

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 18

JANUARY, 1933

No. 1

CINNABAR AND ASSOCIATED MINERALS FROM PIKE COUNTY, ARKANSAS*

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INTRODUCTION

During the early part of the summer of 1931, quicksilver ores were discovered in Pike County, southwestern Arkansas. While engaged in a petrographic examination of a suite of these ores for Dr. George C. Branner, State Geologist of Arkansas, I encountered several interesting mineral occurrences and relationships that appear to merit description. Prospecting is being carried on both in the central and eastern part of the county, near the towns of Crawford and Jackfork. A furnace is now in operation and economic appraisals of the deposits are being made.

The Mississippian and Pennsylvanian sandstones and shales, which cover the area, have been intensely folded and faulted. Miser and Purdue,¹ who have described the geology of the district, include an excellent map with their report.

RELATIONSHIP OF THE CINNABAR TO THE COUNTRY ROCK

The ore bodies are in the form of veins and disseminated masses in the lower part of the Jackfork quartzitic sandstone of Mississippian age. The veins follow, for the most part, the fractures and bedding planes of the sandstone, a gray to buff rock which has been firmly cemented with secondary quartz. The quartz grains measure, on the average, 0.1 mm. in diameter and have a well rounded appearance as if waterworn. Other detrital minerals present in the country rock include tourmaline, zircon, muscovite, chlorite, badly altered feldspar fragments, and occasional small grains of rutile. The feldspar has often been sericitized and rounded rock fragments are not uncommon. Most of the extensive fractures in the sandstone have been filled with vein quartz and it is in the interstices of these grains that the chief ore mineral, cinnabar, is

* Published by permission of the State Geologist of Arkansas.

¹ Miser, H. D., and Purdue, A. H., *Geology of the DeQueen and Caddo Gap quadrangles, Arkansas: U. S. G. S. Bull.* 808, 1929.

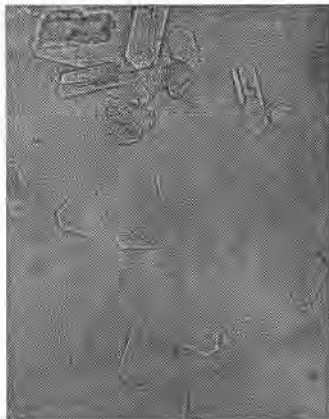


FIG. 1. (\times ca. 130 diameters). Euhedral crystals of dickite mounted in Canada balsam. The crystals are slightly out of focus so as to bring the Becke line just within the crystal boundary, thus emphasizing the outline.

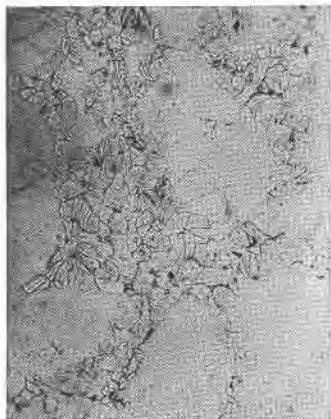


FIG. 2. (\times ca. 100). Showing well developed dickite crystals in the vein quartz.

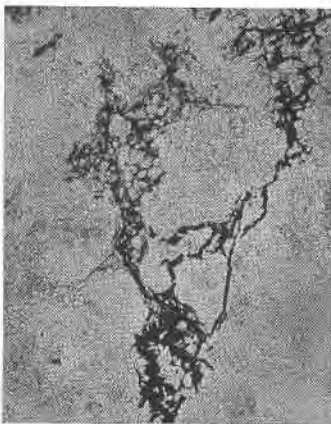


FIG. 3. (\times ca. 100). The iron-bearing dickite has formed in the interstices of the vein quartz and is cut by irregular stringers of cinnabar (opaque). The normal dickite of lower double refraction replaces the quartz grains.

