

*The crystallography and dehydration of Torbernite.*

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## I. CRYSTALLOGRAPHY.

**M**EASUREMENTS for torbernite have been given by numerous observers; the results are, however, of rather early date, and although the values for the ratio  $a:c$  are generally in fair agreement with the results here stated, the degree of accuracy of these measurements is not always indicated. Moreover, several minor difficulties arise, and it has been suggested that some of the early descriptions refer to the allied species, zeunerite; both species are optically uniaxial and possess almost the same axial ratios; they can, however, be distinguished by means of their refractive indices. The ordinary index of all the specimens here described has been determined by the Becke method; that for torbernite is 1.591, for the zeunerite from Schneeberg, approximately 1.62. A few torbernites possess a slightly higher index which may be due to the presence of zeunerite in isomorphous mixture, as is suggested by the presence of arsenic in some analyses.

It has been possible to examine much of the original material described by Lévy in his catalogue of the Heuland-Turner Collection (3). Before the early measurements are discussed, an account will be given of measurements made on three well-crystallized specimens of torbernite, with the object of determining more closely the crystalline form of this mineral.

*The Axial Ratio of Torbernite.*

*Specimen No. 1*<sup>1</sup> (fig. 1).—The locality of this specimen is not recorded. The crystals are scattered over white porous quartz; they are turbid and somewhat olive-green in colour, but the refractive index is normal

<sup>1</sup> No. L 1911, Museum of Practical Geology (Ludlam Collection).

and the faces are symmetrically developed and unusually free from striations and oscillatory growth. Examination of a basal cleavage flake showed that the turbidity is due to selective staining of the faces  $l(112)$  during the growth of the crystals, which therefore have an 'hour-

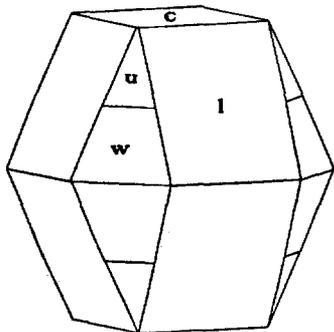


FIG. 1.—Crystal of Torbernite.

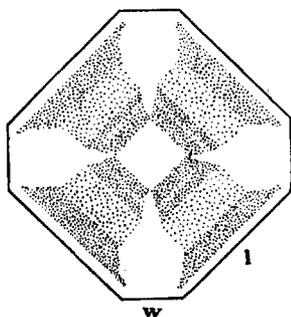


FIG. 2.—Section through crystal of fig. 1.

glass' structure; the last layer to be deposited seems to have been free from colouring matter. The appearance of a section near the middle of the crystal is shown in fig. 2.

The form  $l(112)$  is normal in character, but the faces  $e(101)$  are replaced by two vicinal faces separated by an angle of about  $1^\circ$ ; these are generally equally developed, but at times one or other may be almost

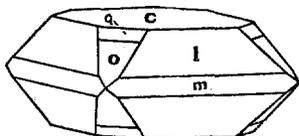


FIG. 3.

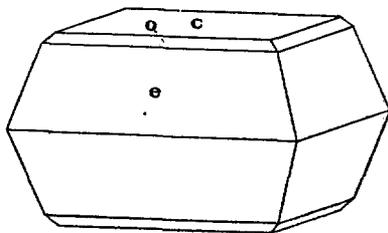


FIG. 4.

Crystals of Torbernite.

suppressed. Special care was taken to determine whether either of them was the true face  $e(101)$ ; the readings show conclusively that neither face occupies the simple position, nor are they equally inclined to  $e(101)$ , they will therefore be termed  $u$  and  $w$ , without assigned

indices. A summary of the readings obtained from five crystals is given below.

