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On Crystals of Percylite, Caracolite, and an Oxychloride of Lead (Daviesite), from Mina Beatriz, Sierra Gorda, Atacama, South America.

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#### [Read January 22nd, 1889.]

Some time ago a specimen studded with small but well developed crystals of a sky-blue mineral, supposed to be percylite, was offered for the British Museum collection: the rarity of percylite and the excellence of the crystals on this specimen rendered a careful examination desirable. The specimen had been obtained from the Mina Beatriz, Sierra Gorda: on a large-scale chart, kindly placed at my service some years ago by Mr. George Hicks, of Newquay, Cornwall, Sierra Gorda is shown situate between the Bay of Mejillones and Caracoles, about 20 or 30 miles from the latter; longitude 69°29' W. of Greenwich, latitude 22°55' S.: at the truce of 1884 possession of this district was temporarily assigned to Chili.

On measurement one of the crystals proved to belong to the cubic system, and to be limited by the faces of the rhombic dodecahedron, octahedron and cube, those of the latter being subordinate in development; on other crystals the cube was seen to be a predominating form : the mineral is without action on polarised light : by help of the blowpipe the presence of copper, lead and chlorine was recognised : hence the crystals are doubtless percylite.

The crystals are sprinkled upon calcite which presents here and there large cleavage-faces, and is coated in parts with a white powder containing both calcium and sulphuric acid : limonite and crystals of chlorargyrite are also present.

On the mention of a wish to see other specimens from the same mine for the purpose of determining the associations of the percylite, 37 other specimens were sent for examination. The following minerals were recognised :—Cleavable masses of sulphide of lead (galena), massive sulphate of lead (anglesite) very dark in colour, yellow coatings of antimonate of lead (bindheimite), chromate of lead (crocoite), molybdate of lead (wulfenite) in very small crystals, sometimes yellow, sometimes red: fine cubo-octahedra of chloride of silver (chlorargyrite), and crystalline iodide of silver (iodargyrite): massive silicate of copper (chrysocolla), and pulverulent blue carbonate of copper (chessylite): quartz, both in minute crystals and massive : a powder giving the reactions of sodium sulphate: pulverulent limonite: calcite in small encrusting crystals and cleavable masses: gypsum both pulverulent and cleavable.

One of the wulfenite crystals was measured and found to have the form of the pyramid  $e\{011\}$ , the two apices being replaced by relatively large faces of the basal pinakoid  $e\{001\}$ , and the four lateral quoins by pairs of small faces of the pyramid  $n\{111\}$ . (Fig. 1, Plate VIII.)

These minerals, percylite included, have all been recognised by Raimondi as occurring also in Peru, where most of the lead minerals, as is pointed out in his treatise, are secondary products resulting from the decomposition of the widely occurring bournonite and galena.

A single specimen from Mina Beatriz shows numerous small crystals, the nature of which was not at first apparent. They are deposited on a matrix which consists largely of massive anglesite associated with massive percylite, and is coated with bindheimite.

The crystals reach occasionally a millimetre in diameter : they are either colourless or patched with green, are hexagonal in development, and have the shape represented in Fig. 2. The hexagonal basis is a dull face rounded in the direction of the adjacent pyramidal planes, and affords no measurements on the goniometer : the other faces are bright and smooth, but generally give more than one image. The most satisfactory measurements obtained from three crystals lead to the following angles :---

- ax 50°8' (mean of the 11 angles 49°56', 49°58', 49°59', 50°0', 50°3', 50°6', 50°9', 50°13', 50°18', 50°18½', 50°28').
- xx 36°59′, 37°3′, 37°6′: 37°23′, 37°28′: 37°42½′: 37°56′.
- aa 58°48', 59°3', 59°58', 60°26', 61°13', 58°51' or 59°27' (alternative images), 59°27' or 60°3', 60°20' or 61°50'.

