DIABOLEITE FROM MAMMOTH MINE, TIGER, ARIZONA

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In a paper published in 1938 on the "Geology and Ore Deposits of the Mammoth Mining Area, Pinal County, Arizona," N. B. Peterson included a description of the minerals found there by him up to that time and a discussion of their paragenesis and origin. To the long list of minerals given by Peterson, there may be added a number of rare species, some of which were previously known and others which have been brought to light by recent development of the mine. These minerals are under investigation at the University of Arizona and at Harvard University, and their complete description will, it is hoped, be published in the near future. At the present time one of them, diaboleite, which seems to be of peculiar interest, has been rather fully studied, and this paper is intended to present only the results of this study.

The materials under examination have been supplied to the Harvard Mineral Collection by Edwin Over, and we are under obligations to him for the opportunity to study so large a suite of specimens. Among them have been identified the following species not found in Peterson's list:—

Atacamite	Matlockite
Boleite	Phosgenite
Caledonite	Pseudoboleite?
Diaboleite	A mineral related to Hydrocerussite
Embolite	

Dioptase has been described in a paper by Galbraith and Kuhn (1940) of the University of Arizona.

Leadhillite is mentioned in Dana's *System of Mineralogy* on the authority of Penfield but without description. It is not uncommon in our specimens.

Linarite is briefly described by Guild (1910), but no idea is given there of its importance in the paragenesis of the Mammoth Mine minerals.

The last two minerals will be included in our future studies.

DIABOLEITE

The name diaboleite was proposed by L. J. Spencer (1923) for a new oxychloride of lead and copper found embedded in mendipite from the old, abandoned lead mines of the Mendip Hills, England. His material was scanty and the description was, therefore, incomplete; but it was

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sufficient to firmly establish the identity of the new species. It is a peculiar pleasure to be able to complete this description through the study of the abundant material found in the Mammoth Mine. It is also hoped that the more complete knowledge of this mineral and the intended study of members of the percylite-boleite group associated with it may clear up somewhat the perplexing relations between them.

Diaboleite is tetragonal and hemimorphic. No general form is present so that from morphology alone the crystal class might be either tetragonal-pyramidal (wulfenite class) or ditetragonal-pyramidal. In the Weissenberg and Laue *x*-ray photographs, however, there are vertical planes of symmetry which prove it to belong to the latter class, 4*mm*. This class has hitherto had no representative among minerals. Diaboleite is always in crystals which range from thin plates a mm. across to stout, stubby crystals up to 1.5 cm. in diameter. The platy habit dominates and, since crystals are usually attached to the cavity wall by an edge, the plates generally show in cross section the marked hemimorphic development.

The evidence of hemimorphism is of two sorts:—

(*a*) unlikeness of the upper and lower basal planes,
(*b*) unlikeness of pyramid development at the opposite ends of the vertical axis.

(*a*) The basal plane is smooth and reflecting in small crystals—more apt to be striated or replaced by vicinal pyramids in larger ones. It is rarely equally developed at both ends and the end of its larger development has been arbitrarily chosen as the lower or negative end. On many of the better, small crystals the negative pedion is relatively large and is smooth or marked by a square series of striae parallel to the axes, while the positive pedion is either lacking entirely or is a tiny square passing into a more or less curved vicinal second-order pyramid of low slope.

(*b*) The pyramids of diaboleite are of both the first and second orders. The first-order series is with rare exceptions confined to what has been chosen as the upper or positive extremity of the crystal. The second-order series is present on both terminations and is of more complex zonal development, always including the second-order prism.

Diaboleite crystals are of superb quality, the faces even when minute giving brilliant single reflections. Nine crystals were measured completely, each being set up twice to permit the study of both terminations. The unit cell was chosen in accordance with the *x*-ray study, detailed below, and angles of four forms, {101}, {201}, {111}, and {112} were employed in the calculation of the elements. The values are collected in Table 1, only faces giving perfect reflections being employed.

