Meta-torbernite I, its physical properties and relation to Torbernite.

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IN a general account of the properties of torbernite given by the present author in this magazine in 1916 (Reference 5, see below, p. 47) it was shown that the transition from torbernite to the first dehydration-product, known as meta-torbernite I (meta-kupferuranit), was dependent on the temperature and the vapour-pressure, and that the boundary of the stability area lay only a little outside the range of ordinary atmospheric conditions; the transition-point of torbernite in contact with water was determined as 75° C.

In continuation of this work, an experiment was made to ascertain the loss in weight that accompanies the transformation at room-temperature. A quantity of 1 gram of torbernite was weighed in a crucible after being exposed to the water-vapour above sulphuric acid solutions of successively increasing concentration. On crossing the transition-curve, at a vapour-pressure corresponding with an acid-strength of approximately 55 per cent. H_2SO_4, no loss in weight was observed, nor did the optical properties change as in the crystals previously examined; not until the mineral was placed over concentrated acid did a loss in weight set in, and the change was then very slow, 0·06 gram being lost during three months. Weighings made at intervals after this show that after more than a year the weight had become apparently constant, the loss being 10·1 per cent. On the formula $Cu(UO_2)_2(PO_4)_2 . 8H_2O$ the loss of five molecules of water corresponds with a loss in weight of 9·6 per cent., but it is not possible to lay any stress on results obtained over so strong an acid, since the transition-pressures of all the compounds in question are evidently indefinitely low; while the rates of transformation are probably to a similar extent prolonged, for the pressure-difference under which water-vapour is transferred from the mineral to the acid is necessarily extremely small.

The mineral used for the above experiment was kindly put at the author's disposal by Mr. Arthur Russell, and represents the well-known 'torbernite' from Gunnislake in Cornwall; but it is clear that it cannot be identical with the torbernite on which the earlier transition-curve was determined. In 1919 N. L. Bowen (6) measured the optical constants of a variety of torbernite 'from Spain and from Cornwall' which exhibited anomalous birefringence, being isotropic for green light, and he concluded that it was a torbernite that had undergone spontaneous dehydration and was identical with meta-torbernite I artificially prepared. The optical properties of the Gunnislake material agree with Bowen's description, and there can be no doubt that this mineral, so long known to collectors, is really meta-torbernite I and is not identical with the mineral on which the accepted constants for torbernite have been determined.

Physical properties of Torbernite and Meta-torbernite I.

It has been possible to obtain fairly complete, though approximate, physical data for the two minerals; for ease of comparison these are summarized in the following table :—

		Sp. gr.		Refractive Indices			$c : a.$
				$\omega.$	$\epsilon.$		
Torbernite	...	3·22	...	1·592	1·582	...	2·97
Meta-torbernite I—	...			...		...	
artificial	...	3·67	...	—	—	...	—
natural	...	3·68	...	1·623	1·625	...	2·28

Specific gravity.—The published results range from 3·29 to 3·72 (Dana) and no doubt confusion has arisen between the two varieties. In methylene iodide (3·3) torbernite floats, while meta-torbernite I sinks. The densities given were determined on carefully purified coarse powders from the Gunnislake material and from a well-crystallized specimen of ordinary torbernite (locality not known). Results.—Torbernite, G = 3·229, 3·219. Meta-torbernite, Gunnislake, 3·700, 3·683; artificial (see below) 3·67.

Optical properties.—The indices given in the table are for sodium-light; those for torbernite are quoted by Bowen (6), and those for meta-torbernite are from the complete dispersion-curves determined by the same author. Both minerals are pleochroic, being pale blue for light vibrating normal to the base and green for that vibrating in the basal plane. The index for meta-torbernite is very near that for zeunerite,

but the two minerals differ in birefringence, in angles, and in crystal-habit. The interference-colours of torbernite are irregular on account of the green colour and also of the absorption-spectrum, those of meta-torbernite are quite anomalous.

Crystallography.—The Gunnislake mineral occurs in rosettes or sheaf-like aggregates of approximately parallel square plates, bounded by the planes of a low pyramid, $d(102)$. The latter are rarely measurable, but a few crystals afforded rough measurements for the angle $c : d$, the mean of six readings being $48° 48'$ (highest, $49° 21'$; lowest, $48° 30'$). The axial ratio $c : a$ is, therefore, 2·28; the calculated value for $c : e(101)$ being $66° 22'$, while that for torbernite is $71° 52'$. The pyramid has been made (102) in order to exhibit the morphotropic relation with torbernite. No confusion has arisen between the two minerals as regards crystallography, for all the later measurements relate to torbernite alone ; some early readings given by Phillips and Miller (see ref. 5) may possibly have been made on the other variety, though no crystals of the habit described by those authors have so far been encountered.

Chemical composition.—The various published analyses (1) agree upon the formula to be assigned to the phosphate molecule in torbernite, but there is much confusion as to the degree of hydration. Y. Buchholz (4) concluded that the true formula contained $12H_2O$, but that four molecules were readily lost in the desiccator, and that consequently the earlier analyses might well show a variable water-content, depending on the means taken to dry the mineral. To this source of confusion must now be added the occurrence of meta-torbernite itself in nature. In order to confirm the suggested formulae, a weighed amount of torbernite was dehydrated by heating under water to $100°$ C. for several hours. The mineral was placed in a density-bottle, so that the specific gravity could be determined both for the original mineral and for the alteration-product, the bottle being filled up and weighed after cooling. In this way the error due to air entangled in the turbid altered mineral was avoided. The meta-torbernite was finally dried and weighed in a Gooch crucible.

