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SCHUETTEITE, A NEW SUPERGENE MERCURY MINERAL*

E. H. BAILEY, F. A. HILDEBRAND, C. L. CHRIST AND J. J. FAHEY
U. S. Geological Survey, Menlo Park, Calif., and Washington, D. C.

ABSTRACT

Basic mercuric sulfate, $HgSO_4 \cdot 2HgO$, has been found as a supergene mercury mineral in several quicksilver deposits in the more arid parts of the western United States, and is a common product on dumps of burnt ore and bricks from old mercury furnaces. This new mineral is named schuetteite after Curt Nicolaus Schuette, mining engineer, geologist, and specialist on mercury deposits.

As schuetteite has been found in natural occurrences only as thin films, it has been identified by comparing its x-ray pattern with that of basic mercuric sulfate prepared in the laboratory. Crystal, chemical, and microscopic data have been obtained chiefly from similar material occurring in greater abundance in dumps and old furnace bricks.

Schuetteite is canary yellow in color, but it differs from the yellow mercury oxychlorides in that it does not darken on exposure of bright light. No crystals suitable for goniometric or precession camera work have been found, but minute tabular hexagonal crystals lying in a flat position were observed to be dark between crossed nicols. The writers, knowing the mineral was hexagonal, indexed the x-ray powder patterns by using a simple and direct method, which appears not be in general use, involving the known chemical formula and density. The hexagonal mineral has a cell with $a = 7.07_0$ Å, $c = 10.9_5$ Å (both ± 0.01 Å) and a calculated density of 8.36 gm/cm^2. The observed specific gravity is 8.18.

Optically schuetteite is uniaxial, negative. Both indices of refraction are well above 2.10; birefringence is moderate to high. It is slightly pleochroic with E = orange-yellow and O = greenish-yellow.

In natural occurrences schuetteite has been found on cinnabar surfaces exposed to sunlight. It is believed to have formed through direct oxidation of cinnabar by oxygen-bearing surface water with sunlight providing energy to cause the reaction. $HgSO_4$ may be an intermediate product.

On dumps of burnt ore and on furnace bricks the basic mercuric sulfate forms beneath the surface and a different reaction is required. In these places it appears to result from the action of strongly acid sulfate waters on metallic mercury. This reaction requires higher acidity and more strongly oxidizing conditions than are normally met in nature; in those natural environments where such conditions might occur, mercury generally is present as a sulfide rather than as the native element. It therefore seems unlikely that quicksilver deposits have anywhere been appreciably leached or enriched by either of the processes that lead to the formation of the basic mercuric sulfate.

INTRODUCTION

Schuetteite, a new mineral with the composition of basic mercuric sulfate, $HgSO_4 \cdot 2HgO$, has been found in small amounts in natural occurrences in several quicksilver deposits in Nevada, and in single localities in California, Oregon, and Idaho. The same material occurs in abundance on bricks of old Scott-type quicksilver furnaces and on dumps of furnaced ore in many other places. Its identity in natural occurrences has been

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established by comparing its *x*-ray pattern with the pattern of basic mercuric sulfate prepared in the laboratory.

It seems fitting that this new mercury mineral, which is the first to be discovered[1] since 1910 (Canfield, Hillebrand, and Schaller, 1910), be named for Curt Nicolaus Schuette (pronounced sh$\overline{\text{oo}}$′ tê), mining engineer and geologist, who has devoted much of his life to the study of mercury deposits. He has written reports on quicksilver mining and economics (Schuette, 1931*a*), on the metallurgy of quicksilver (Duschak and Schuette, 1918; Schuette, 1931*b*, 1931*c*), the geology of quicksilver deposits of Oregon (Schuette, 1938) and of the world (Schuette, 1930). He also has successfully operated several of the largest quicksilver mines in the United States.

