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THE DEHYDRATION OF HEMIMORPHITE

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ABSTRACT

The thermal dehydration of hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) has been studied by single-crystal *x*-ray methods. Loss of the molecular water below 550° C. causes only slight change in the rest of the structure. At about 700° C., the hydroxyl water is lost, and there is an oriented conversion to β-Zn_2SiO_4; below 960° C. there is a second oriented conversion to α-Zn_2SiO_4 or willemite. γ-Zn_2SiO_4 does not appear to be formed. Both orientation relationships have been established and the unit cell of β-Zn_2SiO_4 determined. The structure of β-Zn_2SiO_4 is probably derived from a distorted tridymite- or cristobalite-like framework in which half of the silicon is replaced by zinc and additional atoms of zinc introduced into suitable interstices. Possible mechanisms for the two oriented conversions are discussed, and are compared with those known or believed to occur in similar reactions of silicates containing other cations.

INTRODUCTION

It has long been known that hemimorphite loses its water in two stages (Zambonini, 1908), and that this is explained by the ionic constitution $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ which was established by *x*-ray structure analysis (Ito and West, 1932; Barclay and Cox, 1960). Faust (1951) studied the dehydration process using differential thermal analysis. Using a heating rate of 10–12 deg./min., he found endotherms at 393–657° C. and 740° C. and an exotherm at 971° C. He attributed the first endotherm to loss of molecular water, and the second to loss of hydroxyl. He obtained indirect evidence that the 740° C. product was γ-Zn_2SiO_4 and that the 971° C. exotherm was due to the conversion of this phase into α-Zn_2SiO_4 or willemite. Roy and Mumpton (1956) also determined a DTA curve and found an endotherm at about 730° C. They reported that heating to above 600° C. caused no change in the *x*-ray pattern, but that static heating at 710° C. caused partial breakdown.

The polymorphism of Zn_2SiO_4 has been studied partly because of the luminescent properties of the various polymorphs. Willemite appears to be the only stable form; it is rhombohedral and gives a green fluorescence. Schleede and Gruhl (1923) were the first to demonstrate the existence also of a β-form, having a yellow fluorescence, and of a γ-form, having a red fluorescence. They used *x*-ray powder photographs. During the next twenty years several investigators concluded, either that the β- and γ- forms did not exist, or that they were amorphous. However, Rooksby and McKeag (1941) confirmed the existence of the β-form and published better *x*-ray powder data for it, though they were unable to obtain convincing evidence for the existence of the γ-form. Ingerson, Morey and Tuttle (1948) prepared single crystals of all three polymorphs and reported their optical properties; the β- and γ-forms were both biaxial. Sabatier (1952) described a polymorph which he called pseudowillemite. This was apparently cubic and so not identical with any of the other forms. These metastable polymorphs have usually been made by cooling mixtures of Zn_2SiO_4 composition rapidly from 500° C. or above. They invert to willemite on sufficiently prolonged heating at 850° C. or above. Faust (1951) found that if his DTA run on hemimorphite was stopped at 761° C., a small exotherm occurred almost immediately on cooling, and that the cooled product was β-Zn_2SiO_4. He attributed the exotherm to inversion from the γ-form, which he considered to have been formed on dehydroxylation at 740° C.

No single-crystal study of the thermal decomposition of hemimorphite has been reported. The present work was done in the hope of obtaining information about the mechanism of the process and perhaps also about the structures of the metastable polymorphs of Zn_2SiO_4.

EXPERIMENTAL

A sample of hemimorphite from Ogdensburg, Sussex County, New Jersey, (BM 1924, 643) was used. It consisted of colorless prisms with elongation *c* and cleavage (110), referred to the usual orthorhombic axes (*a* 8.37, *b* 10.67, *c* 5.10 Å; Barclay and Cox, 1960). For all *x*-ray work, filtered copper radiation was used. Single-crystal examination of the sample showed that it had substantially the same cell parameters as those given above.

Crystals were heated in air for 5–15 hour periods at 550°, 725–760° and 960° C. They were then cooled, either rapidly by placing them on a metal surface, or slowly at about 20 deg./min. *X*-ray rotation photographs were taken of the cooled crystals about the prism axis. In all cases it was found that partial or complete oriented conversion to new products had occurred. Appropriate oscillation or Weissenberg photographs were taken in each case to determine the nature of the product and its orientation relative to that of the starting material.