*Specimen No. 2*<sup>1</sup> (fig. 3).—Rather thick, tabular crystals, transparent and of brilliant lustre, are closely grouped over the surface of white quartz. The locality is given as Redruth, but the name of the mine is not recorded. The pyramid  $l(112)$  exhibits good faces, but those of  $o(103)$  are often striated horizontally, and a vicinal face  $q$  occurs next the base, or in oscillatory growth. The reading for  $o(103)$  is slightly below the calculated value, but importance cannot be attached to this in view of the irregularity of the faces in this zone. The faces of  $m(110)$  are normal. The readings obtained from three crystals are summarized below.

*Specimen No. 3*<sup>2</sup> (fig. 4).—The locality is not recorded. The crystals are quite transparent and are very well developed. The faces of  $e(101)$  are striated and the readings are unreliable even when apparently good images are obtained; the faces of  $o(103)$ , though narrow, give simple images for which the mean angle agrees very closely with the calculated value.

The readings obtained from this and the two preceding specimens are summarized in the following table:

Specimen.	Angle.	Limits.		Mean.	No. of readings.	Calculated.
No. 1. (Five crystals.)	$c : u(h0l)$	70° 17'	70° 50'	70° 33'	16	vicinal
	$c : w(h0l)$	71 43	72 4	71 50	10	vicinal
	$c : l(112)$	64 19	64 43	64 33	22	*64° 34'
No. 2. (Three crystals.)	$c : o(103)$	44 21	44 39	44 31	11	44 45
	$c : q(h0l)$	43 26	43 45	43 33	5	vicinal
	$c : l(112)$	64 21	64 49	64 35	16	*64 34
	$c : m(110)$	89 12	90 36	89 59	9	90 0
No. 3. (Three crystals.)	$c : o(103)$	44 39	44 56	44 47	8	44 45
	$c : e(101)$	71 3	71 45	71 18	13	71 25

<sup>1</sup> No. L 1890, Museum of Practical Geology (Ludlam Collection).

<sup>2</sup> No. L 1947, Museum of Practical Geology (Ludlam Collection).

The calculated angles are based on the mean angle  $c'l = 64^{\circ} 34'$  for the first two specimens. The corresponding axial ratio is:

$$a:c = 1:2.974.$$

The suggestion has been made by Koksharov (9) and by Walker (11) that the symmetry of torbernite is really pseudo-tetragonal, like that of autunite. The deviation from tetragonal symmetry, if present, is very small, and on account of the irregularity of growth the question cannot be decided with sufficient accuracy by the measurement of cross-zones on the crystals here described. If the faces of  $e(101)$  and similar forms really belong to two closely similar zones it might be expected that the readings would be most frequent for two slightly separated values instead of for the mean. No trace of such a grouping could be found, the mean reading is also the most frequent reading, and the crystallographic evidence available is therefore in favour of the view that torbernite possesses a true axis of fourfold symmetry, a view which is very strongly supported by the optical properties and dehydration.

#### *Comparison with earlier measurements.*

The early measurements for torbernite are to be found chiefly in the text-books; they are numerous; in many cases, however, it is difficult to ascertain the experimental evidence for the readings given, and there can be little doubt that the existence of several forms has never been confirmed by actual measurement. The results given by a number of authors are summarized in the following table. The angular measurement from the base is given under each symbol so that the extent to which the readings agree may be compared. Calculated values are placed in brackets, and, in the case where an author's results are completely consistent with theory but no indication of the fundamental angle is given, it has been thought best to indicate all the angles as theoretical. The sign  $\times$  signifies that the angle of an earlier author is repeated.

