THE STABILITY RELATIONS OF CINNABAR AND METACINNABAR*

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ABSTRACT

The stability relations of cinnabar and metacinnabar have not been well understood. Metacinnabar, or black HgS, has been supposed to occur in nature as a metastable substance found in weathered portions of mercury ore deposits. Cinnabar, or red HgS, was considered to be the only stable modification of HgS. However, the results of the present study indicate that pure red HgS, cinnabar, inverts to black HgS, metacinnabar, at 344° C., at one atmosphere pressure. The inversion is comparatively rapid and is reversible for pure HgS. The presence of small amounts of iron, zinc, or selenium in the metacinnabar structure retards the inversion of metacinnabar to cinnabar at temperatures at which cinnabar is stable. In addition, the presence of iron or zinc in the metacinnabar depresses the inversion temperature: iron, to as low as 305° C.; and zinc, to as low as 240° C.

Studies of ores and protores containing both cinnabar and metacinnabar show that in general metacinnabar was deposited earlier than cinnabar. Metacinnabar does not appear to be an alteration product of cinnabar, but some cinnabar is the product of the inversion of metacinnabar. Conclusions from study of ores and protores are consistent with conclusions from the laboratory study of equilibrium relations of cinnabar and metacinnabar.

INTRODUCTION

The relationship of cinnabar, red HgS, to metacinnabar, black HgS, has been inadequately studied and has been poorly understood. Moore, who first described metacinnabar in 1872 (6), recognized that the metacinnabar in the specimens he studied had been deposited earlier than associated cinnabar, but he thought that metacinnabar was amorphous. Penfield first demonstrated that metacinnabar is crystalline and correctly assigned it to the sphalerite group (8, p. 452–453). Lindgren (5, p. 463) regarded metacinnabar as a supergene mineral found principally in altered mercury ore deposits. Lindgren's opinion was widely accepted, although later workers have observed that some metacinnabar is earlier than accompanying cinnabar (Ross, 10, p. 51; Bailey and Phoenix, 2, p. 137; and Eckel and Myers, 3, p. 97–98). Studies by the present authors

indicate that metacinnabar is a hypogene mineral which in most instances was deposited earlier than associated cinnabar.

Previous Experimental Work

Allen, Crenshaw, and Merwin (1) studied aspects of the chemical and thermal behavior of HgS, with the aim of determining the conditions under which cinnabar and metacinnabar are formed. Red HgS and black HgS were heated in evacuated vessels in the presence of substances such as ammonium sulfide and sulfuric acid, at temperatures ranging from 100° C. to 570° C., for times varying from one-half day to five days. After cooling the samples were examined under the microscope for evidences of inversion. Red HgS was reported to be unchanged, but black HgS was either partially or completely altered to red HgS. Allen, Crenshaw, and Merwin concluded that red HgS was stable at all temperatures up to 570° C. and that metacinnabar was not stable under any of the conditions of their experiments. They found the thermal behavior of HgS to be rather confusing, however. They reported that HgS, initially red, heated to 445° C. appeared black to the naked eye, but after the samples were ground fine and examined under the microscope they were seen to be made up mostly of cinnabar. The black color of the unground samples was apparently caused by a thin layer of metacinnabar on the cinnabar particles. No satisfactory explanation was presented for the appearance of black HgS, which had formed from red HgS in contradiction to their conclusion that red HgS was the stable phase at 445° C. The suggestion was offered that black HgS deposited from the vapor in the container when the container and contents were quenched.

The equilibrium pressures of the reaction $n\mathrm{HgS_{(solid)}} \rightarrow n\mathrm{Hg_{(gas)}} + \mathrm{S}_{n\,\mathrm{(gas)}}$ were measured by Rinse at temperatures ranging from 331° C. to 651° C. (9, p. 28–32). HgS samples were heated in a sealed glass instrument, one end of which was a hollow glass spring which coiled or uncoiled in response to unbalanced pressure between the interior and exterior of the instrument. The internal pressure was estimated by measuring the external pressure required to bring the spring to a zero position. Table 1 presents Rinse's data.

Rinse noted that red HgS became black when heated above 400° C., and he showed that the HgS had acquired the specific gravity of metacinnabar. By the use of an undescribed method of plotting his data, he deduced that red HgS inverts to black HgS at 386 ± 2° C. However, Rinse mentioned that HgS heated for three days at 347° C. became black and possessed a specific gravity intermediate between cinnabar and metacinnabar. He applied the theory of allotropy as expounded by Smits (11) to explain the appearance of metacinnabar below the supposed inversion

TABLE 1. RINSE'S VALUES FOR THE DISSOCIATION PRESSURES OF THE REACTION
$n\mathrm{HgS}_{(\mathrm{solid})} \rightarrow n\mathrm{Hg}_{(\mathrm{gas})} + \mathrm{S}_{n(\mathrm{gas})}$ AS A FUNCTION OF TEMPERATURE