The following additional experiments were carried out:

1. A crystal about 0.5 mm long was held at one end in a metal clamp and heated momentarily at the other end in a very small gas flame burning from a glass capillary. The resulting pseudomorph contained the 550° C. product at one end and the 960° C. product at the other. Subsequent Weissenberg photographs of this crystal provided valuable supplementary information about the relative orientations of these two products.

2. High-temperature single-crystal photographs were made at 650°

and 750° C., using a device similar to that described by Dent and Taylor (1956) as modified by Barclay and Donaldson (1961).

3. X-ray powder photographs were made of samples that had been cooled rapidly and slowly from 750° C. A single-crystal camera 6 cm in diameter was used to permit direct comparison with rotation photographs.

RESULTS

Modified hemimorphite

The crystal heated at 550° C. gave patterns of sharp spots substantially identical with those of the original hemimorphite, but with slightly altered cell dimensions (a 8.25, b 10.75, c 5.10 Å). The a-axis had thus contracted while the b-axis had expanded. Comparison with weight-loss and DTA evidence (Zambonini, 1908; Faust, 1951) shows that this product is a modified hemimorphite, $Zn_4Si_2O_7(OH)_2$, from which the molecular water has been lost. A crystal examined at 650° C. using the high-temperature camera gave the same pattern, with slight further modifications attributable to thermal expansion.

The 725–760°C. product: β-Zn_2SiO_4

Some crystals cooled from these temperatures contained a little modified hemimorphite, but all consisted wholly or mainly of a different product which was subsequently shown to be β-Zn_2SiO_4. This product showed markedly preferred orientation. In rotation photographs about the prism axis, all but a few very weak reflections fell on the same layer lines as those of the hemimorphite, showing that the repeat distance in this direction is approximately preserved. Zero, first, and second-layer Weissenberg photographs were obtained, and gave the following results:

1. Most of the reflections could be indexed on a geometrically orthorhomic cell with a 8.40, b 5.10, c 32.2 Å, which was all-face centered. There were two orientations, with a common b-axis parallel to the prism direction (Fig. 1). The intensities of corresponding hkl and $hk\bar{l}$ reflections were unequal, and the symmetry is therefore monoclinic or triclinic. Corresponding hkl and $h\bar{k}l$ reflections were of equal intensity, but there was no evidence as to whether or not this was caused by twinning; further elucidation of the symmetry would only be possible with true single crystals. $00l$ reflections occurred only for $l=8n$. The unit cell is therefore built up from eight elementary layers each 4.025 Å thick, and the larger c-axis is caused by the way in which these are stacked.

2. A few reflections, some of them strong, would have had to have

been assigned non-integral *l*-indices on this cell. They could be explained if a second polytype of the same substance was present, in the same two orientations. This is composed of the same elementary layers as the first, and has the same *a*- and *b*-axes, but *c* is a different multiple of 4.025 Å. Not enough reflections were observed for the value of *c* to be definitely established, though there were indications that it was either 5 or 10 times 4.025 Å.

3. A few reflections, all very weak, demanded doubled values either of *a* or of *b*. The true unit cell for the main polytype therefore had *a* 16.8, *b* 10.2, *c* 32.2 Å.

The relative proportions of the two polytypes varied in different crystals cooled from 725–760° C., though the 8-layer one always predominated. The relative porportions did not seem to be correlated with the rate of cooling. A high-temperature photograph was taken of a crystal which had been heated to 750° C. in 10 minutes and then maintained at that temperature during a 5-hour exposure. It showed the presence of both polytypes and of no other phase. The crystal was cooled and a further photograph taken. This was identical with the first, apart from the effect of thermal contraction.