Density of torbernite used	...	...	...	3·219
Density of altered mineral	...	...	...	3·67
Weight of torbernite	...	...	...	1·3568
Weight of altered mineral	...	...	...	1·2603
Loss in weight	...	...	...	...	0·0965

The percentage loss on transition to meta-torbernite is thus 7·11, the

calculated value ($12H_2O$ to $8H_2O$) being 7·1. The formula for meta-torbernite I must, therefore, be taken as

$$Cu(UO_2)_2(PO_4)_2 . 8H_2O,$$
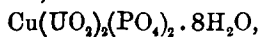
while torbernite itself contains $12H_2O$.

Structural Relations.

The occurrence of natural crystalline material removes all doubt that meta-torbernite I has a perfect crystalline structure. In the transition from torbernite we have, therefore, a morphotropic change that can be brought about, not only by a re-growth in the new form, but by the direct removal of water from the crystal-network, which at the same time undergoes a homogeneous deformation and assumes new constants proper to the lower hydrate. It has already been remarked (5) that the water is removed by way of the edges of the crystals and is apparently unable to escape through the basal planes, and also that parallel growths of barium chloride on the basal plane have been recorded for both substances. There is thus every reason to think that the horizontal dimensions of the two crystals are similar, and that the additional water is held in layers that alternate with basal layers having the constitution of meta-torbernite. If this is the case, the morphotropic change should consist in a decrease in the vertical axis of the crystal to an extent proportional to the change in molecular volume due to the transition. From the data already given, the molecular volume of torbernite is 313, that of meta-torbernite is 254; the ratio $c : a$ for torbernite is 2·97, that for meta-torbernite is 2·28. Thus the ratio of volumes is 0·81, that of the c-axes is 0·76. In view of the inaccuracy of the crystal measurement for meta-torbernite this may be regarded as a satisfactory confirmation of the above conclusions.

Properties of the water of crystallization.—In view of the simple morphotropic relation described above, it may be permissible to assume that the difference between the physical properties of the two forms is due simply to the addition of water, and that the properties of the meta-torbernite molecule persist without substantial modification in the space-lattice of torbernite. The four molecules of water then occupy in the crystal a molecular volume 59, and the molecular volume of H_2O is 14·75; the density is consequently 1·2, while that of the free liquid is 1·0. This value corresponds with that found in many hydrated salts, e. g. in the phosphates described by Dufet (2) and in the sulphates described by Tutton (3).

Turning to the refractive power, from the data given above, the values calculated for the two formulae generally used are :—

Gladstone & Dale.   Lorenz & Lorentz.

$$M_d = (n-1) \cdot \frac{m}{d}.$$ $$\{k\}_d = \frac{n^2-1}{n^2+2} \cdot \frac{m}{d}.$$

for torbernite   ...   183   ...   ...   104·5
for meta-torbernite I ...   158   ...   ...   89·8

For the four molecules lost the mean molecular refractive power for H_2O is 6·25 on the first formula and 3·67 on the second. The values calculated for pure liquid water are 6·00 and 3·77 respectively. The refractive power is thus unaltered by the condensation and is approximately additive as in the case of the double sulphates (3).

Occurrence.

In nearly all the well-known occurrences the mineral is torbernite. Meta-torbernite has not yet been found well crystallized, the best material being from Gunnislake; it is reported also from Spain (6), and is to be observed on a few other specimens as a platy incrustation without crystal boundaries and with a somewhat pearly lustre. Superficial alteration and even complete transformation of torbernite crystals is not uncommon, as in some Redruth material, but the absence of cracks and turbidity in the Gunnislake mineral makes it clear that these crystals have been deposited from solution in their present form and have not been subsequently dehydrated. Although the transition-curve for torbernite is very well defined, no proof has yet been obtained that the transformation is reversible, and it is thus possible that the meta-torbernite may have been deposited under conditions represented by a point within that curve. Both minerals are very insoluble in water, and a solution would, therefore, easily become supersaturated with respect to both forms. Crystals of either, when once deposited, seem to be stable indefinitely in contact with water at ordinary temperatures.

References.

1. J. D. Dana, System of Mineralogy, 6th edit., 1892, p. 856. (References are given to analyses by various chemists.)

2. H. Dufet, Étude crystallographique et optique des phosphates, etc. Bull. Soc. franç. Min., 1887, vol. 10, p. 77.

3. A. E. Tutton, Potassium, rubidium, and caesium salts . . . double sulphates. . . . Journ. Chem. Soc., 1896, vol. 69 (1), p. 344.

4. Y. Buchholz, Das Wassergehalt des Kupferuranits. Centralblatt Min., 1903, p. 362.

5. A. F. Hallimond, The crystallography and dehydration of torbernite. Mineralog. Mag., 1916, vol. 17, p. 326.

6. N. L. Bowen, Abnormal birefringence of torbernite. Amer. Journ. Sci., 1919, vol. 48, p. 195.