Phillips, 1823. (1)	Naumann, 1828. (2)	Hausmann, 1847. (4)	Miller, 1852. (5)	Dufrénoy, 1856. (6)	Greg and Lettsom, 1858. (7)	Hessenberg, 1864. (8)	Koksharov, 1866. (9)	Schrauf & Dana, 1872. (10)	A. F. H. (11)
—	—	—	—	—	—	—	—	—	<i>w</i> 71° 50'
—	<i>P</i> (71° 31')	—	—	—	—	<i>P</i> 71° 22'	<i>o</i> 71° 7'	<i>e</i> (71° 11')	<i>e</i> (101) 71° 18'
—	—	—	—	—	<i>u</i> 70° 26'	—	—	—	<i>u</i> 70° 33'
<i>c4</i> 68° 10'	—	—	<i>r</i> (68° 15')	$\frac{1}{2}b$ x	<i>r</i> x	—	—	<i>r</i> (69° 2')	—
—	—	<i>f</i> (63° 22')	—	—	—	—	—	<i>f</i> (62° 56')	—
—	—	—	—	—	—	—	<i>y</i> (55° 33')	<i>y</i> (55° 44')	—
—	—	—	<i>e</i> (51° 25')	<i>b</i> <sup>1</sup> x	<i>e</i> x	—	—	<i>ε</i> (51° 31')	—
—	—	<i>e</i> (44° 55')	—	—	—	—	<i>x</i> 44° 21'	<i>o</i> 44° 23'	<i>o</i> (108) 44° 47'
<i>c3</i> 42° 50'	—	—	—	—	<i>o</i> 43° 15'	—	—	—	<i>q</i> 43° 33'
—	—	—	—	—	—	$\frac{2}{10}P$ 41° 50'	—	<i>z</i> (41° 22')	—
<i>c2</i> 39° 20'	—	—	<i>s</i> (39° 53')	$\frac{3}{2}b$ x	<i>s</i> x	—	—	<i>s</i> (39° 59')	—
<i>c1</i> 34° 28'	—	—	—	—	—	—	—	—	—
—	—	—	<i>x</i> (32° 4')	<i>b</i> <sup>2</sup> x	<i>x</i> x	—	—	—	—
—	—	<i>d</i> (30° 53')	—	—	—	—	—	<i>x</i> (30° 25')	—
—	—	—	—	—	—	—	—	—	<i>p</i> (111) 77° 21'
—	—	—	—	—	<i>v</i> 72° 25'	—	—	<i>v</i> (72° 12')	—
—	<i>p</i> (64° 42')	—	—	$\frac{4}{5}a$ 64° 22'	<i>l</i> x	—	—	<i>l</i> (64° 17')	<i>l</i> (112) 64° 34'
<i>a2</i> 46° 0'	—	<i>c</i> (46° 36')	—	$\frac{3}{5}a$ (46° 10')	<i>t</i> x	—	—	<i>t</i> (46° 4')	—

## Notes on the preceding table.

[The numerals correspond with those in the list of references at the end of this paper, and with those at the head of the columns in the table.]

- (1) Phillips says in the preface, 'in no instance has it been attempted to correct the geometry of nature'. The angles are therefore to be taken as observed values.
- (2) Naumann's two values are in theoretical agreement; they are remarkably close to the later results, but it is not clear which form was measured.
- (3) No angles are given in the Heuland-Turner catalogue; it seems probable that the figures are based on measurements which were used by Miller (5) and by Dufrénoy (6).
- (4) Hausmann's values are in theoretical agreement with those of Naumann (2) (see Koksharov's paper (9)).
- (5) These angles are in theoretical agreement; the original measured angles are not given.
- (6) Dufrénoy says that these angles are based on Lévy's manuscript notes on specimens in the Turner Collection. The values are those given by Miller (5) with the addition of the forms  $a_1^2$  and  $a_2^2$ , which do not accord with the rest, but are themselves in theoretical agreement. The latter values are defended by Lévy, and agree with those of other observers. The figures and symbols agree with those in the Heuland catalogue (8).
- (7) Miller's angles are again quoted, with those of Lévy (3) and three new forms.
- (8) For the first time the actual observation is fully recorded; the angle  $71^\circ 22'$  is based on twelve measurements from five Redruth crystals; the number of readings for the other face is not given.
- (9) Koksharov's result is based on a number of measurements on crystals from Cornwall and from Schlaggenwald. The material was not very good, for two measurements were rarely obtained from the same crystal. Wolf Island, Lake Onega, is quoted as the locality for one specimen which is not here described. In conclusion, the author strongly emphasizes the discordance between these results and the angles given by Miller.
- (10) Schrauf wrongly quotes Wolf Island as the locality for Koksharov's material. The only new measurement given was obtained from one small Cornish crystal, and it is this angle which is taken as fundamental by Dana; the value lies between the rather widely separated results of Hessonberg and Koksharov. The suggestion is made that the early measurements of Lévy were in part made on crystals of zeunerite, the angle obtained by Schrauf for this substance agreeing with Miller's angles. Later measurements have not supported this view, the angle for zeunerite being fairly close to that for torbernite. No zeunerite was found among the English specimens examined for the purpose of the present paper.

