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ON PARAMELACONITE, AND THE ASSOCIATED MINERALS.

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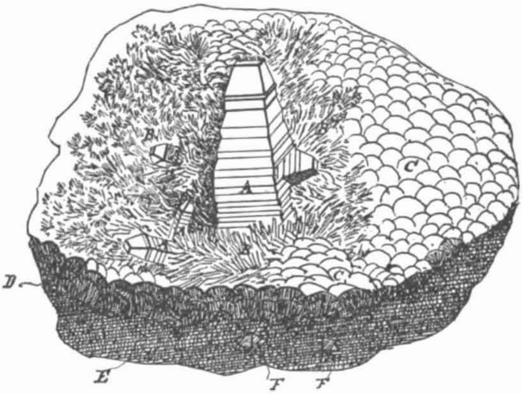
On his recent visit to the Copper Queen Mine at Bisby, Arizona, Dr. A. E. Foote obtained possession of two specimens showing crystals, which he could not associate with any known species except Anatase. The locality and association, however, speak strongly against the presence of that or any other form of the Titanium dioxide. These specimens have since passed into the collection of Mr. Clarence S. Bement who has kindly permitted me to examine and study them.

One of these specimens has been deemed of sufficient importance to be represented in the adjoining figure as a whole, to show the relation of the associated minerals. It is drawn to natural scale.



We see as the central figure a monolithic crystal (A) lying flat upon the supporting surface, but so that the pyramidal termination is entirely free and symmetrically developed. To the left there are three more pyramidal crystals of the same kind, but of smaller stature. These crystals are characterized by the most brilliant metallic adamantine luster, and purplish-black color. The crystals stand in relief against a back ground of minute acicular crystals of deep blue color (B). Upon the crystals are patches of a beautiful light greenish or silvery-white substance, which have not been individualized in the drawing, as color only could bring them out properly. The nature of both these substances will be discussed below. Under (C) are represented small, brownish-black mamillæ of limonite, shown in section at (D), exhibiting a distinct radial structure. This layer of limonite passes rapidly into a granular mixture of limonite and cuprite (E) of brownish-red color and in this we see imbedded at (F, O) crystals of native copper. Since we find both blue crystals and silvery patches on the large crystals, the genetic relation appears as follows, E, F & D, C, A, B.

The second specimen is about 3 x 4 inches in size. It looks as if it had formed at one time a part of the same large slab of which the first specimen is a fragment. Some twenty odd beautiful crystals like (A) but of smaller size, not over ½ inch in length, are either lying flat or stand erect upon the mamillary mixture of limonite and cuprite. One large blue crystal (B) and several bundles of the same are stretched across the black crystals. The latter are covered in part, mostly upon the strongly striated faces with the greenish-silvery substance mentioned above, which coating produces the impression of a patina on dark bronze.

1. *The black crystals.*—Symmetry. The habitus is strongly tetragonal. Each crystal represents uniformly a combination of (001) (111) (110). The plane (001) is very generally square, sometimes a narrow oblong. The pyramidal faces are broad and smooth at the apex, but are invariably striated parallel to the main plane of symmetry. The luster is so strong on these planes, that one easily overlooks this striation; but it shows with a small magnifying power. One or two pyramidal faces are usually broader than the others. In one of the measured crystals one face is 4 mm., two 2 mm.; one 1 mm. The horizontal edges are generally the resultants of combination of pyramid with prism. I have noticed, however, in a few crystals these edges formed by pyramidal faces alone. The habitus and color of these crystals strongly resemble that of the black or blue-black Anatase. All this might be deceptive, however. To determine the symmetry three crystals were measured, two of the larger (20 mm.) one very small one (2 mm.)

Whilst the faces are very splendent, the striation causes multiple images, sometimes of equal luminosity, and sometimes a mere shredded spectrum. Descloizeaux's artifice of covering the faces gave only a partial relief. It seems to be safest, therefore, that I record here the reflection images observed, and give my readers the opportunity, as well as the means, to decide whether my interpretation of the observed facts is, under the circumstances, the correct one.