PHYSICAL PROPERTIES

The color of schuetteite is canary yellow, which along with its association with other mercury minerals permits its ready recognition in the field. Specimens exhibit a range in color from greenish-yellow through a shade that exactly matches the color of most carnotite to a somewhat orangey-yellow in the coarsest crystals found in old furnace bricks. Its color may in places resemble the color of the mercury oxychlorides, eglestonite and terlinguaite, but both of these darken rapidly on exposure to sunlight whereas the yellow color of schuetteite remains unchanged.

The hardness appears to be about 3 on Mohs' scale, as determined by dragging minute grains of schuetteite, under a glass slide, across the surface of gypsum and calcite cleavage plates. However, as the mercury mineral is quite friable and readily reduced to dust, this test may not have yielded accurate results.

The specific gravity is 8.18, determined by using a 5 ml. fused silica Adams-Johnston pycnometer and applying a vacuum to remove air from a finely ground sample of synthetic schuetteite. The calculated density is 8.36 gm./cm.^{3}, based on composition and size of the unit cell.

OPTICAL PROPERTIES

Schuetteite is uniaxial, negative. Basal hexagonal plates observed under the oil immersion lens are sensibly dark between crossed nicols, but are much too small to yield an interference figure. Both indices of refraction are well above 2.10; the birefringence is moderate to high. All sections are yellow; however, crystals are slightly pleochroic with E = orange yellow and O = greenish yellow.

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[1] The name moschellandsbergite was introduced in 1938 by Berman and Harcourt (1938) for amalgam with a composition of Ag_2Hg_3; however, this is regarded as a redefinition of previously known material rather than a new discovery.

CRYSTALLOGRAPHY

Microscopic examination and *x*-ray diffraction studies reveal that schuetteite is hexagonal, but no crystals suitable for goniometric or precession camera work have been found. Natural occurrences of the mineral consist of thin earthy films, in many places accompanied by opal. Although the material found on bricks of demolished furnaces generally is sufficiently crystalline to exhibit a sparkle from minute crystal faces, the crystals are so clustered as to prove unsuitable for determination of the crystal morphology. Material from the dump of the Oceanic mine contained some minute crystals that were thin hexagonal plates and others that had a small hexagonal prism and steep hexagonal dipyramidal (?) faces. To confirm the apparent hexagonal character of schuetteite an attempt was made by Marie Lindberg, of the U. S. Geological Survey, to prepare electron diffraction patterns from the basal plates. However, no pattern could be obtained, probably because the thin plates were quickly volatilized by the electron beam.

X-RAY DATA

As the habit and uniaxial character of schuetteite suggested that the mineral was hexagonal, an attempt was made to index the *x*-ray powder pattern, assuming hexagonal symmetry. This attempt was entirely successful.

The initial derivation of the values of a and c of the hexagonal cell from the observed powder pattern data was made in a direct and simple way, using the known chemical formula and density. The volume of a hexagonal cell, V(Å^3), is related to the density, ρ(gm./cm.^{3}), the formula-weight of the compound, F.W. (gm.), the number of formula-weights per unit-cell, Z, and the interplanar spacings $d_{10.0}$ and $d_{00.1}$ (both in Å), by the following expression:

$$\mathrm{V} = (2/3^{1/2})d^2_{10.0}d_{00.1} = \frac{Z \times (\mathrm{F.W.})}{6.023 \times 10^{23} \times \rho \times 10^{-24}} \tag{1}$$