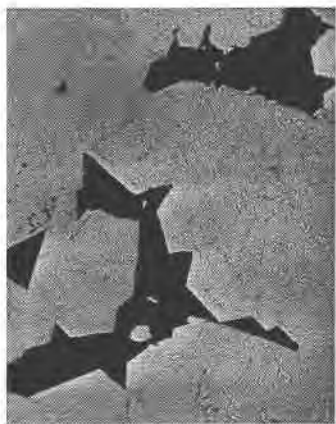


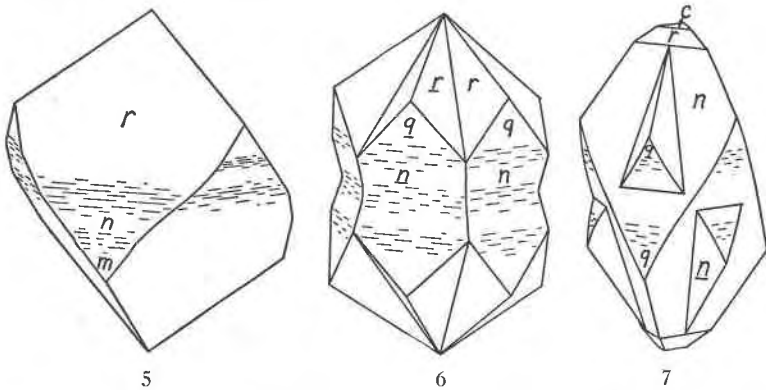
FIG. 4. (\times ca. 100). The cinnabar (opaque) has formed around the quartz crystals which are replaced by the dickite.

found. The cinnabar has been deposited after the formation of the vein quartz for cinnabar often completely surrounds the quartz grains. In some instances very fine veinlets of cinnabar cut grains of vein quartz, but this is comparatively infrequent. In such cases the ore has probably filled small fractures caused by later movement. Although most of the ore is in the vein quartz, the country rock adjacent to the veins also carry stringers of cinnabar.

In some places the veins are separated from the country rock by narrow zones of gouge material. This crushed rock does not contain any cinnabar nor does the country rock close by; even when the ore is present in the vein bordering on the crushed zone.

EUHEDRAL CRYSTALS OF CINNABAR

Closer to the surface euhedral crystals of cinnabar occur in vuggy openings and along some of the bedding planes of the sandstone. These are generally twins although simpler untwinned individuals have been noted. The crystals vary in size from 1 to 7 mm. in length and are usually more or less malformed.



FIGS. 5, 6, 7. Clinographic projections of euhedral crystals of cinnabar. An attempt has been made to show the rounded and striated appearance typical of these crystals. Forms noted: $r\{10\bar{1}1\}$, $n\{20\bar{2}1\}$, $q\{40\bar{4}1\}$, $m\{10\bar{1}0\}$, and $c\{0001\}$.

The untwinned crystals are smaller and more perfectly formed than the twinned individuals. Although this observation may not be true for a larger number of specimens, it seems to be most often the case among those examined. As can be seen in Fig. 5, the simple

² According to Buckley and Vernon, the hexagonal prism and not the rhombohedron is the space lattice in cinnabar. Four indices rather than three should therefore be used. Buckley, H. E. and Vernon, W. S., *Miner. Mag.*, vol. 20, p. 382, 1925.

crystals are rhombohedrons, the unit rhombohedron $r\{10\bar{1}1\}$ predominating with the steeper rhombohedron $n\{20\bar{2}1\}$, and the prism $m\{10\bar{1}0\}$ occurring as modifications.²

The twinned crystals, Figs. 6 and 7, are of the penetration type with the c -axis as the twin-axis. In addition to the forms present in the simpler crystals, another rhombohedron, $q\{40\bar{4}1\}$, the pinacoid $c\{0001\}$ and the trigonal trapezohedron $\kappa\{42\bar{6}3\}$ are present. Similar twinned crystals have been described by Tschermak³ from Nikitovka, Russia, and by Termier⁴ from Ouen-Shan-Tschiang, China. The penetration-twinning of crystals having the trapezohedron present is apparently very rare; for with the exception of the Nikitovka occurrence, which Tschermak describes as being twinned in the same manner, it is not known to have been found elsewhere. The unit rhombohedron almost always merges into the steeper rhombohedrons; the effect being a curved face. Some difficulty was encountered in accurately measuring the crystals as the faces, in addition to being curved, are often dull and striated. The differences between the values of the measured and recorded angles must be attributed to this cause.

TABLE OF INTERFACIAL ANGLES

	Measured	Recorded
cr (0001) \wedge (10 $\bar{1}$ 1)	53°34'	52°54'
rn (10 $\bar{1}$ 1) \wedge (20 $\bar{2}$ 1)	17 30	16 24
cq (0001) \wedge (40 $\bar{4}$ 1)	78 00	79 18
$r\kappa$ (10 $\bar{1}$ 1) \wedge (42 $\bar{6}$ 3)	21 05	21 30
rr (10 $\bar{1}$ 1) \wedge (01 $\bar{1}$ 1)	75 00	74 12

SECONDARY QUICKSILVER MINERALS

A number of interesting secondary quicksilver minerals are found closely associated with the cinnabar. Both calomel and native mercury in the form of globules fill many of the near surface cavities. Also, small amounts of a greenish-yellow mineral occur with the calomel as irregular masses. Fragments of this, mounted in Canada balsam, prove to be completely isotropic at room temperature. This mineral is eglestonite, previously described from Terlingua, Texas,⁵ and San Mateo County, California.⁶

² Tschermak, G., *Min. u. Petr. Mitth.*, vol. 7, p. 361, 1886.