The general aspect of the crystals and the magnitudes of the angles made it probable that the mineral was identical with one described in 1886, in a posthumous paper of Professor Websky,<sup>1</sup> and named by him caracolite: the habit of both is the same, and the means of correspondingly variant angles are given by him as

ax 50°8', xx 37°44', and aa 60°36'

respectively. The approximate chemical formula assigned by Wcbsky, on the basis of a qualitative examination of the crystals and a quantitative analysis of the mixed matrix, is  $2Na_2SO_4 \cdot PbCl_2 \cdot PbO \cdot H_2O$ .

The crystallised crust, from which the crystals occasionally project and which is apparently of the same material, was found on blowpipe examination to contain the elements sodium, lead, chlorine and sulphur found by Websky in caracolite: further, transparent particles picked from the minute fragments removed by a needle-point from the crust were found to be similarly acted upon by water; they become white and opaque and are partially dissolved, the solution giving a rich yellow colour to a Bunsen flame. It may be added that on spontaneous evaporation minute squarefaced crystals, with occasionally a pyramidal depression, are deposited from the solution: they are without action on polarised light, and are probably sodium chloride. The part insoluble in water dissolved slowly and almost completely on warming for some time in dilute nitric acid. The identity of the mineral with caracolite is thus beyond doubt.

Websky found that when the crystals were examined in polarised light they afforded aggregate depolarisation, and that when reduced to minute splinters, not before, a sharp line of demarcation between distinct individuals was visible. From this he inferred that the hexagonality is due to twin-growth.

We may observe that in its crystalline habit and its angles caracolite is very similar to mimetite, which has been proved to be optically biaxal and thus only pseudo-hexagonal in its facial symmetry; the corresponding angles for that mineral are given by Brooke and Miller as :---

ax 49°6', xx 38°12', aa 60°0' :

<sup>&</sup>lt;sup>1</sup> Sitz. Ak. Berlin : 1886, p. 1045.

further, the angles of the principal zone a x o of caracolite are nearly those of the prominent zone b d c of anglesite, b d (010.012) being for that mineral 50°37½'. On one of the crystals from Mina Beatriz very minute faces are visible in the zone a a, and truncate the edges of the prism: other crystals still on the matrix show a face replacing one of the edges of the pyramid x. On Websky's crystals a confirmation of the twinstructure was afforded by the occasional furrowing of the edges of the pyramid.

On the specimen which furnished the caracolite, and in the immediate neighbourhood of some of the crystals, was a small cavity only two millimetres in diameter, from the sides of which very minute elongated clear colourless crystals, of vitreous to adamantine lustre, were seen to project. No crystals of the same kind were visible on other parts of this or on any of the remaining specimens. The material from which they spring is colourless or white at their bases, but farther away has a brownish tinge : the latter part was found to contain the elements lead, sodium, chlorine, and sulphur present in the caracolite, though the proportion of sulphur seemed to be less and thus to suggest an admixture of caracolite with one or more minerals less rich in sulphuric acid. The crystals are less than one millimetre in length, and are about one-sixth of a millimetre wide : they are still smaller in thickness.

When mounted for measurement on the reflecting goniometer and viewed with the highest power, they were seen to be very well developed, some being terminated by numerous minute faces. Ten crystals were measured and found to belong to the orthorhombic system; but only five gave results of value for the determination of the parametral angles: the faces often give more than one good image, and on one crystal prismfaces which ought to be parallel are inclined at an angle of  $176^{\circ}$ - $177^{\circ}$ .

