

## *A thermal study of thaumasite.*

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[Taken as read 2 June 1960.]

*Summary.* A differential thermal analysis curve of thaumasite shows an endothermal peak at 206° C., corresponding to the loss of H<sub>2</sub>O and CO<sub>2</sub>, and a weak exothermal peak at 709° C., corresponding to recrystallization to a mixture of anhydrite and larnite, as is shown by X-ray powder photographs of material heated to 950° C. Improved powder data for thaumasite are given: the three strongest lines are at 9·66, 3·79, and 4·58 Å., and the cell-dimensions are *a* 10·992, *c* 10·311 Å.

THE sample of thaumasite used in this work is from Bull Runn Quarry, Centerville (Virginia), and was put at our disposal by R. A. Highbarger. It is a paragenesis of this mineral with apophyllite and a chlorite identified as pennine. The apophyllite occurs in large tetragonal crystals, which are transparent and colourless to light green; they are well formed, with {100} and {001} only, and the pennine occurs as small grains or as a dark green film covering them.

Among the apophyllite crystals is a very pure white mass of thaumasite formed by a great number of little crystals, of an average size 0·280 × 0·048 × 0·033 mm., which as seen under the microscope are completely transparent and colourless; they are well formed, of prismatic, almost acicular habit, in which the faces of the prism are observed (figs. 1-3). They are not pleochroic, with straight extinction, low refraction, and moderate birefringence (0·039).

The indexed powder data for thaumasite, obtained with Cu-K $\alpha$  radiation in a 229·2 mm. diameter camera of the Guinier-DeWolff type, is given in table I; intensities were measured with an integrating microphotometer. The indexing is based on a unit cell with *a* 10·992, *c* 10·311 Å.; previous values are: *a* 10·90, *c* 10·29 Å., Aminoff (1933); *a* 10·95, *c* 10·30 Å., Welin (1956); *a* 11·03, *c* 10·40 Å., Knill (1960). The three strongest lines of the powder photograph are 9·66, 3·792, and 4·582 Å.

A differential thermal analysis of the thaumasite has been made with the apparatus of the Inorganic Chemical Laboratory at the Faculty of Science, University of Barcelona.

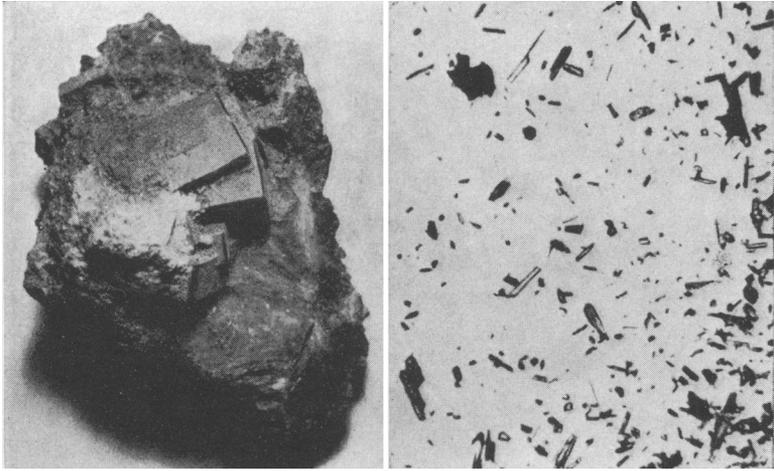


FIG. 1 (*left*): Specimen of thaumasite, with apophyllite and pennine. The white mass among the tetragonal prisms is the thaumasite.

FIG. 2 (*right*): Crystals of thaumasite; approximately  $\times 20$ .