Red HgS		Black HgS			
Temp. in ° C.	Pressure in mm. Hg	Temp. in ° C.	Pressure in mm. Hg	Temp. in ° C.	Pressure in mm. Hg
333	1.1	331.5	1.45	440	34.0
345.5	1.95	351	2.7	447.5	40.7
351	2.1	357	3.35	457.5	53.0
356	2.8	359.5	3.7	472	73.8
360	3.1	365	4.2	479.5	86.4
362	3.3	373	5.35	491	115.3
371.5	4.7	378	6.4	501.5	147
378.5	5.95	383	7.4	521	221.5
		392.5	9.6	540	340
		395	10.55	564	526
		400	12.0	582	740
		409.5	15.4	599	983
		422.5	22.35	633	1766
		429	25.75	651	2385

temperature. From thermodynamical considerations, however, it appears most unlikely that metacinnabar could form from cinnabar as a result of a reaction in the solid state below the true inversion temperature. Therefore, Rinse's determination of the inversion temperature seems to be in error. Furthermore, inspection of his data, plotted in Fig. 1 as pressure versus temperature, shows no well defined intersection of the curve for cinnabar with the curve for metacinnabar. His measurements are not sufficiently reliable to permit an exact determination of the inversion temperature.

Treadwell and Schaufelberger (12, p. 1938) estimated the inversion temperature to be 400° C. by heating red HgS in capillary glass tubes for several hours at controlled temperatures. They noted that cinnabar heated at 375° to 385° C. became black, but x-ray examination revealed only a trace of metacinnabar. Treadwell and Schaufelberger theorized that the metacinnabar had deposited from the vapor phase during the quenching of the sample. They demonstrated the slowness of the inversion of metacinnabar to cinnabar under the stability conditions of cinnabar. For example, black HgS heated at 250° to 300° C. for 30 hours was only partially transformed to cinnabar.

Professor W. S. Fyfe, of the Department of Geology, University of California, Berkeley, California, noted that red HgS transformed to black HgS at 290° C. and 80 bars water pressure (oral communication).
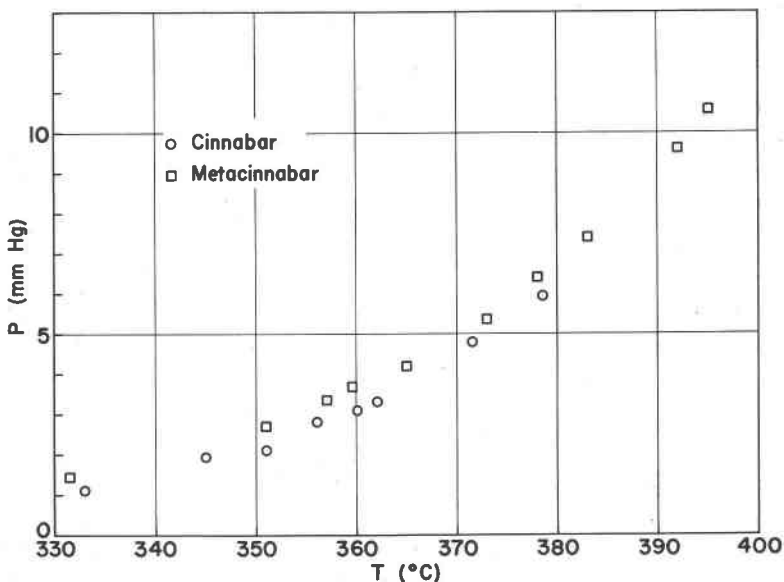
Fig. 1. A plot of a portion of Rinse's temperature-pressure determinations for the reactions $n\mathrm{HgS_{(red)}} \rightarrow n\mathrm{Hg_{(gas)}} + \mathrm{S}_{n\mathrm{(gas)}}$ and $n\mathrm{HgS_{(black)}} \rightarrow n\mathrm{Hg_{(gas)}} + \mathrm{S}_{n\mathrm{(gas)}}$.

However, Fyfe's experiments were carried out with natural cinnabar, which may have been impure, and he used steel containers to hold the experimental mixtures. Both of these factors may have had an effect on the inversion temperature (see p. 480–481, this paper).

Present Experimental Work

The solubilities of black HgS and red HgS in $\mathrm{Na_2S}$ solutions were determined by the authors at 25° C., 50° C., and 75° C. at one atmosphere pressure (3, p. 18). The solubility of black HgS, though greater than that of red HgS at all three temperatures, decreases more rapidly with increasing temperature than the solubility of red HgS (Fig. 2). Extrapolating the data to higher temperatures shows that at some temperature above those examined by us, the solubilities of the two forms can be expected to become equal. Inasmuch as the two forms would then be capable of coexisting in stable equilibrium in contact with the same solution at one temperature, that temperature would be the inversion temperature. The inversion temperature could not be determined accurately from the solubility data, however, because the angle of intersection of the extrapolated curves is small and small experimental errors greatly affect the location of the intersection.