For schuetteite, F. W. = 729.90, and $\rho = 8.18$ (taking the density equal to the observed specific gravity). Substituting these values into (1), we obtain:

$$d_{10.0} = (11.328\, Z^{1/2})/d^{1/2}_{00.1} \tag{2}$$

or

$$hd_{h0.0} = (11.328\, Z^{1/2})/(ld_{00.1})^{1/2} \tag{3}$$

Several values of the observed d-spacings from Table 1 were tentatively assumed to represent $d_{00.1}$, and values for $d_{10.0}$ were calculated from (3), for several values of Z. By the use of this method it very soon became apparent that the observed values of 6.13 Å and 3.35 Å, of Table 1, represent $d_{10.0}$ and $d_{00.3}$, respectively, and that $Z=3$. From a consideration of a large number of the observed spacings, the unit-cell constants that best fit all the data were selected as $a=7.07_0$ Å and $c=10.0_5$ Å (both ±0.01 Å). All possible $d_{hk.l}$ were calculated on the basis of these unit-cell constants, using the expression

$$\frac{1}{d_{hk.l}} = \left[\frac{4}{3a^2}(h^2+hk+k^2)+\frac{l^2}{c^2}\right]^{1/2};$$

the calculated spacings are listed in Table 1. The calculated density is 8.36 gm./cm.^{3}, which compares favorably with the measured specific gravity of 8.18. It will be noted from Table 1 that there are no systematic extinctions leading to a rhombohedral cell. In addition it will be noted that with the exception of the very weak line of spacing 9.5 to 9.6 Å, all the observed reflections of the type $00.l$ obey the criterion $l=3n$ only.

The line of spacing 9.5 Å occurs on powder pattern photographs made with Cu/Ni radiation just at the edge of the region of heavy scattering around the central beam, and consequently it is difficult to measure it accurately, or even to decide whether it is, in fact, present in some of the films studied. Attempts made to record the line on diffractometer tracings and on powder pattern photographs using Cr/V radiation were unsuccessful.

If it is assumed that the line is due to a constant impurity such as some decomposition product of $HgSO_4 \cdot 2HgO$, then the criterion holds that for $00.l$ reflections $l=3n$ only and that schuetteite contains a 3_1, 3_2, 6_2, or 6_4 axis and has one of the ten space groups compatible with these screw axes listed in International Tables (1952). If, on the other hand, the 9.5 Å line is truly the 00.1 line, then schuetteite has a pseudo screw axis of the kind listed above. Such a pseudo screw axis would be due to the arrangement of the relatively heavy mercury atoms.

Although the method expressed by (3) above is perfectly general, where the chemical formula and density are known and the symmetry is suspected, and is quite easy to apply in practice, it does not seem to be in common use.

CHEMICAL PROPERTIES

The assignment of the chemical formula of $HgSO_4 \cdot 2HgO$ to schuetteite is based on the identity of its x-ray pattern with that of the artificial compound, which can be readily prepared by adding water to solid mercuric sulfate after the equation:

$$3\,HgSO_4 + 2\,H_2O \rightarrow HgSO_4 \cdot 2HgO + 2\,H_2SO_4$$

TABLE 1. *X*-RAY DATA FOR SCHUETTEITE—$HgSO_4 \cdot 2HgO$
HEXAGONAL; $a = 7.07_0$ Å, $c = 10.0_5$ Å (BOTH ±0.01 Å)