³ Termier, P., *Bull. Soc. Fran. Min.*, vol. 20, p. 204, 1887.

⁵ Moses, A. J., *Am. Journ. Sci.*, [4] vol. 16, pp. 253-63, 1903.

⁶ Rogers, A. F., *Am. Journ. Sci.*, [4] vol. 32, pp. 48-50, 1911.

In places, the cinnabar has been thinly coated with metacinnabar,⁷ the black, secondary sulfide of mercury. When the thin, opaque coating is heated with sodium carbonate in a closed tube, small globules of mercury result. The use of a polished surface provides no additional information as the polishing process employed destroys the coating. Allen and Crenshaw⁸ state that metacinnabar is formed when descending dilute acid solutions come in contact with precipitating agents such as sulfides and organic matter. Broderick⁹ has demonstrated experimentally that these waters must have a chloride composition, because sulfates, the only other salts likely to form, immediately hydrolyze to form an insoluble basic salt.

DICKITE AND OTHER ASSOCIATED MINERALS

Dickite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), a mineral of the kaolin group and a polymorph of kaolinite and nacrite, is universally present in both the quartz veins and the fractures and bedding planes close to the surface. Singly terminated quartz crystals projecting from the walls of these fractures are very often covered with the dickite. In the hollows between the quartz crystals, places especially favorable for uninterrupted growth, the dickite is best developed, individual crystals measuring up to 0.15 mm. in length. The crystals are tabular in habit, occasionally twinned, and commonly form pseudo-hexagonal book-like aggregates. The optical character is biaxial positive with the optic plane normal to the crystal edge. The three principal indices of refraction, obtained by the immersion method, are $n_\alpha = 1.560$, $n_\beta = 1.565$, and $n_\gamma = 1.567$, all $\pm .002$. The maximum double refraction is thus .007 with a possible maximum error of $\pm .004$. The greatest extinction angle found was 15° .

The optical properties of dickite, while distinct from those of the non-kaolin minerals, are nearly similar to those of nacrite. As the dispersion and optical character may or may not be the same for these two minerals, the only certain difference optically is the maximum angle of extinction. Ross and Kerr,¹⁰ who have made a special study of the minerals of the kaolin group, find that the

⁷ Metacinnabar is preferred to metacinnabarite, used in Dana, and is believed to be the more consistent usage.

⁸ Allen, E. T., and Crenshaw, J. C., *Am. Journ. Sci.*, [4] vol. 34, p. 341, 1912.

⁹ Broderick, T. M., *Econ. Geol.*, vol. 11, p. 645, 1916.

¹⁰ Ross, Clarence S., and Kerr, Paul F., *The kaolin minerals: U. S. G. S. Prof. Paper 165E*, 1930.

x-ray diffraction patterns of the three minerals, kaolinite, dickite and nacrite are quite distinctive. An *x*-ray diffraction pattern of the kaolin mineral from this locality, furnished through the kindness of Dr. Kerr and interpreted by him, establishes beyond doubt the identity of this mineral as dickite. Although many of the dissimilarities in the *x*-ray diffraction patterns become apparent only upon close measurement, a few can be detected by inspection. See Fig. 8.

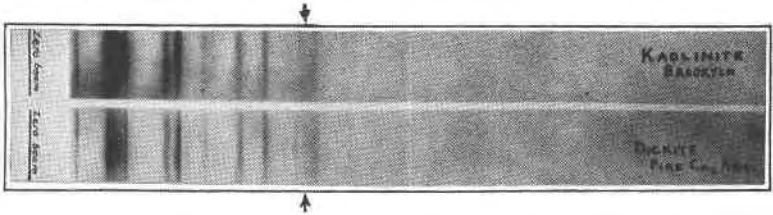


FIG. 8. X-ray diffraction pattern of the dickite associated with the quicksilver ores in Pike Co., Ark., with a comparison pattern of kaolinite from Brooklyn, N. Y. Some of the more apparent differences in the arrangement of the lines are marked by arrows. (Photographed by Paul F. Kerr.)

In the vein quartz, the dickite is observed replacing the quartz grains themselves as well as being present in the interstices. Often this interstitial dickite assumes a brown-yellow color and possesses a somewhat higher double refraction than the normal variety, leading to the suspicion that iron may be present in solid solution. A quantitative determination of iron by chemical means would be of little value as some iron stain is also present.