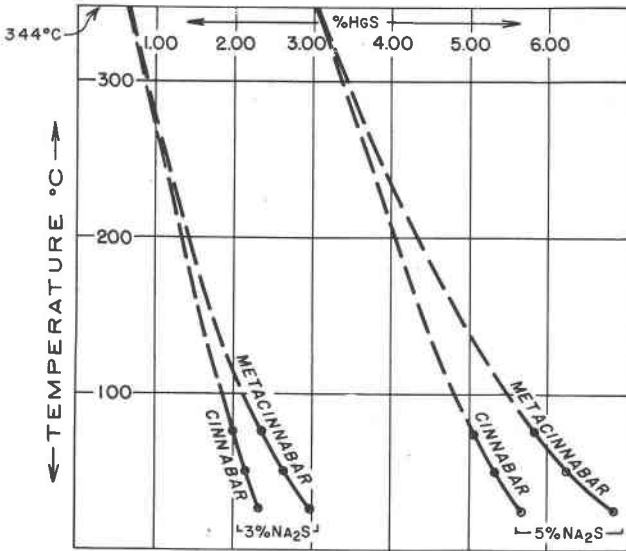The inversion temperature was therefore measured by more accurate

Fig. 2. The solubility of cinnabar (red HgS) and metacinnabar (black HgS) in 3% and 5% sodium sulfide solutions at 25° C., 50° C., and 75° C. as determined by Dickson and Tunell. Solid lines connect experimentally determined points, and broken lines represent curves extrapolated to intersect at the inversion temperature, 344° C.

direct methods. The first method involved heating Baker and Adamson reagent grade red HgS in a series of sealed evacuated glass tubes at controlled temperatures ranging from 320° C. to 380° C., each for a period of one week. The cooled samples were examined by the x-ray spectrometer to detect the presence of metacinnabar. The inversion temperature determined in this way is 344° C. ± 4° C. Attempts were made to measure the inversion temperature by heating black HgS, but the transformation of black HgS synthesized in the laboratory to red HgS proved to be so sluggish that runs of excessive duration would have been required to effect the inversion. For example, only a small part, perhaps 5%, of black HgS heated for three weeks at 330° C. was converted to red HgS.

A second method of determining the inversion temperature involved the use of a temperature gradient furnace designed by Kennedy and Dickson for the purpose of studying dissociation pressures of metal sulfide reactions. A capillary glass tube was filled with red HgS and heated in such a manner that a temperature gradient of about ten degrees per inch existed along the tube. The furnace used to establish the temperature gradient is illustrated in Fig. 3. The alundum core of the furnace was wound with three platinum wire coils: a rear coil (not used in our experiments) to maintain a constant temperature zone; a middle coil to estab-
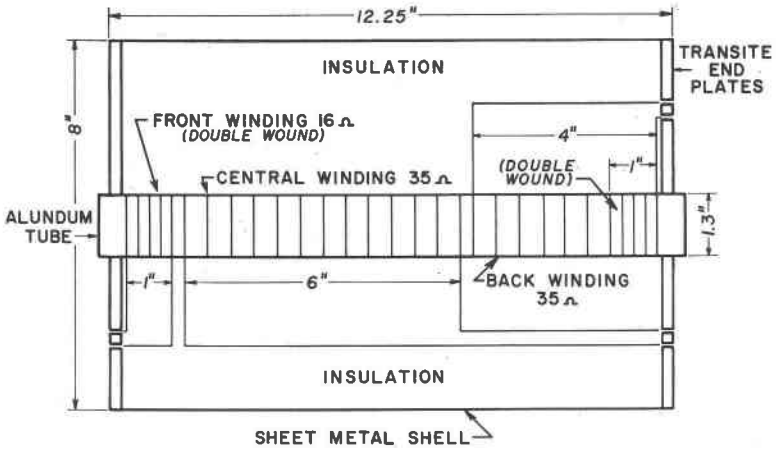
FIG. 3. Cross-section view of temperature-gradient furnace used to determine inversion temperatures. (Apparatus designed by Kennedy and Dickson.)