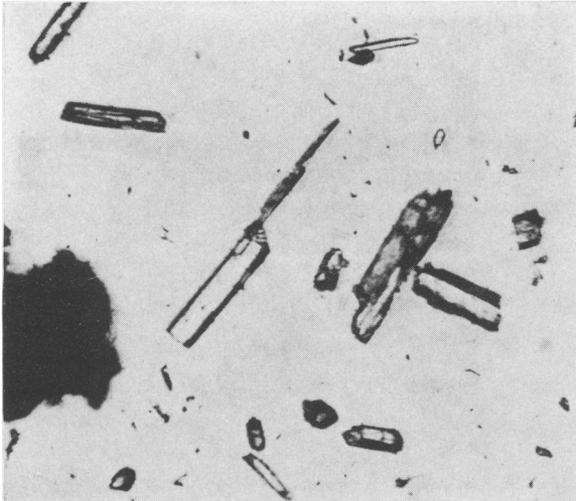


FIG. 3. Crystals of thaumasite; the top left-hand part of fig. 2 at a higher magnification, approx.  $\times 80$ .

TABLE I. Indexed X-ray powder data for thaumasite from Bull Runn Quarry, Centerville, Virginia, U.S.A. Cu-K $\alpha$  radiation, camera diameter 229.2 mm. Indexed on cell-dimensions  $a$  10.992,  $c$  10.311 Å.