TABLE 1. DIABOLEITE: CALCULATION OF ELEMENT p_0

	No. of faces	ϕ	ρ	ϕ Range	ρ Range	p_0
101	20	0°02′	43°07½′	0°00′– 0°07′	42°52′–43°18′	0.9366
201	20	0 02	61 54	0 00 – 0 04	61 47 –62 02	0.9364
112	20	44 55	33 28½	44 53 –45 00	33 22 –33 35	0.9352
111	9	44 58	52 56½	44 53 –45 00	52 52 –53 08	0.9364

The mean value of p_0 derived from the values of the last column is 0.9361, which is used in the calculation of the angles given in Table 2.

It is interesting to compare these results with what Spencer was able to observe on his poor and minute crystals. He reported $c\{001\}$, $a\{100\}$, $e\{101\}$ and $o\{307\}$. $a:c=1:0.95$, derived from the appoximate angle ce of 43½°. Spencer's {307} with co 22½° is probably our {102}, $cr=25°03'$.

TABLE 2. DIABOLEITE: ANGLE-TABLE

Tetragonal, ditetragonal-pyramidal 4*mm*.

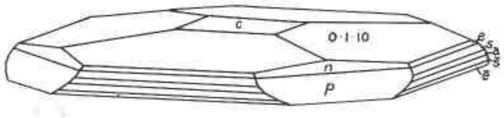
$c=p_0=0.9361$

Lower	Upper	ϕ	ρ	A	$\overline{\text{M}}$
$\bar{c}$	*c* 001	—	0°00′	90°00′	90°00′
	a 010	0°00′	90 00	90 00	135 00
	m 110	45 00	90 00	45 00	90 00
$\bar{r}$	*r* 012	0 00	25 05	90 00	72 33½
$\bar{e}$	*e* 011	0 00	43 06½	90 00	61 49
$\bar{s}$	*s* 021	0 00	61 53½	90 00	51 25
$\bar{n}$	*n* 112	45 00	33 30	67 01½	90 00
	p 111	45 00	52 56	55 39	90 00

HABIT OF THE CRYSTALS

A tabular habit prevails and, as the crystals are attached by an edge, it is rare to find one complete. Very small ones, however, are nearly so and are often perfectly square tables or regular octagons in outline. The lower base is large and plane, generally bounded on the edges by narrow line faces of second-order pyramids and prisms. On but two of the very numerous crystals examined was there a trace of first-order pyramids on the lower end and then it was the form $\bar{n}\{11\bar{2}\}$.

The upper termination is apt to be dominated by the pyramid $n\{112\}$. This face or {111}, by impinging on the lower base, truncates the corners of the tablets to give the octagonal outline. Only exceptionally is the prism of the first order developed, but when it is the faces are as brilliant as are those of the more common second-order prism. Sometimes the polar edges of {112} are truncated symmetrically by narrow faces of {012}. More commonly, however, the upper termination consists in large



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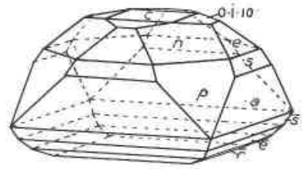

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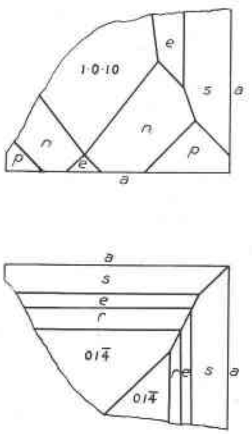

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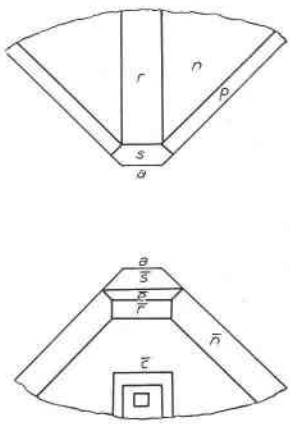

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FIG. 1. Crystal of diaboleite from Mammoth Mine. Above, $c\{001\}$, $a\{010\}$, a vicinal pyramid {0.1.10}, $e\{011\}$, $s\{021\}$, $n\{112\}$ and $p\{111\}$. Below $\bar{c}\{00\bar{1}\}$ dominant, $\bar{e}\{01\bar{1}\}$ and $\bar{s}\{02\bar{1}\}$. Commonest type.