lish a temperature gradient over the central portion of the tube; and a front coil to allow manipulation of the temperature gradient. The power input to each of the coils was controlled by separate phase-shifting thyratron controllers. Inside the alundum core was a stainless steel tube (Fig. 4) which provided a thermal mass and smoothed the temperature distribution. Alumel-chromel thermocouples were precisely spaced at intervals along the steel tube, sunk in receptacles in holes in the steel which allowed placement of the thermocouples close to the glass tube. Temperatures along the steel tube could be adjusted by varying the power delivered to the separate heating coils.
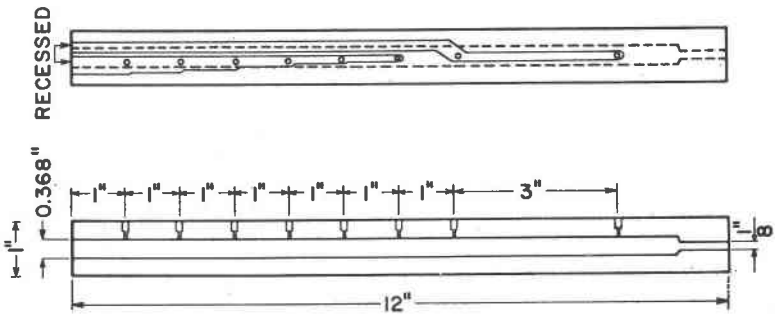

FIG. 4. Schematic diagram of stainless steel tube designed to fit in alundum tube of the temperature gradient furnace. Upper drawing is a plan view showing thermocouple wells and longitudinal grooves in which thermocouple leads were placed. Lower drawing is a cross-sectional view showing placement and shape of thermocouple wells.

The experimental procedure was to place a thick-walled capillary glass tube filled with red HgS in the stainless steel tube and to allow the glass to attain the temperature of the steel. The position of the boundary between unaltered red HgS and black HgS was observed at regular intervals of time. No migration of the boundary was observed after 24 hours of exposure to the temperature gradient, but to ensure complete reaction the capillary was left in the apparatus for four days. At the end of four days the capillary was withdrawn, air quenched, and the boundary between red and black HgS was located within one-tenth of an inch. The temperature which had existed at the boundary before removal of the capillary tube was obtained by thermocouple measurements of temperature made before the tube was withdrawn. An inversion temperature of $344°$ C. $\pm 2°$ C. was obtained in this way. The presence of metacinnabar in the darkened HgS was confirmed by x-ray examination.

Differential thermal analyses of red HgS, kindly carried out for us by Dr. J. F. Burst at the Shell Development Company, Houston, Texas, revealed that an endothermic reaction, presumably the inversion of red HgS to black HgS, was initiated at $355°$ C. and completed at $381°$ C. The differential thermal analyzer heats the sample rapidly, in this case at a rate of ten degrees Centigrade per minute. The inversion of red HgS to black HgS proceeds slowly at or near $344°$ C. and it is to be expected that the inversion temperature determined by such rapid heating would be higher than one obtained by slow heating.

Dr. R. A. Rowland, also of the Shell Development Company, Houston, Texas, measured for as atomic planar spacings of HgS at temperatures above $300°$ C. by use of the oscillating-heating x-ray diffractometer (13, p. 118–119). Temperatures were not measured accurately enough to permit a determination of the inversion temperature. However, Dr. Rowland confirmed the inversion of red HgS to black HgS at elevated temperatures, and further demonstrated that the crystalline phase actually existing at the elevated temperatures is metacinnabar.

That cinnabar inverts to metacinnabar on heating has therefore been experimentally well established. Why did such careful workers as Allen, Crenshaw, and Merwin fail to observe the inversion? The answer seems to be that black HgS produced by heating pure red HgS above $344°$ C. reverts rapidly to red HgS on cooling below $344°$ C. The actual process of reversion can be observed. Fine-grained HgS crystals, made by heating red HgS in a sealed evacuated glass tube at $350°$ C. were black when first cooled to room temperature, but on standing for about one-half hour changed to red. Grinding freshly-made black HgS appeared to accelerate the reversion to red HgS.

A further illustration of the reversion process was the behavior of

freshly-made black HgS while being examined by the x-ray spectrometer. A diagnostic part of the 2θ region for cinnabar and metacinnabar ($30°$ to $32°$, copper Kα radiation) was scanned at two minute intervals and the peaks representing the diffracted x-ray beams were plotted on graph paper by means of a strip chart recorder (Fig. 5). The first scanning showed a metacinnabar peak and a cinnabar peak of about the same height; subsequent scannings showed progressively decreased heights of metacinnabar peaks and increased heights of cinnabar peaks. Peak heights are directly proportional to the amount of each phase in the sample and thus the ratio of the amount of cinnabar to the amount of metacinnabar increased with time. Presumably if the sample had been examined while still hot there would have been only a metacinnabar peak, as in the case of Dr. Rowland's experiment, but between the end of the heating process and the first scanning by the spectrometer there was about a 30 second delay owing to the time required to grind the sample and sediment it on a glass plate.

The fact that black HgS, formed by heating pure red HgS above $344°$ C., reverts rapidly to cinnabar on cooling probably explains why Allen, Crenshaw, and Merwin did not discover that cinnabar inverts to metacinnabar at high temperatures.

