liberated as tiny bubbles that appear on the surface of the crystals a few minutes after the addition of concentrated HCl. In $1+1$ HCl heated to about $70°$ C., the CO_2 is evolved much more rapidly. The mosesite had previously been treated with HNO_3, in which it is insoluble, in order to remove any calcite impurity.

The effect of various reagents on mosesite was tested by placing single grains with bright crystal faces in small test tubes with the reagent at room temperature. After eight days each solution was tested for Hg. None was found with H_2SO_4 (concd. or $1+1$), HNO_3 (concd. or $1+1$), acetic acid (concd. or $1+1$), oxalic acid, or water. Some mercury was dissolved by HCl (concd. or $1+1$); the concentrated HCl caused the formation of a white coating (HgCl) in one hour; the dilute acid gave a white coating in 24 hours.

SPECTROGRAPHIC ANALYSIS

A qualitative spectrographic analysis was made by Murata of mosesite from Huahuaxtla before quantitative analysis by chemical means was undertaken. The spectrogram revealed the presence of several per cent of molybdenum in this sample. This led to a spectrographic analysis of the type material and of mosesite from El Doctor, Mexico. Molybdenum

was not detectable in the type material (from Terlingua, Tex., U.S.N.M. 93292) and was present only in tenths of a per cent in the sample from El Doctor. The latter, however, was found to contain several per cent of arsenic, presumably as arsenate.

The dark outer portion and the light inner core of crystals from Huahuaxtla were separated and found by quantitative spectrographic analysis to contain 0.54 per cent and 2.1 per cent Mo, respectively.

A summary of the results of the spectrographic analysis is given below:

TABLE 3. SPECTROGRAPHIC ANALYSES OF MOSESITE FROM MEXICO

Per cent	Huahuaxtla (U.S.N.M. 105159)	El Doctor (U.S.N.M. 105522)
X0:	Hg	Hg
X:	Mo	As
0.X:	Si Al	Si Al Mg Ca Mo
0.0X–0.00X:	Fe Mg B V Ca Ba Cu	Fe B V Ag Mn
Not found:	As Mn Ag	Cu Ba
Not found in either:	Sb Sn Zn Cd Ge In Tl Pb Bi W Co Ni Cr Ti P Na Sr Y La Be	

DESCRIPTION OF MEXICAN MOSESITE

Mosesite from the two new localities in Mexico, Huahuaxtla and El Doctor, is very similar in appearance and occurrence to the original material from Terlingua, Tex. The crystals range in size from a fraction of a millimeter up to about 2 mm. and are attached to small dogtooth calcite crystals lining vugs in limestone.

The crystals are octahedral, but only rarely in single crystals. The usual habit is complex intergrowths of many crystals, resulting in nearly spherical aggregates. A few single octahedrons were noted, some of them modified by a cube, and a few simple spinel-type twins.

The color of the mosesite is variable, ranging from yellow through amber to nearly black. Some crystals are zoned, with a core of glassy amber-colored mosesite and a softer, lighter-colored surface layer. These two zones differ in molybdenum content, as already discussed, but they give identical x-ray powder patterns. The outer, lighter-colored zone seems to be a surface alteration. Powder patterns of the light- and dark-colored crystals are also identical. The cause of this variation in color is not known.

The index of refraction of mosesite from Huahuaxtla is greater than 1.95, and the mineral, like that from Terlingua, is anisotropic at room temperature.

OCCURRENCE AND ASSOCIATION

The mercury mines of Huahuaxtla have produced in the past an abundance of oxidized mercury minerals. Unfortunately, no adequate collection of these minerals has been preserved, but terlinguaite, montroydite, eglestonite, and calomel have been recognized. According to reports, rich masses of these minerals were charged into the retorts for distillation, including quantities of pure montroydite crystals, some of which exceeded an inch in length. Beautiful specimens, some of them containing as many as 10 recognizable varieties of colorful crystals, were consumed in this manner.

The commercial ore bodies at Huahuaxtla occur along ribs of brecciated limestone that formed along the rolls of a low-dipping fault plane. Limestone forms the footwall, and carbonaceous shale the hanging-wall of the fault (Gallagher and Perez-Siliceo, 1948). The chief ore mineral is cinnabar, but metacinnabar is also present and in some places abundant. Marcasite, pyrite, and stibnite are rare. Native mercury is abundant in places and some of it is associated with the oxidized minerals, suggesting their derivation from native mercury rather than from cinnabar.

The mosesite was found in a small cave in the workings of the Huahuaxtla mine known as Pozo Rico. These workings lie immediately below the Aurora tunnel about 100 meters from the entrance. It was reported that Pozo Rico yielded much native mercury, some of which was ladled directly into flasks. The small natural cave appeared to be a solution cavity in a zone of fractured limestone. This irregular cave, about 16 meters long, was lined with a crust of buff-colored steep rhombohedral calcite crystals. Sparsely scattered over these calcite crystals at one end of the cave were small octahedral crystals or aggregated octahedrons of mosesite.

Mosesite was also found with native mercury on calcite from El Doctor, State of Querétaro, Mexico. El Doctor is a famous old silver camp that was active more than a century ago. In the same district are old mercury mines, some of which were operated on a small scale during World War II. Nothing is known of the geology of these mercury deposits other than that they are enclosed in limestone. The specimen available to us contained a number of vugs in limestone lined with steep rhombohedral calcite crystals. A second generation of prismatic calcite crystals sometimes encrusted the first. Sulfur-yellow octahedral crystals or crystal groups of mosesite are scattered sparsely over the first generation calcite. Some irregular solution cavities in the limestone contain montroydite and native mercury.

Genesis

Mosesite may be easily synthesized by treating HgCl with dilute ammonium hydroxide. The reaction is shown by the equation:

$$4NH_4OH + 4HgCl \rightarrow 2Hg + Hg_2NCl \cdot H_2O + 3H_2O + 3NH_4Cl.$$
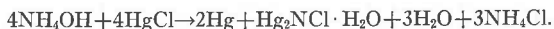
In terms of mineral components this would be equivalent to the reaction of ammonia-bearing waters with calomel, yielding native mercury and mosesite. As calomel, mosesite, and native mercury are all found at Terlingua and Huahuaxtla, it is quite probable that the mosesite was formed in just this way, probably at very low temperature because the synthesis may be done at 25° C. The other anions found in mosesite, that is, molybdate, sulfate, arsenate, and carbonate, can be accounted for by anion exchange.

Substantial concentrations of ammonia have been found in thermal waters associated with mercury deposits of Sulphur Banks mine, Lake Co., Calif. (Waring 1915, and Allen and Day, 1927). The presence of tarry organic matter in mercury deposits of many different localities has been discussed by Ross (1942). Such organic matter or its precursors may have been the original source of the ammonia required for the formation of mosesite. At the Huahuaxtla mine, the ammonia may have come from the highly carbonaceous shales lying immediately above the Pozo Rico cave.

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