In the following figure 2, I have reproduced the observed images obtained from the two larger crystals:

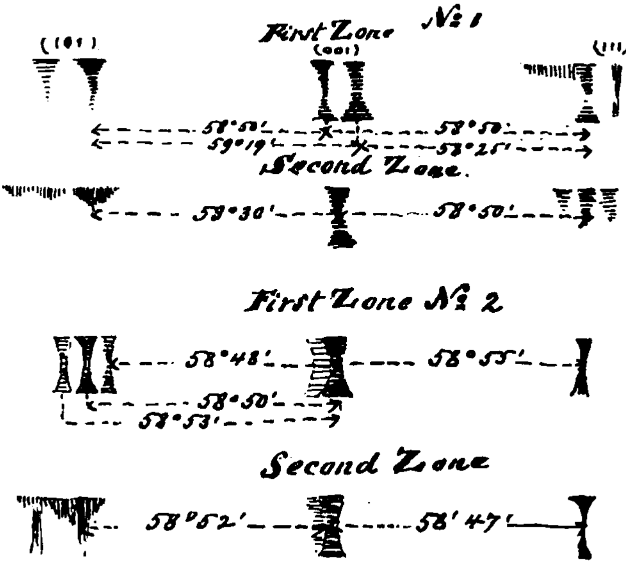


Fig. 2.

The inspection of this figure seems to allow but one interpretation, to wit that the symmetry is *tetragonal* and that the angle (001): (111) = 58° 50'. Now we have for Anatase according to V. Kockscharow (001) : (101) = 60° 38' a difference of 1° 48'.

Does this mean isomorphism of the two species? The Anatase of some localities shows only one pyramid but the cleavage is parallel to this pyramid and it is made the fundamental pyramid for this reason. I have not been able to trace any cleavage planes in the crystals under discussion. Neither basal nor pyramidal nor prismatic. This seems to oppose the notion of isomorphism. Assuming the observed pyramid as (101) then the primary pyramid follows with 66° 58' 12"

and C = 1·6643.
against C = 1·7799 in Anatase.

I have taken, of course, V. Kockscharow's value, because I obtained from a very fine Brazilian anatase (Mr. Bement's collection) for the basal edge. 43° 20' (Koenig.) (43° 24' V. Kockscharow.) Groth bases his C value 1·7344 (Tabell. Uebers. 3 Aufl.) on a much larger angle.

The hardness of the mineral on the smooth basal plane was found equal to that of Apatite. The color on the faces is purplish-black, on the fracture pitch-black. The fracture is uneven, to flat conchoidal. The luster is brilliant metallic-adamantine. The substance is opaque. The streak is black. The specific gravity was found at 20° C = 5·833. The determination made with 0·8487 g. in Pyknometer. The entire crystals, weighing 1·132 g., gave on Jolly's balance two readings, of which the above is the arithmetic mean. Unless crystals, weighing at least 3 grs. be used, the values derived from Jolly's balance are not sufficiently reliable, according to my experience.

In a strong oxidizing flame, a splinter of the mineral is rounded at the edges. In reducing flame, melts easily and yields metallic copper. With the fluxes a blue glass in O fl. Dissolves in HCl with a yellow, in NHO^3 with a blue color. With $NH^4(HO)$ a very slight brown precipitate.

A preliminary analysis made with 48·2 mg. gave CuO = 46·1 Fe^2O^3 = 2·0. It is evident in this instance that the iron does not belong to the mineral, as the greater part of it was left undissolved by dilute nitric acid as a brown red, scaly powder, therefore, probably Hematite. The material used in determining the specific gravity was crushed in a steel mortar. It was then seen that the material was not homogeneous. Whilst the large bulk was black, there could be seen three red spots. They denoted the presence of cuprite, which, of course, was not strange since the mineral sits on cuprite. It was not thought advisable to remove this admixed cuprite mechanically. But if really the mineral is CuO, then the analysis must give an excess if Cu^2O be present.

0·2031 gr. gave 0·2045 Cu^2S.
0·0014 Fe^2O^3.

$$\begin{aligned} CuO &= 100{\cdot}58 \\ Fe^2O^3 &= 0{\cdot}64 \\ \hline &\ 101{\cdot}32 \end{aligned}$$

Here is then an excess of 1·32, which is Oxygen, and this corresponds to 11·8 of Cu^2O.