X-ray powder data for β-Zn_2SiO_4

X-ray powder photographs of samples cooled either quickly or slowly from 750° C. gave identical results (Table 1). They were indexed by direct comparison with photographs obtained on the same camera from single crystals rotated about the prism axis, due account being taken of relative intensities estimated from Weissenberg photographs. The powder patterns were somewhat diffuse because of the combined effects of small crystallite size and a large *c*-axis. Few of the lines are due to single reflections, and only the main contributions to each line are listed in the indexing. To a fair approximation, the data are those of the 8-layer polytype, though reflections from the other polytype probably contributed appreciably to the lines at 3.55, 1.64 and 1.43 Å. If a sufficiently high proportion of the other polytype were present, one would expect a line at 2.57 Å to appear.

Formation of willemite

X-ray photographs from single crystals that had been heated at 960° C. showed the reflections of willemite (α-Zn_2SiO_4). These had strongly preferred orientation. A rotation and a complete set of 10° oscillation photographs about the prism axis were taken. They showed that the willemite had been formed in four orientations, which are given in Fig. 1. Hexagonal axes (*a* 13.96, *c* 9.34 Å) will be used throughout this paper

Table 1. *X*-Ray Powder Data for β-Zn_2SiO_4

Observed CuKα: $\lambda = 1.542$ Å			Calculated	Observed (Rooksby & McKeag, 1941)[3]		Observed (Sabatier, 1952)	
Spacing (Å)	Relative intensity[1]	Indices[2]	Spacing (Å)	Spacing (Å)	Relative intensity	Spacing (Å)	Relative intensity[1]
		$20\bar{2}$	4.07			4.29	vw[4]
4.07	s/b			4.10	5		
		008	4.03			4.05	s
				3.646	5		
3.55	vs/b	$11\bar{5}$	3.61			3.52	vs
				3.502	6		
3.29	vw	206	3.30	3.238	5		
		$20\bar{8}$	2.91	3.067	3		
2.86	ms/b						
		119	2.77	2.846	8		
						2.57	w[4]
		022	2.51	2.531	6		
2.48	vvs/b	311	2.45	2.493	6	2.47	vs
		11.11	2.44	2.454	3		
2.31	vvw	$31\bar{5}$	2.30	2.210	4		
		224	2.10				
2.12	w			2.114	4	2.11	w
		$40\bar{2}$	2.08				
		226	2.02				
2.02	w	$22\bar{6}$	2.02	2.022	4	2.00	w
		00.16	2.01				
		11.15	1.93				
1.8–1.9	vvw/d	20.16	1.82				
		$22.\overline{10}$	1.81				
1.64	w/b	40.12	1.65	1.635	5	1.61	m
		$22.\overline{14}$	1.59				
1.57	vvw			1.559	3		
		11.19	1.58				
				1.517	4		
1.52	mw	51.7	1.51			1.50	m
				1.488	3		
		$11.\overline{21}$	1.45	1.430	3		
1.43	m					1.41	m
		31.19	1.40	1.420	3		
1.242	vw						
1.112	vw						
1.007	vw	00.32	1.006				
0.939	vw						

[1] s = strong, m = moderate(ly), w = weak, v = very b = broad, d = diffuse.

[2] Referred to the geometrically orthorhombic pseudo-cell with *a* 8.40, *b* 5.10, *c* 32.2 Å.

[3] Very weak lines (intensitites 2 or under) omitted.

[4] Lines unindexable on a cubic cell with *a* 7.03 Å.

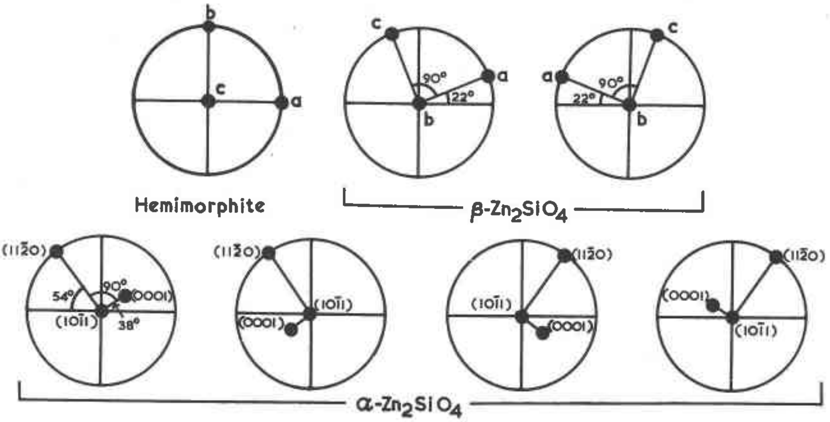

FIG. 1. Orientation relationships between hemimorphite, β-Zn_2SiO_4, and α-Zn_2SiO_4 or willemite, shown in stereographic projection onto a plane normal to the prism axis. For clarity, angles are shown in only one of the four equivalent orientations of the α-Zn_2SiO_4.

for willemite. For all four orientations, $(10\bar{1}1)$ was normal to the prism axis.