The parametral angles are

#### 011.010 58°58', 101.001 25°32', 110.100 51°33', and the parametral ratios are a:b:c = 1.2594:1:0.6018.

The prism-zone is constant in character, the prism m {110} having always two opposite edges replaced by the faces of the pinakoid a {100}; the latter faces are generally larger than those of the prism. As the crystals have one end of the prism in the matrix, only one extremity is terminated by faces. In two cases the crystal is terminated by the basal pinakoid c {001}, as shown in Fig. 3: in another crystal the basal pinakoid is absent and its place is taken by two domes f {101}, g {301} (Fig. 4): in another appear small faces of a third tautozonal dome h {501}, a fourth dome e {031} in the perpendicular zone, and also octahedrid forms r {521}, v {221}, t {121} and s {211}, giving rise to the zones a r v t,  $m_1 r_1$  $g s t e \bar{m}_1, m_1 s_1 f d t'_1 \bar{m}_1, r h r_1$  (Figs. 6 and 7); in this crystal the forms v eare represented only by single and very minute faces. On the termination of another crystal (Fig. 6) the dome d {011} presents itself, and is associated with the forms cfr and other faces too rounded to have definite indices assigned to them. Several of these minute faces give a faint image of the slit when observed with the  $\delta$ -eyepiece of a Fuess-goniometer, but most of them not only give no image of the slit but are themselves only visible when the slit is removed, and all the light transmissible by the collimator is made use of: the angles can then be measured by the method of maximum illumination, and with a certain amount of precision owing to the smoothness of the minute faces. The forms observed were  $a \{100\},\$ c {001}, d {011}, e {031}, f {101}, g {301}, h {501}, s {211}, t {121}, v {221}, r {521}: a stereographic projection of the poles is given in Fig. 7.

When the face a is striated, its striæ are perpendicular to the edges of the prism.

One crystal has a face of the form f {101} on the end which had been in the matrix, and that face may possibly be due to cleavage.

The following is a list of calculated and observed angles :----

	0	0
Angles.	Calculated.	Observed.
am	51°33′	Mean 51°33' (50°58', 51°1', 51°9½',
		$51^{\circ}29\frac{1}{2}', 51^{\circ}29\frac{1}{2}', 51^{\circ}31', 51^{\circ}38',$
		51°35′, 51°38′, 51°44′, 51°44′, 51°44′, 51°45′,
		51°58', 52°12': all images)
cd	<b>31°2</b> ′	31°8' image
af	64°28′	64°51' image
cf	25°32′	25°
ag	84°54'	34°21' image
fg	<b>29°34'</b>	29°2′, 29°24′, 29°36′
hg	<b>12°11'</b>	11°30', 11°51'
Ĵ)	51°5′	51°37′
ar	<b>33°13</b> ‡′	83°2011' image
rv	$25^{\circ}22'$	26°33′
$vt_1'$	48°24′	47°22′
rt	<b>39°48</b> ′	39°22′, 39°39′, 40°21′
$tt_1'$	33°58′	33°21′

Angles.	Calculated.	Observed.
mr	<b>31°45</b> ½'	$30^{\circ}14' - 31^{\circ}44'$ band of images
rg	<b>27°</b> 35′	<b>27°40'</b> , <b>28°18'</b>
mg	<b>5</b> 9°20′	59°25' image
$ys_1$	<b>25°</b> 59′	26°28′
$s_1 t_1$	$\mathbf{27^{\circ}54}$	27°27′
$t_1 e'$	20°0½′	20°37′
ms	45°3‡′	45°42′
sf	$29^{\circ}23\frac{1}{2}'$	$28^{\circ}23': 29^{\circ}: 29^{\pm}^{\circ}$
mf	$74^{\circ}27'$	74°9' image
fd'	$\mathbf{39^{\circ}22'}$	<b>3</b> 9‡°
ft'	64°49′	65°45′
md	66°11′	66°22' image : 66°, 66‡°
mf'	<b>105°38</b> ′	105°7′
$rr_1$	49°51′	49°50' image
as	<b>5</b> 0°41′	50 <u>3</u> °

As no correspondence could be found between the angles of these crystals and those of any known mineral, it became necessary to determine as completely as possible the characters of the mineral without trespassing too much on the material in the minute cavity : as the matrix might not be identical in its composition with the projecting crystals, the experiments must of necessity be made on the crystals themselves.

The following results were obtained :---

1. A crystal sinks quickly in a liquid of specific gravity exceeding 3.

2. On examination in parallel polarised light, the edges of the prism are seen to be parallel to a direction of extinction.

3. In convergent polarised light no optic axes are visible through the face a.

4. By means of a quartz-wedge it was found that for the face a the direction of the prism-edge is that of the least optic elasticity.