In the last column of the table, stating my own results, only the

observed values for well-defined forms are given. Inspection of the table will show that few, if any, of the other forms are based on sufficient evidence to justify their inclusion in the list, especially in view of the confusion which has occurred between the different species of this group.

*Material described by Lévy.*

The early observations by Lévy (3) were made on material in the Heuland-Turner Collection. The majority of these specimens passed into the Ludlam Collection, and it has been possible to identify most of the figured specimens, which still bear numbers corresponding with those in Lévy's catalogue. The crystals are not always so well formed as might be concluded from the figures, and it is clear that the forms given have not in all cases been confirmed by measurement. The

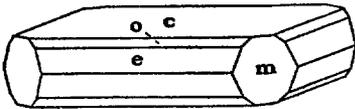


FIG. 5.

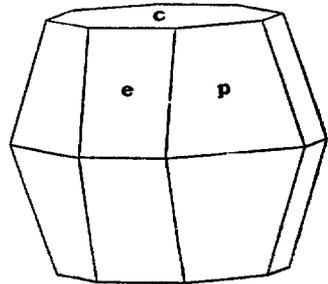


FIG. 6.

Crystals of Torbernite.

angles given later in Dufrenoy's work (6) are evidently those on which the figures are based, the high indices attributed to the pyramids  $a_1^6$  and  $a_2^6$  resulting in a very abnormal appearance in the drawings.

Measurements now made on crystals from these specimens have not confirmed the system of angles given for the forms (101), (103), &c., for the readings agree with those given in the first part of the present paper, and the form  $a_1^6$  becomes (112). The form  $a_2^6$  has not been found; it is not figured by Lévy, and it seems probable that it is based on an observation on bassetite. The habit of the crystals on most of these specimens is rather variable, and neighbouring crystals sometimes differ widely, especially in the extent to which the corners are modified by the pyramid  $l$  (112). Lévy's figures must be regarded as representing the general shape of the crystals, the forms encountered on

several crystals being brought together in the figure representing the specimen; in some cases the crystals are too small to have allowed any certain identification of the faces. The best crystal<sup>1</sup> from these specimens is represented in fig. 5.

*The forms  $c4$  and  $p(111)$ .*

The very steep form  $p(111)$ , which has not previously been recorded for this mineral, was observed on crystals partially invested with bassetite.<sup>2</sup> A drawing of one of these crystals is given in fig. 6.

The form  $c4$  of Phillips requires special consideration, since the early system of angles attributed to torbernite appears to have been based on measurements in agreement with the value of  $68^{\circ} 10'$  assigned by Phillips to this face. Good readings for such a form have not been obtained in the course of the present measurements, but there is no doubt that some crystals have yielded confused images in this position. The faces are dull and altered and have the size and development of the common form (101). It seems probable that the reading is due to reflection from a coating of alteration product, and does not therefore represent a true form belonging to torbernite.