The indices of refraction of the brown-yellow variety are $n_{\alpha} = 1.560$, and $n_{\gamma} = 1.572$, $\pm .002$, giving a maximum birefringence of $.012$, $\pm .004$. The birefringence was also determined by means of a Berek compensator, eliminating a possible total error of $.004$ which may result from the use of index liquids. The compensator values were $.004$ for the normal dickite and $.006$ for the brown-yellow variety. The discrepancy between the compensator values and the values obtained through the use of index liquids can only be explained by assuming that some of the dickite, which is soft, has been removed during the grinding of the section, rendering it thinner than the more resistant quartz which was used to determine the thickness of the section.

The brown-yellow dickite occurs as irregular stringers between the grains of the vein quartz, indicating that the iron-bearing solutions affected only the dickite along the more permeable parts of

the vein and not that replacing the quartz. Most of the cinnabar has undoubtedly been deposited soon after the dickite was formed because veinlets of cinnabar cut patches of dickite. Occasionally, however, cinnabar veinlets continue as veinlets of dickite, the transition from one to the other being almost imperceptible. As dickite is regarded of hydrothermal origin,¹¹ the close association of dickite with cinnabar, typical of all specimens examined, strongly indicates a hydrothermal origin for these deposits.

Goethite is present as a colloform coating on a number of the quartz crystals near the surface. Hyalite opal has formed both on the quartz and the goethite, partly as colloform crusts and partly as thread-like masses resembling spider-webs. A small amount of stibnite associated with stibiconite has been noted in one instance. The stibiconite is an alteration product of the stibnite and the bladed appearance of the latter is preserved in the stibiconite. Small particles of cinnabar are present in the stibiconite and as there are all gradations between these particles and the massive cinnabar, the cinnabar must be later than the stibnite.

The dickite is often gashed as if a mineral had been removed by solution. Though these gashes appear somewhat regular in outline, a possible determination of their former content by angular measurement of the gashes proved unsuccessful.

SUMMARY

After the folding and faulting of the region, hydrothermal solutions rose along the fractures and fissures of the Jackfork quartzitic sandstone, depositing vein quartz, dickite and cinnabar in the order named but with some local overlapping. The dickite replaces the vein quartz and is in turn cut by thin veinlets of cinnabar. The solutions and vapors which formed the cinnabar were probably of an alkaline nature. Later, descending acid solutions altered the cinnabar, producing the secondary quicksilver minerals, meta-cinnabar, calomel, and eglestonite. The same solutions are, in all probability, also responsible for the high iron content in some of the dickite. Opal was the last mineral to form.

ACKNOWLEDGMENTS

The writer is indebted to Dr. Austin F. Rogers, under whose guidance this work was done, and whose many helpful suggestions

¹¹ Ross and Kerr, *Op. cit.*

and criticisms have been greatly appreciated; to Dr. Paul F. Kerr for photographing and interpreting the x -ray diffraction pattern; and to Dr. George C. Branner for permission to publish this article.

CRYSTALLOGRAPHIC DATA ON MELLITE

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I

Mellite is one of the few organic minerals. Its formula is $\text{Al}_2\text{C}_{12}\text{O}_{12} \cdot 18\text{H}_2\text{O}$, which corresponds to a hydrous salt of the hexa-carboxylic mellitic acid, and is thus far the only representative of the benzene ring in the mineral kingdom. It occurs in coal seams in middle Europe and Russia; the tetragonal crystal form is frequently nicely displayed by very simple face combinations. In Goldschmidt's "Atlas der Kristallformen" only the following forms are listed: (001), (010), (110), (011), and (111). The crystals are semi-transparent with a honey-yellow color, from which the mineral takes its German name, Honigstein. As far as the authors are aware no recent investigation of this mineral is on record. Des Cloizeaux in his "Manuel de Minéralogie" (vol. 2, p. 70) gives a good description of it, but in more recent textbooks very little space is devoted to it.

Through the courtesy of Professor F. Bernauer, Technische Hochschule, Berlin-Charlottenburg, several beautiful, small crystals from Artern in Thuringia were sent to us for x -ray investigation.

II

Rotation photographs with the crystal rotating about the a -axis and the c -axis were obtained by using Fe- K_α -radiation. From these photographs it was found that the primitive translations along these directions were:

$$\begin{aligned} a_0 &= 22.0 \text{ \AA} \\ c_0 &= 23.3 \text{ \AA} \\ a_0/c_0 &= 1.055 \end{aligned}$$

Since the crystallographic axial ratio a'/c' is given as 0.7463, this means that the crystallographic a -axis should be rotated 45° in order to correspond with the internal symmetry of the crystal, the crystallographic axial ratio being obtained by dividing the true axial ratio by $\sqrt{2}$.