The rapidity with which pure black HgS reverts to red HgS on cooling in the laboratory raises another question: How is it possible for metacinnabar to persist at ordinary temperatures, as it does in nature, and in some cases in the laboratory? In an attempt to answer this question the effect of impurities in the system was investigated.

Analyses show that naturally occurring metacinnabar contains elements such as iron, zinc, and selenium, sometimes in major amounts. Table 2 presents analyses of metacinnabar taken from *Dana's System of Mineralogy, Seventh Edition* (7, p. 216); it is noteworthy that the specimens of metacinnabar contained in addition to mercury and sulfur at least one of the elements mentioned above and some contained two. Few reliable analyses of cinnabar have been reported in the literature, but several specimens analyzed by the writers contained less than 0.1% nonvolatile impurities. By contrast, homogeneous metacinnabar from the Mt. Diablo mine, California, contained 0.5% iron.

Samples of red HgS were heated in the presence of iron sulfide, zinc sulfide, and selenium, respectively. These substances acted to retard the reversion of metacinnabar to cinnabar; freshly formed metacinnabar made in this way did not revert to cinnabar, but remained unchanged after being kept for months at room temperature. The metacinnabar was only metastable, however, and could be converted to cinnabar by allowing it to stand in contact with sodium sulfide solutions.
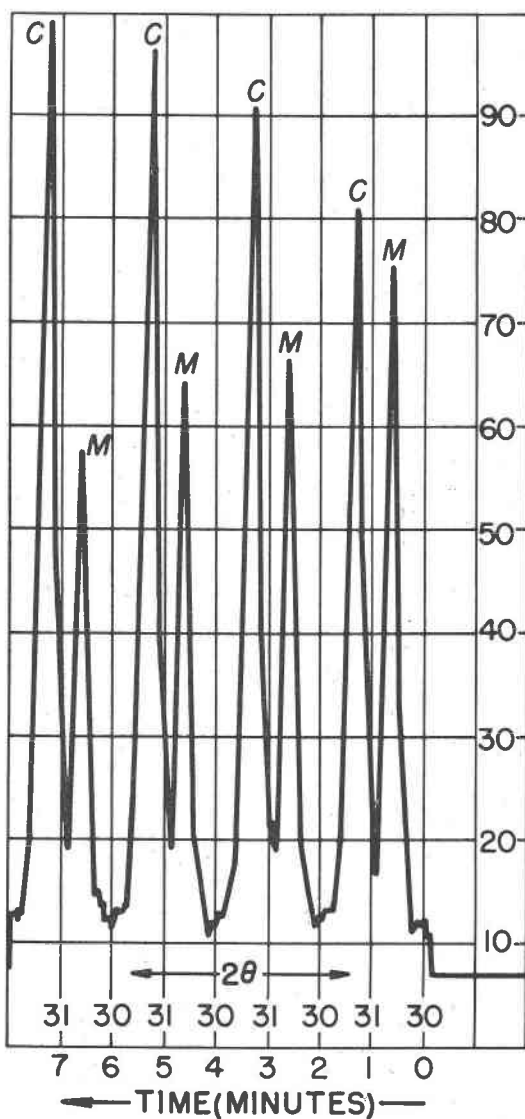
FIG. 5. X-ray spectrometer measurements of diffraction peaks of HgS heated previously above 344° C., the inversion temperature of red and black HgS. The 2θ region from 30° to 32° was scanned at two-minute intervals. Peaks labeled M represent the 2.92 Å spacing of black HgS, and peaks labeled C represent the 2.85 Å spacing of red HgS. The intensities of the diffracted beams are proportional to areas under the peaks, and are direct functions of the amounts of the phases present in the sample. Note the increase in the height of C and the decrease in the height of M with the passage of time. Cu Kα radiation was used.

TABLE 2. ANALYSES OF METACINNABAR LISTED IN DANA'S
SYSTEM OF MINERALOGY, 7TH EDITION, PAGE 216

	1	2	3	4	5	6
Weight % Hg	86.22	77.68	79.73	79.69	83.38	81.83
Weight % Fe		5.36	trace	1.04		
Weight % Zn			4.23	3.32	2.17	
Weight % Se			1.08			6.49
Weight % S	13.78	14.97	14.58	14.97	14.24	10.30
Rem.		1.41			0.52	
Total	100.00	99.42	99.62	99.02	100.31	98.12

1. Pure HgS.
2. Felsöbánya, Transylvania. Rem. is insoluble.
3. Guadalcazar, Mexico (guadalcazarite).
4. Pola de Lena, Spain.
5. Levigliani, Italy (leviglianite). Rem. is FeO.
6. San Onofre, Mexico (onofrite).