	Measured*				Calculated†	
	Cu/Ni	$\lambda K\alpha = 1.5418$ Å $\lambda K\alpha_1 = 1.5405$ $\lambda K\alpha_2 = 1.5443$				
I/I_0**	$d_{hk.l}$[1]	$d_{hk.l}$[2]	$d_{hk.l}$[3]	$d_{hk.l}$[4]	$d_{hk.l}$	$hk.l$
<5[5]		9.5	9.6	9.5	10.0	00.1
11	6.13	6.11	6.11	6.11	6.12	10.0
22	5.22	5.19	5.19	5.21	5.21	10.1
					5.02	00.2
4	3.87	3.85			3.88	10.2
					3.54	11.0
69	3.35	3.34	3.34	3.34	3.35	00.3
<5		3.33			3.34	11.1
5	3.06	3.04		3.04	3.06	20.0
100	2.92	2.91	2.91	2.92	2.94	10.3
					2.93	20.1
					2.89	11.2
55	2.61	2.60	2.60	2.61	2.61	20.2
					2.513	00.4
3	2.43	2.42			2.432	11.3
<5		2.32		2.32	2.324	10.4
15	2.315	2.30		2.30	2.314	21.0
					2.260	20.3
7	2.25	2.24	2.24	2.25	2.255	21.1
2	2.10	2.09		2.09	2.102	21.2
		2.040			2.048	11.4
					2.041	30.0
					2.010	00.5
3	1.99	1.989		1.989	2.000	30.1
26	1.937	1.933	1.933	1.937	1.942	20.4
<5		1.899	1.899	1.888	1.910	10.5
6	1.900				1.904	21.3
3	1.887	1.881			1.891	30.2
16	1.763	1.762	1.762	1.762	1.768	22.0
<5		1.755		1.755	1.747	11.5
6	1.741	1.737	1.737	1.737	1.743	30.3
6	1.739	1.731		1.731	1.741	22.1
					1.702	21.4
5	1.696	1.695		1.695	1.698	31.0
15	1.674[6]	1.675 1.670	1.675	1.675 1.667	1.680 1.675	20.5 00.6

* The powder patterns made photographically were taken with Debye-Scherrer powder cameras of 114.59 mm. diameter, using the Straumanis technique. The lower cut-off limit is at 2θ of approximately 7° (13 Å).

** Intensities from diffractometer tracing except those marked <5 or <3.

† Spacings calculated for $d \geq 1.5$ Å only.

[1] $HgSO_4 \cdot 2HgO$ from burnt ore dump, Oceanic mine, San Luis Obispo Co., Calif. Diffractometer tracings run between $2\theta = 4°$ and $2\theta = 106°$. Error in peak-position measurement approximately $\lesssim 0.1°$ (2θ).

[2] Synthetic schuetteite prepared by treating $HgSO_4$ with H_2O ,washing and decanting excess H_2SO_4. This product was used for the chemical analysis. Film No. 7532.

[3] Schuetteite furnace deposit from the Chisos Furnace, Terlingua district, Trans Pecos, Texas. Film No. 6362.

[4] Schuetteite from the B. and B. mine, Nevada. Film No. 6355.

[5] Intensities marked <5, or <3 are estimated from powder films.

[6] Doublet.

TABLE 1 (*continued*)

Measured*					Calculated†	
Cu/Ni		$\lambda K\alpha = 1.5418$ Å $\lambda K\alpha_1 = 1.5405$ $\lambda K\alpha_2 = 1.5443$				
					1.674	31.1
					1.667	22.2
<5		1.610 *b*[7]		1.608 *b*	1.616 1.609	10.6 31.2
3	1.610					
					1.584	30.4
18	1.558	1.556	1.558	1.556	1.563	22.3
3	1.528	1.526		1.523	1.531	40.0
					1.518	21.5
					1.515	31.3
					1.514	11.6
10	1.510	1.508	1.508	1.508	1.513	40.1
<5		1.488				
7	1.461	1.459	1.459			
2	1.443	1.441		1.441		
2	1.430	1.427	1.427	1.427		
4	1.404	1.399		1.400		
5	1.389	1.388	1.388	1.388		
2	1.352	1.352	1.352	1.352		
3	1.324	1.321		1.323		
5	1.305	1.302	1.302	1.302		
5	1.297	1.296	1.296	1.298		
7	1.213	1.213 *b*	1.213	1.215 *b*		
2	1.188	1.188				
1	1.181	1.180 *b*				
<5		1.159	1.158	1.163		
6	1.147	1.144 α_1		1.144 α_1		
4	1.144	1.145 α_2				
6	1.125	1.123 α_1	1.124 α_1	1.123 α_1		
4	1.122	1.124 α_2				
2	1.111	1.110		1.110		
1	1.102					
2	1.092	1.094 α_1 1.091 α_2		1.094 α_1		
1	1.073	1.072 *b*		1.071 *b*		
3	1.049	1.047 α_1	1.047 α_1	1.048 α_1		
2	1.045	1.045 α_2				
2	1.013	1.017		1.017		
<3		1.011				
3	1.000	1.001 α_1 .999 α_2	1.001 α_1	1.001 α_1 .999 α_2		
2	0.974	.974 *b*				
		.960 *b*				
		.951 *b*				
		.942 *b*		942 *b*		
		.929 *b*				
		.914 *b*				
		.898 *b*		.898 *b*		

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[7] *b* = broad.