$d$ , Å.	$I$ .	$hkl$ .	$d$ , Å.	$I$ .	$hkl$ .	$d$ , Å.	$I$ .	$hkl$ .
9.66	100	1000	2.0110	18	$\left\{ \begin{array}{l} 32\bar{5}2 \\ 10\bar{1}5 \end{array} \right.$	1.5598	3	$\left\{ \begin{array}{l} 60\bar{6}1 \\ 4370 \\ 4045 \end{array} \right.$
7.075	12	10 $\bar{1}$ 1	2.0010	9	30 $\bar{3}$ 4			$\left\{ \begin{array}{l} 4371 \\ 21\bar{3}6 \end{array} \right.$
5.535	44	11 $\bar{2}$ 0	1.9500	3	40 $\bar{4}$ 3	1.5431	4	$\left\{ \begin{array}{l} 5270 \\ 51\bar{6}3 \end{array} \right.$
5.221	6	0002	1.9285	10	41 $\bar{5}$ 2			$\left\{ \begin{array}{l} 5054 \\ 42\bar{6}4 \end{array} \right.$
4.889	18	$\left\{ \begin{array}{l} 20\bar{2}0 \\ 11\bar{2}1 \end{array} \right.$	1.9200	7	11 $\bar{2}$ 5	1.5384	3	$\left\{ \begin{array}{l} 6170 \\ 5272 \end{array} \right.$
4.582	65	10 $\bar{1}$ 2	1.9070	7	50 $\bar{5}$ 0	1.5338	7	$\left\{ \begin{array}{l} 5054 \\ 42\bar{6}4 \end{array} \right.$
4.355	10	20 $\bar{2}$ 1	1.8945	9	20 $\bar{2}$ 5			$\left\{ \begin{array}{l} 4264 \\ 6170 \end{array} \right.$
3.792	75	11 $\bar{2}$ 2	1.8785	1	$\left\{ \begin{array}{l} 5051 \\ 2244 \end{array} \right.$	1.4715	4	$\left\{ \begin{array}{l} 5272 \\ 2246 \end{array} \right.$
3.623	4	21 $\bar{3}$ 0			$\left\{ \begin{array}{l} 33\bar{6}0 \\ 3253 \end{array} \right.$	1.4580	9	$\left\{ \begin{array}{l} 4373 \\ 5164 \end{array} \right.$
3.529	31	20 $\bar{2}$ 2	1.8430	6	$\left\{ \begin{array}{l} 3144 \\ 4260 \end{array} \right.$	1.4222	6	$\left\{ \begin{array}{l} 4480 \\ 6172 \end{array} \right.$
3.422	36	21 $\bar{3}$ 1			$\left\{ \begin{array}{l} 3361 \\ 5052 \end{array} \right.$	1.3914	3	$\left\{ \begin{array}{l} 5273 \\ 4046 \end{array} \right.$
3.263	20	10 $\bar{1}$ 3	1.7990	8	$\left\{ \begin{array}{l} 4153 \\ 2135 \end{array} \right.$			$\left\{ \begin{array}{l} 7070 \\ 5380 \end{array} \right.$
3.188	15	30 $\bar{3}$ 0			$\left\{ \begin{array}{l} 5160 \\ 0006 \end{array} \right.$	1.3757	1	$\left\{ \begin{array}{l} 4481 \\ 3365 \end{array} \right.$
2.981	4	21 $\bar{3}$ 2	1.7892	10	$\left\{ \begin{array}{l} 3362 \\ 5161 \end{array} \right.$	1.3655	4	$\left\{ \begin{array}{l} 4265 \\ 7071 \end{array} \right.$
2.935	10	11 $\bar{2}$ 3			$\left\{ \begin{array}{l} 4262 \\ 10\bar{1}6 \end{array} \right.$	1.3550	2	$\left\{ \begin{array}{l} 5381 \\ 6064 \end{array} \right.$
2.756	3	22 $\bar{4}$ 0	1.7205	45	$\left\{ \begin{array}{l} 1126 \\ 5162 \end{array} \right.$	1.3515	3	$\left\{ \begin{array}{l} 3256 \\ 6173 \end{array} \right.$
2.714	37	30 $\bar{3}$ 2			$\left\{ \begin{array}{l} 3145 \\ 3363 \end{array} \right.$	1.3415	1	$\left\{ \begin{array}{l} 4374 \\ 4482 \end{array} \right.$
2.6465	6	31 $\bar{4}$ 0	1.7666	8	4261	1.3384	1	$\left\{ \begin{array}{l} 4482 \\ 6280 \end{array} \right.$
2.5950	39	0004	1.7480	4	4044	1.3303	1	$\left\{ \begin{array}{l} 4176 \\ 4176 \end{array} \right.$
2.5630	18	31 $\bar{4}$ 1			$\left\{ \begin{array}{l} 4154 \\ 2026 \end{array} \right.$	1.3227	3	
		$\left\{ \begin{array}{l} 2242 \\ 2133 \end{array} \right.$	1.6920	20	$\left\{ \begin{array}{l} 4263 \\ 6060 \end{array} \right.$			
2.4965	66	10 $\bar{1}$ 4	1.6410	11	11 $\bar{2}$ 6			
2.3571	11	31 $\bar{4}$ 2	1.6254	8	$\left\{ \begin{array}{l} 5162 \\ 3145 \end{array} \right.$			
2.2770	10	20 $\bar{2}$ 4			$\left\{ \begin{array}{l} 3363 \\ 4154 \end{array} \right.$			
2.1885	8	32 $\bar{5}$ 0	1.6152	11	$\left\{ \begin{array}{l} 2026 \\ 4263 \end{array} \right.$			
2.1546	41	4042	1.5822	3	6060			
2.1421	18	$\left\{ \begin{array}{l} 3251 \\ 2243 \end{array} \right.$						
2.1012	22	$\left\{ \begin{array}{l} 3143 \\ 2134 \end{array} \right.$						
2.0665	6	4150						
2.0495	4	41 $\bar{5}$ 1						

The d.t.a. curve obtained is reproduced in fig. 4. An endothermic peak appears clearly defined at 206° C., beginning between 135° and 140° C. and finishing between 255° and 260° C. The peak height or amplitude is 155  $\mu$ V, with a peak width 120° C. and a slope ratio 1.5. The latter is typical and can be used for identification of minerals of the same group as has been shown by Bramao *et al.*<sup>1</sup> Another peak of exothermic character, little intensity, and symmetrical form is situated at 709° C. It has a peak width 46° C., a peak height 6  $\mu$ V, and a slope

<sup>1</sup> L. Bramao, J. G. Cady, S. B. Hendricks, and M. Swerlow, *Soil Science*, 1952, vol. 73, p. 275.