DISCUSSION

The 725–760° C. product: identity, density, and cell contents

The *x*-ray powder pattern of this product agrees substantially with those of Schleede and Gruhl (1923) and of Rooksby and McKeag (1941, Table 1) for β-Zn_2SiO_4, and the identity of the product is thus established. Rooksby and McKeag's pattern contained many more weak lines. This can probably be attributed chiefly to larger crystallite size, though it is possible that a different polytype or combination of polytypes was present.

Table 1 also gives Sabatier's (1952) data for pseudowillemite. They agree closely with the others. Sabatier concluded from his data that his product was cubic, with *a* 7.03 Å, although two lines could not be indexed on this cell. It seems more likely that it was virtually identical with the β-Zn_2SiO_4 obtained in the present investigation. One of the lines which Sabatier could not index had a spacing of 2.57 Å. The presence of this line suggests that the product contained a high proportion of the polytype which was found as a minor constituent in the present investigation.

The β-Zn_2SiO_4 pseudomorphs made from hemimorphite were highly porous but of low permeability to liquids, and it was impracticable to obtain significant experimental values for either density or refractive index. However, Sabatier (1952) reported a specific gravity of 4.22 for pseudowillemite. This value is indirectly but strongly supported by the results of Ingerson, Morey and Tuttle (1948), who showed that single crystals of β-Zn_2SiO_4 had a mean refractive index close to that of willemite. The density of β-Zn_2SiO_4 must therefore be almost the same as that of willemite, which is about 4.2 gm/cc. The orthogonal pseudocell of β-Zn_2SiO_4 with *a* 8.40, *b* 5.10, *c* 32.2 Å therefore contains 16 [Zn_2SiO_4]; the density calculated assuming these cell contents is 4.29 gm/cc.

The sequence of changes on heating hemimorphite

The present results confirm that the molecular water is lost below 550° C. with only minor effect on the rest of the structure. They suggest that the resulting modified hemimorphite changes directly into β-Zn_2SiO_4 at about 700° C., and that this product transforms to willemite below 960° C. They do not support Faust's view that γ-Zn_2SiO_4 is formed at about 700° C. and inverts to β-Zn_2SiO_4 only on cooling. The possibility was considered that γ-Zn_2SiO_4 is merely a particular polytype of β-Zn_2SiO_4. It was rejected, because Schleede and Gruhl's *x*-ray powder patterns for the two modifications differ too much to be explainable in this way. This leaves unexplained the exothermic change which Faust observed to occur on cooling a specimen from 761° C. It could possibly be attributed to a change in polytype of the β-polymorph. Though such a change was not found to occur on cooling in the present investigation, its occurrence might well be influenced by small differences in composition or in experimental conditions. On this interpretation of the results, γ-Zn_2SiO_4 is not formed during the heating of hemimorphite.

The nature of β-Zn_2SiO_4

The present results suggest that β-Zn_2SiO_4 has a structure related to those of tridymite and cristobalite. These modifications of silica have structures based on a trigonal structural element with *a* 5.2, *c* 4.0 Å (Fig. 2a), and to a rough approximation this is also true of β-Zn_2SiO_4. The atomic contents of the structural element are 2 [SiO_2] for tridymite and cristobalite, and 1[Zn_2SiO_4] for β-Zn_2SiO_4. The latter could therefore have a structure derived from that of tridymite or cristobalite by replacing one-half of the silicon by zinc and introducing more zinc atoms into suitable interstices.