FIG. 2. Crystal of diaboleite with forms similar to Figure 1 but much less tabular. A rare type.

FIG. 3. Plans of upper and lower ends of a thin tabular crystal of diaboleite, showing irregularity of quadratic pattern due to single vicinal faces.

FIG. 4. Plans of upper and lower ends of exceedingly thin tabular crystal of diaboleite showing marked hemimorphism, presence of the rare form $\bar{n}\{11\bar{2}\}$ and the square striation pattern on the lower pedion.

part of rounded faces of second-order pyramids of low inclination which are regarded as vicinal forms. Reflections from these faces are poor but seemed to group themselves about positions at angles to the base of about $5\frac{1}{2}°$, $11\frac{1}{2}°$ and 13°. These angles correspond to forms as follows:—

	ϕ	ρ
1.0.10	0°00′	5°21′
209	0 00	11 45
104	0 00	13 10½

They are not regarded as definite forms, but not infrequently they are relatively large and on the larger crystals, where they are unequally developed, they cause the terminations to lose their usual quadratic symmetry. In the drawings they are shown only schematically.

The second-order pyramids of the upper ends of the crystals are three only; *r*, *e* and *s*. All are generally present on every crystal, although one or more may be line faces only. On the lower end the same three forms commonly occur but with them, or replacing one or more of them, other forms were found occasionally as shown below.

	No. of faces	Measured ρ	Calculated ρ
203	2	31°52′ 32 00	31°58′
302	4	54 25 54 07 54 39 54 13	54 32½
401	2	75 06 75 01	75 02½

These forms were never found on the upper termination. The vicinal forms described as belonging to the upper ends of the crystals are occasionally found replacing the lower base. It is not impossible that this is due to twinning, but no evidence could be secured to prove this. Otherwise, there is no evidence of any sort of twin relationship. The crystals often form subparallel aggregates or occur in quite irregular groups. There was no rule apparent as to attachment of the crystal by one or the other end of the polar axis; on the contrary, as has been stated, attachment is generally by an edge.

Diaboleite has a perfect and brilliant cleavage parallel to {001}, but it is not always easy to effect cleavage. The fracture transverse to the tables is conchoidal. Hardness 2½. Specific gravity 5.42 ± 0.01, determined on six separate, very pure crystal fragments on the Berman microbalance. This is much lower than the value given by Mountain (1923)—6.412,* which was determined on 0.1218 gram in the pycnometer; but is consistent with the chemistry and *x*-ray data here presented.

* It seems likely that this figure is due to a mistake in calculation, for the figures to the right of the decimal are in agreement.

The color of diaboleite is a very intense blue with a pale blue streak. It is noteworthy that there are in this series of minerals three others of almost the same deep blue color: azurite, a darker, less clear blue; linarite, not quite so intense and showing cleavage across the edges of the plates instead of parallel to them as in diaboleite; and boleite, which is in cubes with cubical cleavage and having a greenish tint, as compared with the diaboleite. In very thin plates there is sometimes a greenish tone to the blue color.

Optical Properties

Diaboleite is uniaxial negative, with some crystals showing a disturbance of the uniaxial cross, but this may be due to a subparallel aggregation. The irregularity of extinction typical of boleite is completely lacking in diaboleite. Under the microscope thick fragments are a deep blue with the absorption $\omega > \epsilon$ well marked (only in thick fragments). Refractive indices are $\omega = 1.98 \pm 0.01$, $\epsilon = 1.85 \pm 0.01$ (by the immersion method, using phosphorus-sulphur-methylene iodide liquids). The ω value is in agreement with Spencer's original measurement on a natural prism.

X-ray Crystallography

The *x*-ray diffraction study was made on a crystal with dimensions $.1 \times .4 \times .8$ mm. Rotation, 0-layer-line and 1-layer-line pictures were taken about each of the following rotation axes: [001], [100], and [110]. The pictures were very satisfactory for an accurate determination of the unit cell lengths and of the space group, since high-order reflections on the layer-line pictures showed unusually strong intensity. The constants for the unit cell derived from these pictures are:

$a_0 = 5.83 \pm 0.02$ $\qquad V_0 = 185.58$ Å^3
$c_0 = 5.46 \pm 0.02$
$a_0 : c_0 = 1 : 0.937$
$a : c = 1 : 0.9361$ (Morph.)