## II. THE DEHYDRATION OF TORBERNITE.

The perfect cleavages of torbernite render the optical study of the crushed mineral exceptionally easy; the temperature of decomposition in air lies below  $100^{\circ} \text{C}$ ., and the alteration is marked by well-defined changes in the optical properties. Rinne has shown that the first and second products of dehydration, termed by him meta-torbernite<sup>3</sup> I and II, are not, as might be expected, amorphous bodies which retain only the external form of the crystals, but are themselves crystalline, birefringent, and are orientated in parallel position upon the still unchanged inner portions of the mineral. Rinne's description relates to the changes which occur when the mineral is heated in air; the same changes may, however, be realized at lower temperatures by the use of a desiccator. The alteration is dependent, then, jointly upon the temperature and the partial pressure of aqueous vapour in the sur-

<sup>1</sup> Specimen No. L 3806, Museum of Practical Geology (Ludlam Collection).

<sup>2</sup> A description of the specimen (No. L 1901) from Redruth has been given by the author in this volume (1915), p. 231.

<sup>3</sup> 'Metakupferuranit' of F. Rinne.

rounding space. The experiments here described have as chief object the determination of the limits of stability for torbernite in moist air at atmospheric pressure.

*Nature of the alteration.*

It is clear that the changes are due to the loss of water, the only constituent which is volatile at the temperatures in question. The second change, which yields the meta-torbernite II of Rinne, appears to be of the same character as the first; in the open air it occurs at about  $180^{\circ}\text{C}$ ., but over concentrated sulphuric acid the alteration is complete at  $100^{\circ}\text{C}$ . The vapour-pressures involved are thus very low, and it is not proposed to discuss this change further in the present paper.

The first change, to meta-torbernite I, is sharply defined. If the particles are kept in an enclosure in which the vapour-pressure is higher than that indicated by the transition-curve of fig. 7, no change in their properties can be observed. As soon, however, as the conditions in the enclosure transgress the transition-curve a change sets in, which, for the coarse powder used for optical determination, is completed in about six hours. If the particles are brought back to a moister atmosphere the change is arrested; the altered portion does not, however, regain its properties, and the products may therefore be examined freely in the open air.

The square fragments are attacked from the edges, with the formation of a network of fine cracks (along the *a* cleavages) which gradually advances toward the centre until the whole piece is converted into a turbid and friable mass. On immersion in an oil the cracks are filled, the altered particles regain their transparency, and it can be seen that the crystal has exfoliated along the *c* cleavage which has been invaded by flattened air-bubbles; there is, therefore, a considerable contraction along the principal axis, as well as in the directions normal to it.

It is of interest to note that the basal cleavage planes, though presenting by far the greater area, are not directly attacked, for the central portions of the fragments remain clear until they are reached by the change proceeding from the edges. The basal planes appear, indeed, to present a barrier to the passage of water from the crystal-network, a fact which may well be connected with the close structure required for these planes, both by the steepness of the commonly occurring forms and by the perfect basal cleavage.

*Optical changes.*—The altered particles still exhibit an optic axis normal to the basal cleavage; the birefringence is, however, much reduced and is now positive. This in itself may not necessarily imply full crystalline symmetry, for such properties may belong to an assemblage of fibres or plates possessing only the principal axis in common. The experiments of Gaubert, who showed that crystals of barium chloride yield orientated growths upon the decomposition product as well as on the original mineral, indicate that the meta-torbernite has probably a completely crystalline structure in which the basal plane retains the symmetry, and, to some extent, the dimensions, of that in the original torbernite.

The change in birefringence is accompanied by a considerable increase in the refractive index, the ordinary index for meta-torbernite I being higher than 1.610. The extent of the alteration in a particle may be seen by immersing it in oil of the ordinary index for torbernite, in which case the border of altered material appears in relief; or by examining the flake between crossed nicols in convergent light with a lens of wide aperture, when the altered borders, having less birefringence, are relatively dark, while the unchanged torbernite appears to glow with a greenish light.