Zinc readily adopts tetrahedral coordination, and the postulated replacement of silicon by zinc is reasonable. The low symmetry of β-Zn_2SiO_4 suggests that the replacement is regular and not random. However, the interstices which are provided by the tridymite or cristobalite frameworks in their undistorted forms are too large to accommodate zinc

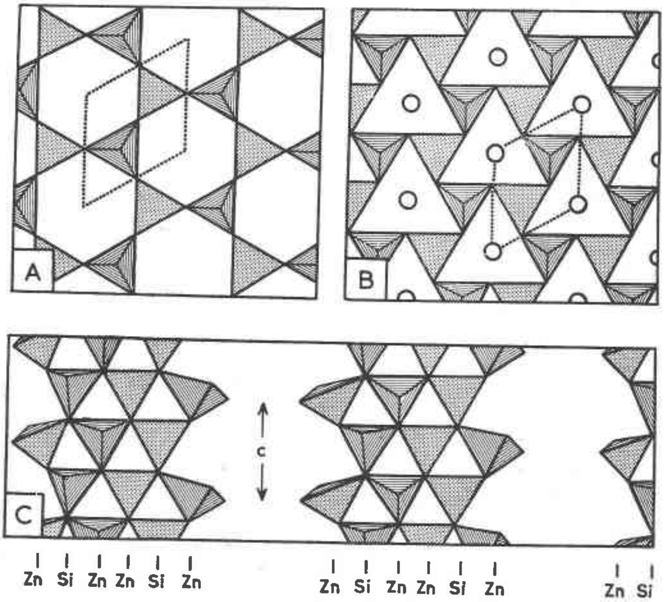

FIG. 2. Arrangements of tetrahedra in a single elementary layer in (A) tridymite or cristobalite (somewhat idealized), (B) $BaAl_2O_4$, and (C) hemimorphite. Tetrahedra with apices pointing in opposite directions are distinguished. In (A) and (B) the trigonal structural element of side 5.1 Å is shown with dotted lines. In (B), open circles represent barium atoms. It is suggested that β-Zn_2SiO_4 structure is composed of layers similar to those in (B).

atoms. Some reduction in their size is caused by distortion of the framework of the kind that is known to occur in $BaAl_2O_4$ (Wallmark and Westgren, 1937, Fig. 2b) and in other structurally related compounds. Evidence that the tetrahedral framework in β-Zn_2SiO_4 resembles that of $BaAl_2O_4$ more closely than that of tridymite or cristobalite is provided by the observed orientation relationships for both the hemimorphite—β-Zn_2SiO_4 and β-Zn_2SiO_4—willemite transitions; this is discussed later.

The kind of distortion of the framework that occurs in $BaAl_2O_4$ does not by itself reduce the size of the interstices sufficiently to make them suitable for an atom as small as zinc; it normally produces interstices suitable for larger cations such as Na, K, Sr, Ba, or Pb (Buerger, 1954). It can only be assumed that in β-Zn_2SiO_4 the presence of tetrahedral zinc in the framework causes further distortion which still further reduces the size of the interstices. The coordination of the zinc present in these interstices is uncertain. By analogy with $BaAl_2O_4$ and other structurally similar compounds, octahedral coordination is perhaps more likely than