To verify the identity of the synthetic material an analysis was made which yielded 88.9 per cent HgO and 11.3 per cent SO_3, which agrees closely with a theoretical 89.0 and 11.0 per cent for the basic mercuric sulfate.

Material from the Oceanic mine dump, which gives an identical powder pattern, was purified for analysis insofar as possible by fine grinding, repeated centrifuging, and flotation. Its analysis is shown in Table 2. The sample proved to be only a little more than 80 per cent pure, with the chief impurities being opal, hematite, and cinnabar. The small amount of cinnabar caused a lowering of the mercury-sulfur ratio. Spectroscopic analysis of the same sample did not reveal other elements to be present in quantities larger than 0.01 per cent.

TABLE 2

Analysis		Recalculated to include only HgO and SO_3	Theoretical $HgSO_4 \cdot 2HgO$
HgO[1]	71.44	87.7	89.0
SiO_2	12.74		
Fe_2O_3	1.22		
TiO_2	0.20		
Al_2O_3	0.54		
CaO	0.08		
MgO	0.06		
SO_3	9.99	12.3	11.0
H_2O*	3.73		
	100.00	100.0	100.0

[1] Weighed as metal after amalgamation with a preweighed gold bar (Fahey, 1937).

* By difference.

OCCURRENCE

Schuetteite has been found as a naturally occurring supergene mineral in six quicksilver mine areas in Nevada, and at single mines in Oregon, Idaho, and California (see Fig. 1). In all of these places it occurs as thin films on surfaces of cinnabar-bearing rocks that are exposed to sunlight. It does not penetrate the rocks except to depths of less than 1 mm. along cracks, and none has been found in the numerous underground workings in these mine areas.

All but one of the Nevada occurrences, and the Idaho and Oregon localities, are at quicksilver deposits of the opalite type (Bailey and Phoenix, 1944, p. 17–21). In these deposits cinnabar generally occurs in a widespread blanket of rock known as opalite, formed by the leaching and silicification of acid tuffs or siliceous sediments. The opalite is cryptocrystalline, and the widely used name is a misnomer as chalcedonic quartz, rather than opal, is generally the predominant mineral. The cinnabar occurs as clouds of disseminated crystals, generally of minute size (Pollock, 1944, p. 2), in favorable layers or along feeder faults. Calomel, mercury oxychlorides, and native mercury have been found at the Opalite mine in Oregon and elsewhere, but they are not common in this type of deposit. Other minerals, except for relict quartz, are generally rare or absent. Some opalite deposits contain alunite, and a few of the rocks found coated with schuetteite contain a little of this mineral. Except for cinnabar, pyrite is the only other sulfur-bearing mineral occurring in opalite deposits, and it is so rare that it has been observed only as a few minute crystals in a single deposit.