The amount of Fe or Zn needed to retard the reversion of metacinnabar was quite small, less than 0.3 per cent. Metacinnabar made by heating an intimately ground mixture of four parts of red HgS to one part of FeS_2 at 520° C. for 16 hours, contained slightly more than 0.1% iron. The metacinnabar formed a solid black cake, conforming in shape to the interior of the glass tube used to hold the sample. A powdery layer of excess FeS_2 remained on the upper surface of the cake. This FeS_2 was removed easily by scraping, however. Before analysis, to ensure that no FeS_2 was mechanically mixed with the metacinnabar the cake was ground fine and the powder was passed through a magnetic separator with sufficient magnetic flux to remove FeS_2. No iron-rich fraction separated. Under the microscope the material was observed to be uniformly black and homogeneous.

As a control (initially red) pure HgS was heated in a sealed evacuated glass tube for 16 hours at 520° C. in the oven alongside the tube containing the red HgS and FeS_2 mixture. A solid, homogeneous, deep red cake formed, similar in shape to the metacinnabar cake previously described. A dissimilar feature of the red cake was that it had fractured into polygonal columns oriented at right angles to the glass tube wall. It is likely that at 520° C. the HgS was metacinnabar, which on cooling inverted to cinnabar. The decrease in volume involved when the metacinnabar inverted to cinnabar probably caused the fragmentation.

As mentioned on page 475, unsuccessful attempts had been made by us to determine the inversion temperature by heating laboratory

prepared metacinnabar. The sluggishness of the reaction was probably caused by the effect of small amounts of impurities introduced during the process used to synthesize the metacinnabar. The metacinnabar was made by precipitation from mercuric sulfide-sodium sulfide solutions. This method resulted in a fine-grained precipitate which probably absorbed impurities from the solution.

The small amount of black HgS which Allen, Crenshaw, and Merwin found in their heated red HgS samples may have resulted from the presence of traces of impurities in the red HgS. That only a small amount of metacinnabar persisted is evidence that their red HgS was quite pure.

In addition to retarding the inversion of metacinnabar to cinnabar, the presence of iron or zinc depresses the inversion temperature. FeS_2 lowers the inversion temperature to at least as low as 305° C., and ZnS to at least 240° C. These temperatures were determined by heating intimate mixtures of red HgS and amorphous iron and zinc sulfides in glass capillary tubes in the controlled temperature-gradient furnace for one week periods. It should be emphasized that the values obtained in this way are upper bounds only. Solid-solid reactions are involved which probably become slower at low temperatures, and the temperatures reported may be merely those at which the reactions become so slow as not to be detectable after one week.

It should be pointed out that the "pure" HgS used in the determination of the inversion temperature contained a very small amount of iron, of the order of 0.01%. Since even very small amounts of impurities may influence the temperature of inversion, the inversion temperature reported for HgS of this iron content may be slightly different from the true inversion temperature of pure HgS.

As mentioned earlier, Fyfe observed that natural cinnabar inverted to metacinnabar at 290° C., under water pressure in a steel bomb. The temperature was lower than 344° C. probably because of impurities, either existing in the original sample or, more likely, introduced from the metal walls of the bomb.

In summary, the laboratory study of the stability relations of cinnabar and metacinnabar has demonstrated that: (1) at one atmosphere pressure pure HgS exists in two stable modifications, cinnabar (red HgS) at or below 344° C. $\pm$ 2° C., and metacinnabar (black HgS) at or above the same temperature; (2) pure metacinnabar reverts rapidly to cinnabar below 344° C.; (3) the presence of Fe, Zn, or Se retards the reversion to cinnabar below the inversion temperature; and (4) the presence of FeS_2 depresses the inversion temperature to at least 305° C., and the presence of Zn depresses the inversion temperature to at least 240° C.

Petrographic Studies

Textural relations of cinnabar and metacinnabar were studied in ores and protores collected at numerous mercury mines and occurrences in California, Oregon, and Nevada. The mineral relations were studied by techniques involving the use of polished sections, thin sections, and polished surfaces. Examination of minerals in cavities by means of the binocular microscope proved to be most informative. Minerals were identified by x-ray methods whenever possible. The textures observed in ores and protores from some of the localities are described briefly in the following pages.