The Laue symmetry group, derived from the presence of three symmetry planes and a 4-fold axis on the layer-line photographs, is $4/mmm$. All general order reflections are present, making the lattice primitive. No special operations are to be noted in the axial directions. Since morphological evidence shows clearly that the 4-fold axis is hemimorphic, the space group is fixed as $P4mm$.

Chemistry

The analysis of diaboleite made by Mr. F. A. Gonyer on the material from Mammoth Mine is in close agreement with that of Mountain in

Spencer and Mountain (1923) on the type material from the Mendip Hills. Both analyses are shown in Table 3. Using the analysis of Gonyer, recalculated to 100%, together with the specific gravity 5.42 and cell volume 185.58Å^3 determined in this study, we obtain the composition of the unit cell, which may be written $2Pb(OH)_2 \cdot CuCl_2$ (Spencer) or $Pb_2CuCl_2(OH)_4$. The derivation of this formula is shown in Table 3. The calculated density is 5.48 as compared with the measured 5.42. The one per cent deviation in these two values indicates the maximum deviation of composition, specific gravity and *x*-ray constants from the theoretical.

TABLE 3. COMPOSITION OF DIABOLEITE

	1	2	3		4	5
PbO	72.09	72.01	72.32	Pb	1.975	72.36
CuO	12.90	12.68	12.73	Cu	0.977	12.90
Cl_2	10.89	11.42	11.47	Cl	1.976	11.49
H_2O	6.14	6.03	6.06	H	4.114	5.84
Insol.	—	.19		O	4.011	
Total	102.02	102.33	102.58			102.59
Less $O=Cl_2$	2.46	2.57	2.58			2.59
	99.56	99.76	100.00			100.00

1. Diaboleite, Mendip Hills. Analysis by E. D. Mountain (1923).
2. Diaboleite, Mammoth Mine. Analysis by F. A. Gonyer on .9 gram.*
3. Analysis 2 recalculated to 100%.
4. Number of atoms in unit cell: volume = 185.58 Å^3; $d = 5.42$, $M_0 = 609.68$.
5. Calculated composition for $Pb_2CuCl_2(OH)_4$.

RELATIONS TO OTHER MINERALS

Counting fragments large and small, several hundred specimens containing diaboleite are at hand in the collection. In the vast majority of them there is no other mineral except quartz and hemimorphite.

The author had the opportunity of making a brief examination of the 500-foot level of the mine, in June 1941, in the company of F. W. Galbraith and by the courtesy of the Mine Manager, Mr. Fozard. Although permitting but a glimpse of the deposit, the visit made it certain that the mineral diaboleite is widely distributed in the Collins Vein of the Mammoth Mine in the 400- and 500-foot levels at least. It occurs with linarite, for which it has been commonly mistaken.

Until more work is done on the general paragenesis it is not possible to place diaboleite accurately in the Mammoth Mine mineral sequence.

* Spectrographic analysis shows presence of Ca, Si, Cr, Fe, in small amounts (less than 0.1%), and Al, Ba, Zn, Mg, Ti in less amounts.

It is, in general, a late mineral, often found in drusy cavities of quartz. With it are commonly to be found cerussite and wulfenite; more rarely dioptase, and implanted upon it are crystals of boleite, pseudoboleite (?) and quartz. In one specimen diaboleite is cut by a tiny vein of hemimorphite, and spherules of needles of this mineral are implanted upon it. The green minerals associated with it have not yet been examined, nor have various acicular white minerals of high luster. Intergrowths of diaboleite and phosgenite were noted which indicated a replacement, but which is the older has not yet been determined. In some cases diaboleite is altered to an aggregate of lighter blue material, but as yet the nature of this product has not been established.

The author desires to state that his part in the study of diaboleite is confined to the crystallography. Dr. Berman measured the optical constants and the specific gravity. The x-ray study was made by C. W. Wolfe. The chemical analysis is the work of F. A. Gonyer.

References

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