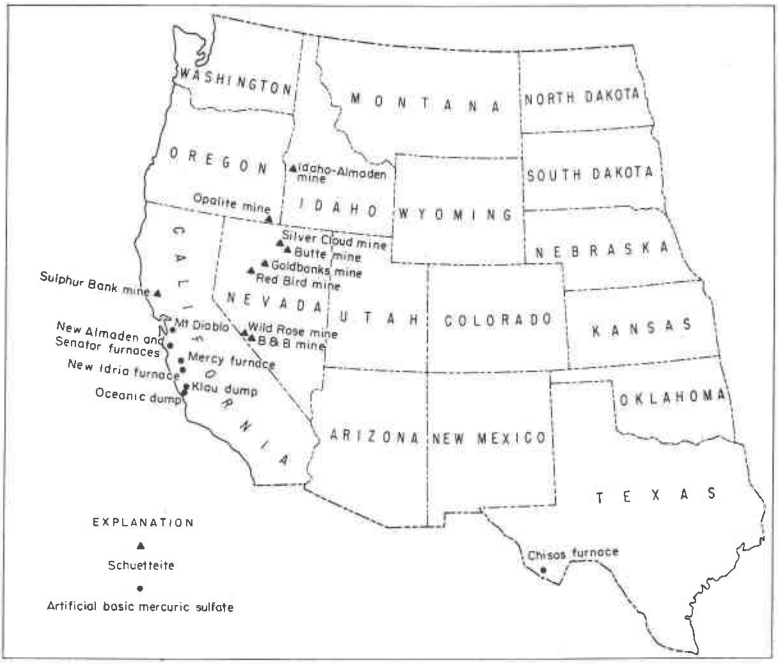

FIG. 1. Index map showing localities where schuetteite has been found, and showing other occurrences of basic mercuric sulfate.

Schuetteite is most easily found at the Silver Cloud mine in the Ivanhoe district about 30 miles north of Battle Mountain, Nevada (Bailey and Phoenix, 1944, p. 61–63). Here an open cut has been stripped to the undulating surface of a particularly hard layer of opalite that only locally contains concentrations of cinnabar. Schuetteite is scattered over this surface, forming nebulous blooms almost a foot in diameter in places where there is also a concentration of cinnabar. The cinnabar has turned black from exposure to sunlight, forming a background on which the thin films of bright yellow schuetteite are readily seen. The open cut was developed to its present depth shortly before the mine was visited by Bailey in 1943; the schuetteite formed between that date and 1956 when it was revisited.

The mineral is also readily found at the B. and B. mine on the east slope of the White Mountains, Esmeralda County, Nevada (Bailey and Phoenix, 1944, p. 67–70). It is most abundant on the steep wall forming the northeastern part of the main glory hole that has been excavated in flat beds of sintery opalite. The glory hole was developed between 1927 and 1930. When Bailey mapped the deposit in 1941 only a little schuetteite was noted in the area, but by 1956 considerable quantities of the mineral had formed. In 1941 it was also collected from loose opalite blocks in the floor of a second pit below the furnace site. Here alunite is present in some of the opalite, and hyaline opal is closely associated with the schuetteite.

Other opalite deposits where schuetteite has been found are the Wild Rose mine, the Velvet working of the Butte mine, and the Goldbanks mine in Nevada (Bailey and Phoenix, 1944, p. 74–75, 56–68, and 170–171), the Opalite mine in southeastern Oregon (Yates, 1942, p. 343–344), and the Idaho-Almaden mine east of Weiser, Idaho (Ross, 1956, p. 95–99).

At the Red Bird mine east of Lovelock, Nevada (Bailey and Phoenix, 1944, p. 167–168) schuetteite was found on a single specimen of rich ore on the waste dump. It selectively coats crystals of cinnabar up to 3 mm. in diameter occurring in a gangue of limestone and quartz.

At the famous Sulphur Bank mine in Lake County, California (Everhart, 1946) thin films of what is probably schuetteite were found on cinnabar-bearing leached basalt between the Northwest Pit and the Basalt Pit. Because of the scarcity of material its identity has not been verified by x-rays. This is an area of continuing hydrothermal activity where the surface waters are highly acid. The environment is comparable to that which prevails in some of the artificial occurrences discussed in the following paragraphs.