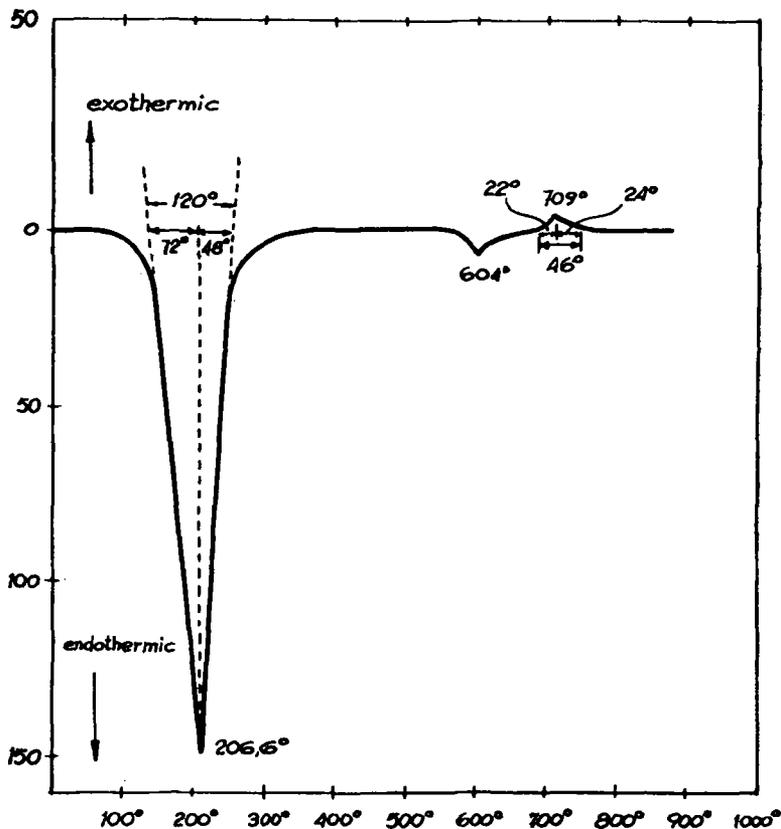


FIG. 4. Differential thermal analysis curve of thaumasite.

ratio 0.92. The endothermic peak situated at  $604^{\circ}\text{C}$ . arises from small quantities of pennine present as an impurity.

The ratio between the two peaks is 7:1 which shows that in the first reaction a quantity of heat is absorbed seven times greater than the one set free in the second. The first peak corresponds to a chemical reaction of first order, whereas the second indicates the consolidation or inversion of a phase.

Previous workers have shown that on heating thaumasite at  $205^{\circ}\text{C}$ . it loses weight by 41.9%, and at  $240^{\circ}\text{--}250^{\circ}\text{C}$ . loses 43.35%; the loss continues to increase up to 50.8% at  $330^{\circ}\text{C}$ . From this temperature up to  $1000^{\circ}\text{C}$ . no further loss of weight is observed.

These temperatures correspond to the great endothermic peak at 206° C., while the exothermic one of small intensity at 709° C. does not correspond to any loss of weight of the sample.

From this can be deduced: that the first peak corresponds to a chemical reaction of the first order, of an endothermic type, as it is the loss of the 15 molecules of water coordinated with Ca, whose total elimination takes place at a temperature situated on its ascendent branch; owing to the disposition of the CO<sub>3</sub> groups, joined to the rest of the structure by hydrogen bonds through the water molecules, these groups decompose during this period, releasing CO<sub>2</sub>, the material remaining completely without H<sub>2</sub>O and CO<sub>2</sub> at about 300° C. And that the second peak, seven times smaller than the first one and of an exothermic type, is due to the consolidation or inversion of a phase.

In order to know the exact happenings, a study has been made of the final phases that are formed when the mineral is heated over 900° C. and below 1 000° C.