The substance of the crystal would thus appear to be a mixture of

$$\begin{aligned} CuO &= 87.66 \\ Cu^2O &= 11{\cdot}70 \\ Fe^2O^3 &= 0{\cdot}64 \\ \hline & \ 100{\cdot}00 \end{aligned}$$

It is a matter of very common observation that large crystals enclose bodies of a different nature, sometimes even force them to participate in the mass arrangement of the predominating molecule. I can find nothing which suggests a process of alteration of either Cu^2O into CuO or the reverse. There is neither metamorphosis nor pseudomorphosis in this case. The black crystals belong substantially to what mineralogists have heretofore called Melaconite or Tenorite. The latest crystallographic work on the form of Tenorite—Melaconite is by Ernst Kalkowsky (Groth. Zeitschr., Vol. 3, p. 279). This author shows by a recalculation that the angular values obtained by Jentsch (Ann. d. Phys u. Chem., Vol. 17) on the crystallized oxyde of Copper occurring as a furnace product at Freiberg, must be considered as identical with those of Maskelyne (Report British Association, 1865) on very minute crystals from Lostwithiel. Jentsch was mistaken in assuming its orthorhombic symmetry and isomorphism with Brookite. But while Maskelyne finds the crystals from Lostwithiel as well as the thin lamellæ from Vesuvius to be *monosymmetric*, Kalkowsky comes to the conclusion, on optical ground, that they are really *asymmetric* although closely approaching the monosymmetric type. Groth (Tabell. Uebersicht, 3 Aufl.) has adopted this view, in so far as he puts an interrogation mark after the word "monosymmetric" and gives the explanation referred to, in a note. He evidently does not believe in an *isometric* form of CuO,—which Dana adopts (System of Mineral, Edition 5) on the authority of J. D. Whitney. The latter had found (Rep. L. Sup., 11·99) cubo-octahedrons of CuO and contended that they were original and not pseudomorphs on the ground that Cuprite was only observed at the same locality in unmodified octahedrons. Such an argument can hardly be sustained. For the cubo-octahedral combination is very common in Cuprite from nearly all known localities. Among some magnificent specimens recently come from the "Copper Queen Mine" I noticed cubo-octahedrons, although the majority of the specimens showed the combination (011) (001) (111)

(122). Unless some more convincing testimony be produced, we are justified in discarding the isometric symmetry as pertaining to CuO. Thus we have only the monosymmetric or possibly the asymmetric system left for the species Melaconite or Tenorite. Aside from all precedent, the tetragonal crystals are so unique in their appearance, that they should be accorded the rank of a very distinct species, and the name *Paramelaconite* is proposed for them.

Among the Melaconite in the collection of the University, there is a specimen with the locality "Arizona." It has been in the collection over twenty years, before the Copper-Queen was located, and very probably is not from Bisby. It is a middle-grain sandstone impregnated with minute black crystals. A similar specimen is in Mr. Bement's collection. I had never examined it critically before, surmising that the form would be the same as that described by Maskelyne. I find that these minute crystals, observed with a magnifying power of 250 diam., show the same habitus, combination, luster and color as the tetragonal crystals from the Copper Queen. There are thus two localities on record for the occurrence of Paramelaconite.

2. *The blue acicular crystals. Footeite—a chloro-oxyhydrate of copper.*—The material to work on was very scant. Dr. Foote sent me broken off crystals from which I was enabled to pick out about 25 mg. of pure material, with which quantitative examinations were made. It was not deemed advisable to disfigure the beautiful specimen (fig. 1) for the sake of more material. None of the crystals weigh over 1 mg. They are either simple or twins. The simple ones represent six sided prisms with pyramidal terminations. The oblique character of the latter is usually well marked. When examined with a power of 150 diameters, it was found that the most complex combination is that represented in fig. 3.

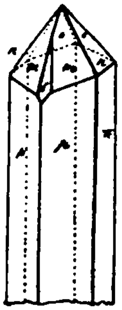


Fig. 3.