Basic mercuric sulfate has also been found in many places where it cannot properly be considered a naturally occurring mineral. Some description of these occurrences seems warranted because the sulfate was apparently formed through a different process than that responsible for most of the natural occurrences. These places include bricks from old Scott-type furnaces formerly widely used for treating quicksilver ore, and dumps of furnaced rock, generally called calcine.

Clots of crystals of macroscopic size form coatings several millimeters thick on the bricks of the dismantled Chisos mine furnace in Brewster Co., Texas. Similar material has been noted in California at the New Almaden and Senator mines in Santa Clara County, the Mercy mine in Fresno County, and the Sulphur Bank mine in Lake County, Mercury sulfate was also referred to as coating the condensers at the Corona mine and the furnaces of the Sulphur Bank and New Idria mines (Bradley, 1918, p. 81, 236). In these occurrences it is in some places closely associated with artificial gypsum, calomel, montroydite, and cinnabar, but metallic mercury, which occurs as droplets in many old furnace bricks, has not been seen with the mercuric sulfate. In contrast to the naturally occurring surface films, the artificial material not only encrusts the bricks but also occurs in pores within them where no sunlight could have penetrated.

The basic mercuric sulfate has been found on calcine dumps in several localities, the most notable of which is at the Oceanic mine in San Luis Obispo County, California. In a part of this dump of burnt ore the sulfate occurs as minute crystals and earthy bunches in a layer of fine-grained debris extending from the surface to a depth of at least $1\frac{1}{2}$ feet. The yellow sulfate amounts to more than 10 per cent of the material in part of the dump, and it constitutes good retort ore containing hundreds, if not thousands, of dollars worth of mercury. The material has been left behind by retort operators, as have the yellow coated bricks in other places, because it is not red like cinnabar and contains no visible mercury. The "gangue" here consists of opal, much of which is attached to the mercuric sulfate, gypsum, cinnabar, iron oxides, quartz, and rock fragments.

The yellow sulfate also has been noted on dump rock at the Klau and New Idria mines, and it forms thin films on rocks near the exhaust end of the condensing stack at the Mt. Diablo mine in Contra Costa County, California.

ORIGIN

The occurrences of basic mercuric sulfate described previously suggest that it forms by two different processes. In the natural occurrences it is closely associated with cinnabar and is limited to environments exposed to sunlight; on bricks and dumps it occurs in areas suspected of containing elemental mercury as well as cinnabar, and that may not be exposed to sunlight. Even though only one questionable natural occurrence fits the latter environment, similar conditions can under unusual circumstances exist in nature and might give rise to appreciable quantities of the mineral through the same process that is responsible for its formation on the dumps.

Because schuetteite forms in the natural occurrences as thin films on cinnabar-bearing surfaces exposed to sunlight, we may conclude that it forms as a result of a reaction involving HgS, sunlight, and a small amount of water containing dissolved oxygen. The surficial water is probably nearly neutral in the mineralized areas where schuetteite occurs, although it may contain locally a little sulfate as a result of limited solution of alunite or the oxidation of pyrite. Some chloride may also be present in the water, but no mercury chlorides or other chlorides have been noted in most of the deposits; even though present chloride would not appreciably aid in dissolving the cinnabar. It thus seems likely the reactions involve only cinnabar, atmospheric oxygen (dissolved in water with a pH a little below 7), and sunlight according to the equation:

$$\text{HgS} + 2\text{O}_2 + \text{energy from sunlight } (h\nu) \rightarrow \text{HgSO}_4$$

The mercuric sulfate with water yields by hydrolysis the basic mercuric sulfate, which has very limited solubility.

If cinnabar, sunlight, oxygen, and water are all that is needed to form the basic mercuric sulfate, one may reasonably ask why the mineral is not more common than it is. The fact that all known occurrences, except the one in the high sulfate environment of Sulphur Bank, are in arid regions suggests the possibility that the amount of sunlight required, or the correct wavelength region of the solar spectrum, or a combination of these two factors, are found only in desert regions. The same explanation can also be applied to the darkening of cinnabar in the sun, which is common in the desert regions yet rarely occurs in the Coast Ranges of California.