Senator mine and Mariposa Canyon prospect

The Senator mine and the Mariposa Canyon prospect, two neighboring localities in the Toquima Range, Nevada, had been examined previously by Bailey and Phoenix, who stated that at the Senator mine "Metacinnabar occurs as coarse crystals in a barite-quartz gangue. Cinnabar occurs as coatings on the metacinnabar, as small veinlets in barite and quartz, and as painty clouds in the kaolinized wall rocks" (2, p. 137). Although Bailey and Phoenix did not explicitly state the time relations involved, it seems apparent from their textural descriptions that they recognized that at least a part of the metacinnabar was earlier than cinnabar. In ore specimens examined by the present writers from both the Senator mine and the Mariposa prospect, mercuric sulfide commonly occurs as rounded grains embedded in a quartz-barite matrix in veins which transect altered granitic rocks. The mercuric sulfide grains are made up of a core of metacinnabar enveloped by a shell of cinnabar. This relation indicates continuous deposition of mercuric sulfide, with early metacinnabar followed by cinnabar. An unusual specimen from the Senator mine shows a clear euhedral barite crystal which contains euhedral crystals of metacinnabar and cinnabar on interior planar surfaces (phantom crystal faces), and on outer faces. The metacinnabar and cinnabar crystals in this specimen are not in contact, but are heterogeneously arranged, and in places are concentrated along lines which apparently represent former crystal edges. During the growth of the barite crystal metacinnabar and cinnabar crystals deposited either simultaneously or in alternation.

Aetna and Knoxville mines

Unequivocal evidence showing that metacinnabar crystals were deposited earlier than associated cinnabar crystals was observed in specimens from the Aetna and Knoxville mines, California. Equant, euhedral metacinnabar crystals in cavities in altered serpentine from both localities

are coated with euhedral needle-like crystals of cinnabar which radiate outward from the surfaces of the metacinnabar crystals (Fig. 6). In some of the Knoxville specimens some elongate cinnabar crystals show near their bases color gradation from typical bright red, through dark red, to black at the junction with metacinnabar (Fig. 7). The cinnabar in these specimens clearly formed after the metacinnabar. The color change at the base of the cinnabar crystals is somewhat difficult to interpret; perhaps conditions during continuous deposition of mercuric sulfide changed rather abruptly from those favoring metacinnabar to those favoring cinnabar.

Some of the metacinnabar crystals in the Aetna specimens are altered to a reddish-black spongy residue about which unaltered cinnabar crystals are arranged in the same way that cinnabar crystals are arranged about unaltered metacinnabar crystals. The metacinnabar crystals apparently were less resistant to chemical attack than the cinnabar crystals. The preferential alteration and removal of metacinnabar suggests that at the time of the attack cinnabar was stable. A common laboratory method of removing small amounts of metacinnabar from cinnabar is to wash the mixture with dilute sodium sulfide solution which selectively dissolves the metacinnabar. Late solutions evidently acted on the metacinnabar and cinnabar crystals in some of the Aetna specimens in a similar way.

New Idria mine

In samples of ore collected at the New Idria mine several kinds of metacinnabar-cinnabar textures were observed which indicate early metacinnabar. For example, alternating thin layers of metacinnabar and dolomite adhere to fracture walls in brecciated sandstone. Overlying the metacinnabar and dolomite layers in the medial portions of the veins massive layers of cinnabar are commonly present. Scattered on other surfaces are small euhedral crystals of metacinnabar covered by layers of cinnabar. Eckel and Myers (3, p. 97–98) on the basis of examination of cinnabar-metacinnabar textures in rocks from the New Idria mine also concluded that the metacinnabar was earlier than the cinnabar.

Mt. Jackson mine

In samples of ore from the Mt. Jackson mine, California, the times of deposition of metacinnabar and cinnabar apparently overlapped. Tiny euhedral crystals of metacinnabar and cinnabar are mixed together in fractures and cavities in strongly silicified rocks. Commonly cinnabar crystals are perched on metacinnabar crystals and nearby in the same cavity metacinnabar crystals are perched on cinnabar (Figs. 8 and 9).

Mt. Diablo mine

C. P. Ross has pointed out that at the Mt. Diablo mine metacinnabar in general appears to have deposited earlier than cinnabar (10, p. 51). Our observations are in accord with those of Ross. Veinlets containing metacinnabar transected by cinnabar veinlets were noted by us, indicating that some metacinnabar is earlier than cinnabar. However, because of the complex mineral sequence in the rocks at Mt. Diablo, and the added difficulty that cinnabar and metacinnabar do not occur together in many of the specimens, the possibility that some or even much of the cinnabar is earlier than some metacinnabar cannot be ruled out.

Amedee Hot Springs, California, and Boiling Springs, Idaho

Metacinnabar and cinnabar occur as thin coatings on calcareous tufa and lake sediments in and about hot spring orifices at Amedee, California, near the east shore of Honey Lake. The rock surfaces over which the spring waters flow are coated by layers of fine-grained cinnabar as much as one-tenth of an inch thick. Overlying the cinnabar is a thinner layer of sooty metacinnabar. The mercuric sulfide forms aprons which extend about 25 feet down slope from the hot spring orifices. The thickness of the layer of mercuric sulfide and the proportion of cinnabar to metacinnabar decrease progressively away from the outlets. In the throats of the hottest vents nearly all the mercuric sulfide is in the form of cinnabar.

A few specimens from Amedee show wispy layers of metacinnabar alternating with thicker layers of cinnabar; in some of these specimens metacinnabar has partially altered to cinnabar, but for most of the cinnabar there is no evidence suggesting that it was not deposited as cinnabar.