5. A crystal boiled for some time in water remains unaltered : water at the ordinary temperature has not the slightest action when the contact is continued during eight weeks.

6. A crystal placed in distilled water in a concave glass and watched with the microscope, dissolves quickly without the least trace of effervescence on the addition of a drop or two of nitric acid.

7. When, instead of nitric acid, sulphuric acid is dropped into the

water, solution without effervescence takes place, but opaque isolated particles are left behind, and these are for a time connected by an invisible substance having the shape of the original crystal, for the opaque particles move simultaneously without changing their relative positions when the watch-glass is tilted to one side.

8. A solution in hydrochloric acid gives no coloration to the flame.

9. Fused with sodium carbonate on charcoal a crystal yields a malleable metallic metal: the products of fusion when moistened with water give no stain to a silver coin.

10. Solutions in nitric acid were subjected to wet tests in capillary tubes with the following results :--Barium chloride gave no visible precipitate : molybdic solution gave neither precipitate nor coloration : silver nitrate gave a minute but distinct turbidity.

11. A crystal in a tube closed at one end was heated in an air-bath at various temperatures up to  $300^{\circ}$  C., but though at the highest temperature the crystal became a shade whiter and the tube became slightly clouded there was no appreciable decomposition: the crystal retained its transparency and the brilliancy of its faces, and its prism-edge remained a direction of optical extinction.

12. A crystal in a tube closed at one end was heated slowly over a Bunsen-burner and carefully watched: up to a considerable temperature no alteration was observed: the crystal then flew to pieces, but the fragments were still clear and colourless: on exposure to a temperature at which the glass began to melt the bits became white and opaque, but remained fairly sharp in outline, though possibly owing to union with the melted glass; there was scarcely any perceptible clouding of the tube.

From the above it follows that the crystals differ from caracolite and the matrix not far from their base: they contain neither sodium nor sulphuric acid, but lead and chlorine enter into their composition. They are distinguished from the native chloride of lead, cotunnite, not only by their angles (which do indeed present some similari:y), but also by their insolubility in water : chemically they must in all probability be an oxychloride of lead.

Several native oxychlorides of lead are already known, namely, fiedlerite of unknown chemical formula, matlockite PbCl<sub>2</sub>·PbO, laurionite PbCl<sub>2</sub>·PbO·H<sub>2</sub>O, and mendipite PbCl<sub>2</sub>·2PbO. Of these the recently discovered fiedlerite belongs, according to the late Professor vom Rath, to the monosymmetric system, and matlockite crystallises in the tetragonal system; further, both have angles quite distinct from those of the crystals under consideration. The rare mineral laurionite,<sup>1</sup> found along with fiedlerite in an ancient lead-slag, described by Köchlin and later by vom Rath, belongs to the orthorhombic system, and presents some similarity in the development of its crystals: it is quite distinct, however, in its angles, and it begins to part with water at a temperature of about 142°C.

There still remains mendipite : this mineral has been found at only two localities, one of them in the Mendip Hills, the other in Westphalia. The white opaque crystals from the neighbourhood of Tarnowitz in Silesia, though known for some time as "chloride of lead" or "mendipite," were long ago proved to be altered cromfordite, and to be more or less changed to cerussite. At both its localities the mineral occurs as columnar cleavable masses, and it has not yet been found presenting crystal-faces. Its assignment to the orthorhombic system depends on the cleavages and optical characters. The only crystallographic element of mendipite known is the angle between its easy cleavages: this is given by Haidinger as 102°27', by Breithaupt as 102°30', by Brooke and Miller as 102°36', and measurement by myself of a single edge gave 102°41'. Now the mean prismangle of the crystals under consideration is 103°6', and though differing from the observed cleavage-angle of mendipite, the difference is not so large, having regard to the variation in the observed angles, as to be convincing in itself of a difference in the specific character of these crystals and mendipite.