The basic mercuric sulfate formed in old furnace bricks and mine dumps is in a high sulfate environment and probably results from the action of strong sulfuric acid solutions on elemental mercury. Although the metal is common in bricks and dumps, it has not been found where the mercuric sulfate is abundant, suggesting it has all been converted to the sulfate. On the other hand the fine-grained cinnabar that occurs with the basic mercuric sulfate on the Oceanic dump appears unetched and unattacked by the solutions that formed the sulfate. In the laboratory, mercuric sulfate can be readily formed by the action of hot concentrated sulfuric acid on mercury but with cold acid the reaction goes very slowly if at all. Preliminary thermodynamic calculations by R. M. Garrels (written communication) suggest mercury sulfate should form only under very strongly acid (pH close to 1) and very strongly oxidizing conditions. Such conditions can occur in nature where pyrite, H_2S, or native sulfur are being rapidly oxidized, but the required pH and Eh are more extreme than is general even in mineralized areas. Under less severe conditions of acidity and oxidation, native mercury is stable, and probably some native mercury found in oxidizing environments is supergene.

SIGNIFICANCE

Mercuric sulfide is notably more stable in the zone of oxidation than are the sulfides of other common metals, and for this reason opinions differ regarding the possibility of oxidation and secondary enrichment of mercury deposits. Broderick (1916) and Emmons (1917) on the basis of laboratory experiments concluded that cinnabar was essentially insoluble in acid sulfate solutions, but they thought mercury sulfide might be transported in chloride solutions and precipitated as a sulfide by reaction with stibnite or a few other metallic sulfides. Krauskopf (1951) concluded that it was unlikely that HgS could be dissolved appreciably in acid sulfide solutions and indicated that conditions required to effect appreciable solubility with chlorides would seldom, if ever, be met in nature. Examples of cinnabar of supposed supergene origin are discussed by Ross (1942, p. 463–464) who suggests the cinnabar in these places has been mechanically transported as tiny suspended particles.

Saukov and Aidinyan (1940) have described experiments in which ferric sulfate and cinnabar were allowed to stand for periods of as long as 60 days in water containing two drops of sulfuric acid. Tests for ferrous iron and dissolved mercury indicated that the iron was reduced and the HgS oxidized to form $HgSO_4$, according to the equation:

$$n\mathrm{HgS} + n\mathrm{Fe_2(SO_4)_3} \rightarrow n\mathrm{HgSO_4} + n\mathrm{FeSO_4} + \cdots$$

Similar experiments with NaCl added yielded much larger amounts of ferrous iron and mercury, which was in solution largely as mercuric chloride. As a result of their experiments and field observations, they believed that cinnabar had been leached in the oxidized zone of some mercury deposits.

The occurrence of the basic mercuric sulfate, schuetteite, indicates that under suitable conditions cinnabar can be converted to mercury sulfate, which hydrolyzes almost completely to deposit the insoluble basic mercuric sulfate. As this reaction involves sunlight and is effective only on the surface in restricted areas, and as it results in very little of the mercury sulfate remaining in solution, it is unlikely that any mercury ore body has been appreciably leached or enriched by this process.

The occurrence of the basic mercuric sulfate in considerable quantity in parts of old dumps, where it is believed to have formed as a result of a reaction of sulfuric acid solutions and mercury, suggests that in areas of very strong acidity and oxidation mercury can be taken into solution as a sulfate and can migrate. Such areas in nature will generally occur where there is a large amount of pyrite or marcasite, and in these areas the mercury is normally present as a sulfide rather than as native metal. It therefore seems unlikely that the restrictive conditions necessary to bring about leaching of native mercury in the zone of oxidation are often met in nature, although under the most favorable conditions this offers a possible mechanism for leaching of mercury ore bodies.

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