A mercuric sulfide occurrence at Boiling Springs, Idaho, very similar to that at Amedee was described briefly by White (14, p. 124–125). Boiling Springs was visited by us during the summer of 1958 and specimens were taken for study. Specimens collected near the hot spring orifices showed layers of cinnabar coating the country rock, overlain in turn by thinner layers of metacinnabar.

The time relations at Amedee and Boiling Springs are the reverse of the usual relation seen elsewhere. Most of the metacinnabar was deposited later than associated cinnabar. The occurrences at Amedee and Boiling Springs are also unusual in that deposition has taken place at the earth's surface very recently, under relatively low conditions of temperature (near 100° C.) and pressure (approximately one atmosphere).

Summary of field and petrographic studies

The field and petrographic studies have demonstrated that: (1) metacinnabar is an earlier mineral than cinnabar as a general rule, although in exceptional circumstances it may be later; (2) in some cases mercuric sulfide was deposited continuously, with early metacinnabar giving way to later cinnabar; (3) in rare instances cinnabar and metacinnabar were deposited simultaneously or in alternation; and (4) metacinnabar was deposited from solutions as metacinnabar, and can not be considered to be an alteration product of cinnabar.

GEOLOGIC CONCLUSIONS

The conclusions resulting from the petrologic studies are in agreement with the determination of the stability relations of cinnabar and metacinnabar by laboratory experiments. That metacinnabar occurs as a hypogene mineral is supported by the petrologic evidence; the conclusion that it occurs as a hypogene mineral is furthermore in accord with the experimental fact that it is stable at high temperatures. The experimental evidence does not preclude the possibility that some metacinnabar in nature has formed metastably even though it was deposited by hypogene solutions.

That metacinnabar should be an earlier mineral than cinnabar appears to be expectable if deposition takes place along with falling temperatures. In this case a high temperature phase should be earlier than a low temperature phase of the same composition.

Textures indicating continuous deposition of mercuric sulfide, with metacinnabar giving way to cinnabar, can be explained in two ways. First, the mercuric sulfide might have been deposited continuously while the temperature dropped from a temperature above the inversion temperature to one below it; or second, deposition may have taken place at a constant temperature, with the concentration in the ore-carrying fluid of a substance such as iron decreasing continuously until at some concentration cinnabar became the stable phase. Probably it is more reasonable to explain continuous deposition of HgS by appealing to falling temperature; if variation in composition of the solutions from which the mercuric sulfide is being deposited commonly determined which phase was formed, reverse relations (early cinnabar and late metacinnabar) should be observed in more specimens than actually is the case.

Simultaneous deposition of cinnabar and metacinnabar could take place stably only if the temperature, pressure, and compositional conditions were precisely adjusted so that cinnabar and metacinnabar were

in equilibrium. Such a delicate adjustment would be expected to occur infrequently in nature and, indeed, textures indicating simultaneous deposition of the two minerals are rare. It is possible, theoretically, for cinnabar and metacinnabar to precipitate together over a temperature interval if the composition of the system varied in such a way as to maintain equilibrium, but this does not appear very probable.

Mineral relationships indicating alternating deposition of cinnabar and metacinnabar imply that these minerals were deposited in an environment of fluctuating chemical and physical conditions. At a given temperature the concentration of substances such as iron or zinc may have fluctuated about certain critical concentrations, or for a given composition, the temperature may have varied above and below the inversion temperature.

The occurrences of HgS at Amedee Hot Springs, California, and Boiling Springs, Idaho, where metacinnabar was deposited later than cinnabar, were both unusual in that deposition has taken place at the earth's surface quite recently. Hot, supersaturated waters have deposited mercuric sulfide at the zone of maximum change in conditions, where temperature and pressure are changing sharply and where there is increased turbulence. The metacinnabar has apparently formed metastably as it does at ordinary temperatures and pressures in the laboratory, probably as a consequence of rapid deposition. Some cinnabar has been formed by the alteration of metacinnabar to cinnabar; it is possible that all of the cinnabar formed in this way, but textural evidences bearing on this point are meager. If some of the cinnabar was deposited as cinnabar, and, as appears likely, if the physical conditions have remained essentially the same during the period of deposition, chemical conditions must have varied to enable fluctuating deposition of cinnabar with metacinnabar.[1]

Acknowledgments

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[1] This paper, being concerned chiefly with cinnabar-metacinnabar relations, has discussed extensively specimens containing both minerals. It should be emphasized, however, that although metacinnabar occurs more commonly than has been generally realized, nevertheless, in most mercury deposits cinnabar is the only mercury mineral present. In general, moreover, the textural evidences indicate that the cinnabar was deposited as such, not as metacinnabar which in turn inverted to cinnabar.

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