*X-ray study on thermal decomposition of thaumasite.* A sample of thaumasite was heated at 950° C. and analysed by X-ray. In the powder diagrams obtained, two phases have been identified: CaSO<sub>4</sub> (anhydrite) and β-Ca<sub>2</sub>SiO<sub>4</sub> (larnite), by means of the A.S.T.M. X-ray powder data file, cards nos. 6-0226, 3-0753, and 3-0761. The data obtained from the sample and the standard data for CaSO<sub>4</sub> and β-Ca<sub>2</sub>SiO<sub>4</sub> are reproduced in table II.

During the past few years several attempts have been made to work out the structure of thaumasite. Brú and collaborators (1954, 1957) have presented a possible scheme of structure.

Simultaneously, E. Welin (1956) has proposed a structure for the mineral, using a sample from Långban, Sweden. He accepts the existence of chains -SiO<sub>4</sub>-Ca-SiO<sub>4</sub>-Ca-SiO<sub>4</sub>- situated along the *c*-axis, with Ca surrounded by six oxygens, lying at the vertex of a distorted octahedron, three of them belonging to SiO<sub>4</sub> and the other three to water molecules. The groups SO<sub>4</sub> and CO<sub>3</sub> would be linked by hydrogen bonds to H<sub>2</sub>O of the octahedron, without direct bonding to the Ca.

The formation of CaSO<sub>4</sub> in the thermal treatment of the mineral seems to be in contradiction with the positions of SO<sub>4</sub> groups in the structure deduced by Welin (1956). In this structure the SO<sub>4</sub> is linked with calcium through a water molecule, which coordinates with calcium without any electric charge and links with SO<sub>4</sub> by a hydrogen bond. Also, in this structural scheme, all the calciums are rigidly joined to chains of SiO<sub>4</sub>. If this were true, one would expect that the final product of the

thermal treatment of the mineral should be only  $\text{Ca}_2\text{SiO}_4$ , the  $\text{SO}_4$  groups being expelled like the  $\text{CO}_3$  groups.

TABLE II. X-ray powder data of heated thaumasite and its interpretation.

Thaumasite heated to 950° C.		CaSO <sub>4</sub> — A.S.T.M. card 6-0226			β-Ca <sub>2</sub> SiO <sub>4</sub> —A.S.T.M.			
<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>hkl</i> .	card 3-0753		card 3-C761	
					<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .
3.466	100	3.498	100	{ 002 020				
3.072	35				3.06	10	3.04	50
2.856	40	2.849	33	210	2.88	10		
2.788	40				2.78	100	2.76	100
2.740	35				2.74	60	2.71	50
2.699	30				2.67	60	2.67	50
2.329	20	2.328	22	{ 202 220				
2.273	20				2.27	40	2.26	50
2.210	20	2.208	20	212				
2.171	30				2.18	80	2.18	75
2.032	15				2.02	20	2.03	50
1.998	20				1.97	20	1.98	75
1.865	30	1.869	15	230	1.89	10	1.89	50
1.800	15				1.79	10	1.80	50
1.743	20	1.749	11	040				
		1.748	10	004	1.70	10	1.70	25
1.648	20	1.648	14	232	1.62	20	1.63	60
1.580	7				1.56	10	1.57	25
1.530	7				1.53	20	1.52	25
1.491	7				1.48	20	1.48	25

The formation of the  $\beta\text{-Ca}_2\text{SiO}_4$  explains the appearance of the peak at 709° C. This silicate is stable between 670° C. and 1 420° C.; it may be supposed that after the elimination of the water and  $\text{CO}_2$  of the mineral, the phase  $\text{CaSO}_4$  becomes consolidated, while the  $\text{Ca}_2\text{SiO}_4$  remains in the  $\gamma$ -form or in some amorphous state, which could crystallize into  $\beta\text{-Ca}_2\text{SiO}_4$  starting at 673° C. This temperature agrees with the starting temperature of the peak.

*Acknowledgements.* I thank Professors DeWolff and Coronas for permission to work in their laboratories, and Dr. Pujol for helping me in obtaining the d.t.a. curve.

#### References.

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