It seemed, however, that the crystals from Mina Beatriz were much more quickly dissolved by nitric acid than were fragments of mendipite : to get an idea of the rate of solution of mendipite, matlockite and cotunnite, minute fragments of those minerals were placed in nitric acid on watch-glasses and left standing at the temperature of the laboratory : the mendipite disappeared in 93 minutes, the cotunnite in 182 minutes, and the matlockite in 215 minutes. As these fragments, though minute, were larger than the crystals under examination, a more direct comparison was made : one of the Mina Beatriz crystals and a cleavage-fragment of true mendipite were placed alongside each other in distilled water and observed with the microscope: the crystal was longer than the mendipite fragment and about the same width, but the two may not have been of exactly equal thickness : the crystal was perfectly clear and free from flaws, while the mendipite was striated by its cleavages and thus not so permeable to light. Nitric acid was dropped on the edge of the water at the spot to which the crystal and fragment both pointed, and would reach the two simultaneously: the

<sup>&</sup>lt;sup>1</sup> Ann. d. k.k. naturhist. Hofmuseums: 1887, Vol. II. p. 188. Sitz. d. niederrhein. Gesell. in Bonn: 1887, Jahrgang 44, p. 149.

crystal disappeared completely in 52 seconds, the mendipite in 142 seconds. If allowance be made for the time taken by the acid to reach the specimens the numerical difference of solubility will appear still greater. The absence of identity of structure would scarcely account for this difference in the rate of action of the nitric acid, for the striated character and lesser compactness of the mendipite should tell in its favour.

Again, a fragment of mendipite heated in a tube closed at one end fuses quite readily and spreads itself over the glass, yielding a product of a yellowish brown colour.

Further, while mendipite, as we have said, has a pair of easy cleavages, the crystals under consideration are without cracks, and when broken under oil still fail to give any cleavage-evidence when examined in the microscope. The crystals break across the prism with a sub-conchoidal fracture, and show no cleavage parallel to the basal plane: the only suggestion of cleavage was that already mentioned, namely, a crystal-face f at the matrical end of a crystal.

Finally, an extremely small fragment terminated by a good basal plane was so placed in a drop of water on a microscopic slide that it could be looked through by convergent polarised light having an axial direction not far from normal to the terminal face : brushes were now seen : the position of one of the optic axes was near the edge, that of the other, owing to the slightly skew position of the fragment, was just outside the field : the plane of the optic axes was perpendicular to the face a : the hyperbolic brush passing through the optic axis in the field was distinctly blue on its concave side, and was not perceptibly coloured on the convex side.

In addition to the native oxychlorides of lead above mentioned, there are at least four others known as artificial products : they have the following formulæ : (3PbCl<sub>2</sub> · PbO), (PbCl<sub>2</sub> · 3PbO), (PbCl<sub>4</sub> · 5PbO), (PbCl<sub>2</sub> · 7PbO).

Since the above observations were made my attention has been called to a description of some mineral specimens from Sierra Gorda, published two years ago by Professor Sandberger,<sup>1</sup> one of the Corresponding Members of our Society. Caracolite, percylite, wulfenite, crocoite and other minerals were recognised by bim: and he further points out that the specimen described by Websky was in all probability brought from the same locality and not from Caracoles itself.

Both Professor Sandberger and myself have failed to confirm the presence of water either in crystals of percylite or caracolite; both minerals give

<sup>&</sup>lt;sup>1</sup> Neues Jahrbuch für Mineralogie, 1886, Vol. I. p. 89; 1887, Vol. II. p. 75.

fumes and a crystalline colourless transparent sublimate when heated in a tube closed at one end, and in the case of percylite at least the sublimate fuses to a colourless liquid.

It being necessary, for purposes of reference at least, to give a name to the oxychloride of lead above described, I venture to suggest the name *Daviesite*, in honour of Mr. Thomas Davies, F.G.S., who has now been associated during upwards of thirty years with the British Museum Mineral Collection, and whose mineralogical experience and Breithauptian eye have ever been willingly placed at the service, not only of his colleagues, but of every one who has been brought into relationship with him.



Grystals from Sierra Gorda.

Mintern Bros. lith.