*Influence of the surrounding medium.*—When torbernite is placed in an enclosure containing air saturated with water-vapour at a temperature higher than 75°C., the change to meta-torbernite I takes place in accordance with the description given above. If, however, the fragments are immersed in water and brought to the same temperature, the birefringence of the resulting meta-torbernite, instead of being positive, is found to be weakly negative. The two slightly different products may be boiled in water for several hours without losing their characteristic birefringences. The temperature of transition does not appear to be influenced by the immersion of the particles, which still break down at 75°C., and the other features of the change are the same. It seems probable that the initiation of the change is dependent simply upon the vapour-pressure of the medium, and that the nature of the medium is of importance only in determining the subsequent course of the rearrangement of the crystal. It is clear that the conditions of experiment require to be stated in the fullest possible way in dealing with alterations of this character.

*Method of Experiment.*

The crushed torbernite was supported in small open bottles in the upper part of the test-tubes which served as desiccators. Six of these

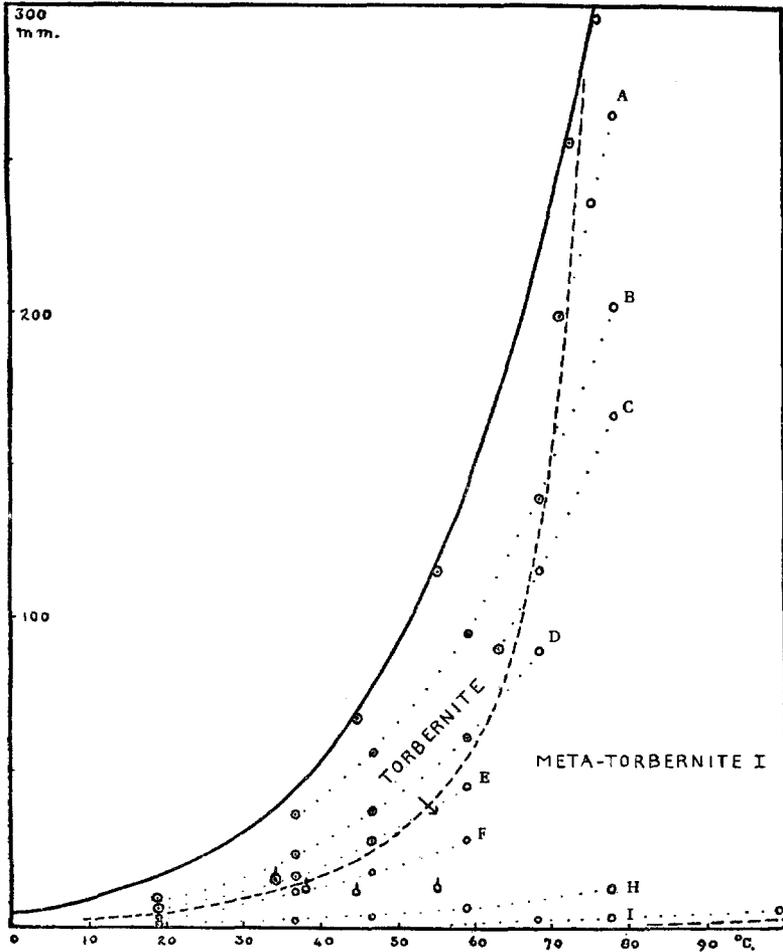


FIG. 7.—Transition-curve of Torbernite.

tubes, each containing about 20 c.c. of sulphuric acid of known concentration, were placed together in a water-bath, the temperature of which could be adjusted within limits of about one degree by means

of a thermo-regulator. After six hours the torbernite in each tube was removed and examined. The mineral in all tubes containing acids of less than a certain concentration was found to be unaltered, while that over the stronger acids had passed into meta-torbernite I. The transition-pressure at the temperature of the bath was thus determined to be between the vapour-pressures of two sulphuric acids in the series. The experiment was repeated several times for various temperatures of the water-bath. The acids used were of those concentrations for which the vapour-pressures are given in the 'Physikalisch-Chemische Tabellen' (Landolt and Börnstein), the values above 35° C. being obtained by extending the curves plotted from the tables.