$m = {}^{1}P$
$o = P^{1}$
$n = \infty\, P$
$d = \infty \bar{P}$
$p = P \infty$
$II = \infty \bar{P} \infty$

d was observed only in two crystals; n is mostly quite small; m and o are always present. The habitus is often tabular, parallel to the plane of symmetry.

$$\Lambda \; p : p = 49^\circ \; (131^\circ)$$

$$\Lambda \; \frac{m}{m} : \frac{p}{p} = 36\tfrac{1}{2}^\circ \; (143\tfrac{1}{2}^\circ)$$

$$\Lambda \; \frac{o}{o} : \frac{p}{p} = 33^\circ \; (147^\circ)$$

These measurements are of course only approximate (being made under the microscope)—the crystal lying on face II. The plane of optical extinction encloses with edge p:p an angle of 7½°. Positive. The system is, therefore, clearly *monosymmetric.*

The twins are either simple like the common form in Selenite, that is composition face $\infty P\infty$ rotation 180°; or two such simple twins perforate each other at right angles with the vertical axis common to both. These form then combinations like those of Harmotome. The broken off ends of such twins show the re-entering angles indicating the existence of a basal cleavage. Heated in a closed tube, a crystal turns black, without losing its shape or even its luster and yields three sublimates. The uppermost is water, the middle one is gray, the lower one green, after cooling. The colorless flame takes the characteristic blue and green colors, when a crystal is brought within its borders. On charcoal the same color phenomena, no smell of arsenic. The tests for sulphuric and phosphoric acids result *negatively.*

For the quantitative analysis only 16·5 mg. were available. This material was placed without pulverizing it, in a mixture of $AgNO^3$ and dil. NHO^3 and digested at about 50°C. The crystals turned white at once and were gradually converted into veritable pseudomorphs of AgCl after the original mineral. They were then broken up, to make sure that a complete decomposition had taken places. AgCl was then filtered upon a 20 mm. filter. From the filtrate the excess of Ag was removed $BaCl^2$ added and allowed to stand over night. Then filtered. Ba removed and Cu precip. by H^2S. The precipitate was dark brown-black. No arsenic present. The filtrate boiled, made ammoniacal, filtered, and to filtrate $MgCl^2$ added. No precipitate. Absent P^2O^5. The weights obtained were:

Ag = 3·5 mg; ashes from $BaCl^2$ precip. = 0·2 mg.
CuO = 11·8 mg; ashes with C^2O^3 = 0·1 mg.

From these figures is deduced the percentage composition.

$$\left.\begin{array}{lcrcr} \mathrm{CuO} & = & 63{\cdot}7 & = & 8{\cdot}12 \\ \mathrm{CuCl}^2 & = & 13{\cdot}5 & = & 1{\cdot}00 \\ \mathrm{H}^2\mathrm{O} & = & 22{\cdot}8 & = & 12{\cdot}6 \end{array}\right\} \text{Molecules.}$$

$$\overline{100{\cdot}0}$$

Hence $8\,[\mathrm{Cu}\,(\mathrm{OH})^2]\,\mathrm{CuCl}^2 + 4\,\mathrm{H}^2\mathrm{O}$.

Footeite has, therefore, as its nearest relative the Thallingite of Church. In the latter the ratio of $\mathrm{Cu}\,(\mathrm{HO})^2 : \mathrm{CuCl}^2$ is 4 : 1.

3. *Malachite, asbestiform.*—It would have been impossible to get enough material with which to identify the peculiar greenish silvery coating from the malaconite specimens. Fortunately there was another specimen of mixed limonite and cuprite, the entire surface of which had such a coating. Here we find it like the finest lint in the depressions of the specimens. The crystals of which this lint-like material is composed, are not fast to the surface on which they lie. With the least touch, whole flakes are detached; but even a big flake will barely weigh one milligram. Under the microscope, the composing crystals can be seen to be needles, tabular, parallel to the clinopinacoid and showing in fact a habitus like the crystals obtained from a boiling solution of calcium sulphate. Each one individualized is light greenish in color and polarizes strongly. The silky metallic luster and white color of the flakes must be owing to interference phenomena.

Brought into a colorless flame, the flake turns shining black and fringes the seams of the flame yellowish red like calcium salts. Neither blue or green colors are visible. The mineral does not contain chlorine. No sulphur present. I managed to get 10 mg. of the clean material; that is to say with 150 diameters I could distinguish a few brown particles of cuprite-limonite only.

This quantity gave

Ignition at beginning of cherry-red heat 3·0 mgs.
$\mathrm{Fe}^2\mathrm{O}^3$ 0·1 mg.
CuO 6·9 mg.

$$\overline{10{\cdot}0}$$

The above composition is exactly that of malachite, and all would be satisfactory if it were not for the color of the flame, for which I can find no explanation.