A few experiments were also made by placing the torbernite in a tube, which was immersed in a water-bath and connected with a flask containing water at a constant lower temperature. The mineral was thus exposed to a vapour-pressure equal to that of the water in the cooler vessel. The results obtained were in agreement with those given by the sulphuric acids and are shown in the diagram (fig. 7). The method was found to be slow and inconvenient and was discontinued.

### *Results.*

The conditions in a tube containing air with a known pressure of water-vapour, at a given temperature, are conveniently represented by a point on a rectangular diagram in which the ordinates measure the vapour-pressure and the abscissae the temperature. Such a diagram expresses the results of the present experiments with sufficient accuracy, and the results have therefore been directly represented in fig. 7. The unbroken line is the vapour-pressure curve of pure water. The pressures over various strengths of sulphuric acid are represented by points in the area below this line. Results for acid of one concentration are joined by a dotted line—the vapour-pressure curve of the acid in question. The following acids were used: A 24.3, B 33.1, C 37.7, D 43.7, E 52.1, F 57.6, H 73.1, I 84.4 per cent.  $H_2SO_4$ . The points within circlets represent the conditions in which the torbernite was found to be unaltered, while the vacant circlets express conditions in which the change to meta-torbernite I had occurred. The area occupied by the first class of points is the stability-field of torbernite under the present conditions. The broken line which has been drawn between the two areas is the transition-curve of torbernite, and the remaining area belongs to the stability-field of meta-torbernite I. A second transition-line

should probably be drawn in the position shown on the right of the diagram, to indicate the change to meta-torbernite II, but the correct values for the very low vapour-pressures involved have not been determined.

The four points marked in the diagram with a small vertical line represent results obtained by the second method described above. Results for acid I (84.4 per cent.  $H_2SO_4$ ) were also obtained at temperatures  $19^\circ$ ,  $37^\circ$ ,  $47^\circ$ ,  $59^\circ C$ . Meta-torbernite I was unaltered at these pressures, which are too low to be included in the diagram.

#### *Conclusions.*

The limits of temperature and vapour-pressure within which torbernite can exist are seen to be very narrow; they are, in fact, little outside the variations which occur from day to day in the condition of the atmosphere. Had the transition-curve lain a little nearer the vapour-pressure curve of pure water, it is clear that the specimens of torbernite would have passed into meta-torbernite I on the first dry day following their removal from the mine. Again, since torbernite is unstable in water at temperatures above  $75^\circ C$ ., at least under ordinary pressure, the dilute solutions to which the crystals were exposed in the upper part of the veins cannot have exceeded this temperature since the formation of the mineral. In view of this very narrow range of stability it is not surprising to find that many specimens of torbernite have undergone more or less complete alteration; but as similar changes are brought about by chemical replacement, especially of the copper, the conclusion cannot be drawn that all these specimens have been subjected to temperatures exceeding  $75^\circ C$ ., it is necessary first to show that the alteration product is meta-torbernite I. Nevertheless it may be regarded as probable that the majority of specimens coated externally with material of higher refractivity have undergone a partial dehydration. It is important to observe that the temperature of an exhibition-case which is liable to exposure to the direct rays of the sun might easily exceed the limit of stability for torbernite, with consequent danger to the specimens. Again, the presence of a hygroscopic body, or of a mineral capable of removing water from the air, becomes a source of danger in a closed case. The decomposition of pyrites, with the formation of the hydrated sulphate of iron, would, for instance, probably suffice for the destruction of torbernite enclosed with it, unless the necessary water was supplied by a sufficiently free communication with the atmosphere.

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