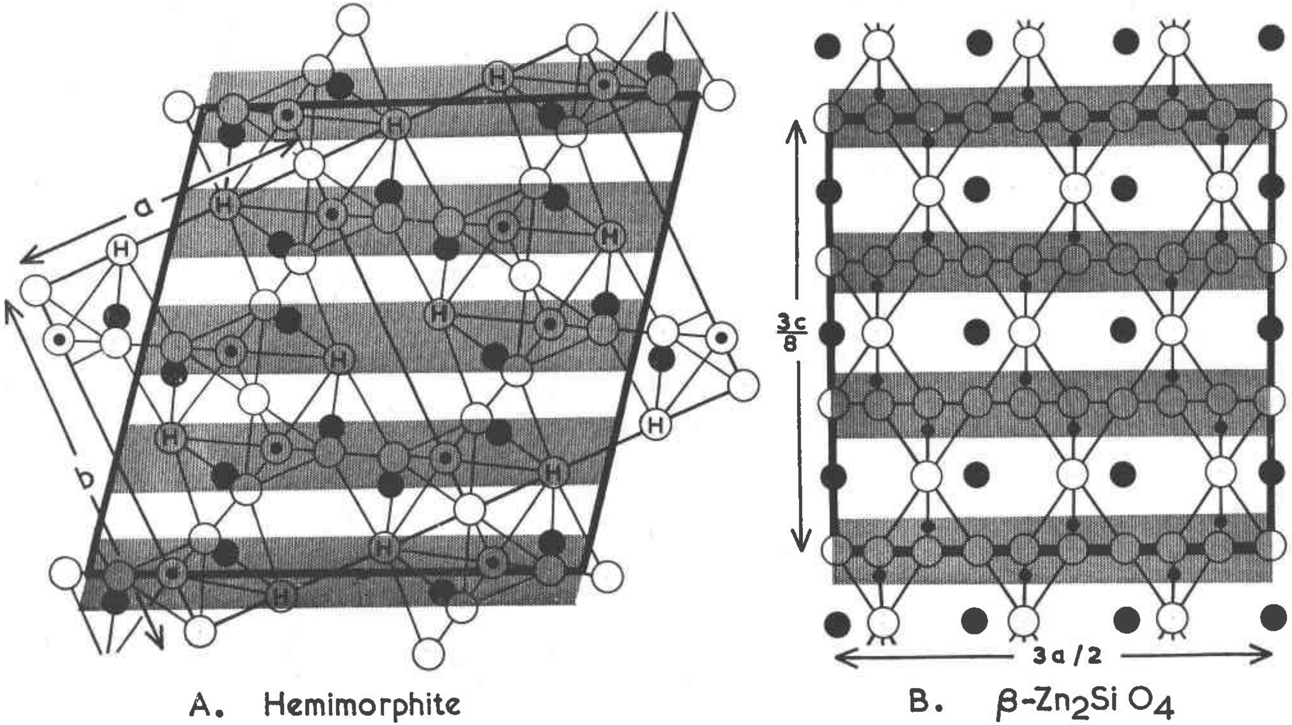

FIG. 3. (A) The structure of modified hemimorphite (slightly idealized), and (B) a general indication of that proposed for the 8-layer polytype of β-Zn_2SiO_4, drawn in the observed relative orientations as seen along the prism axis. Open circles represent oxygen atoms or hydroxyl groups (Ⓗ), thin lines outline SiO_4 or ZnO_4 tetrahedra. Large full circles represent zinc. Small full circles in (A) represent silicon; in (B) they can be either silicon or zinc. All atoms occur once only in the height of the projection (5.1 Å in each case). The significance of the shaded regions and of the heavily outlined pseudo-repeat units is explained in the text.

tetrahedral. This might also explain the apparently low stability of β-Zn_2SiO_4 relative to willemite, in which all of the zinc is tetrahedrally coordinated.

Tridymite and cristobalite show polytypism, which can give rise to large repeat distances in the tridymite *c*-direction (Flörke, 1955). The same phenomena exist in β-Zn_2SiO_4, and can probably be explained in much the same way. It appears profitless to discuss whether the 8-layer polytype of β-Zn_2SiO_4 should be regarded as a derivative of tridymite or as one of cristobalite.

Figures 2B and 3B show a tentative and idealized structure for β-Zn_2SiO_4 based on the reasoning given above. No attempt has been made to distinguish zinc from silicon in the tetrahedral positions, nor to show how the stacking of the structural elements could give rise to any particular polytype. The zinc atoms not forming part of the framework have merely been placed in plausible octahedral positions. A structure analysis made on true single crystals would be needed to settle these questions.

The transformation of hemimorphite into β-Zn_2SiO_4

Figure 3 shows the two structures in the observed relative orientations. The modified hemimorphite (Fig. 3A) is assumed to have the same structure as the original material apart from the loss of the water molecules. Most of the atoms in this structure lie on or near to the (130) planes, in lamellar regions which are shaded in the diagram. In the β-Zn_2SiO_4 (Fig. 3B), most of the atoms lie on or near to the (008) planes, in lamellae which are also shaded. The orientation relationship is such that (001) of β-Zn_2SiO_4 is formed parallel to (130) of the modified hemimorphite. The β-Zn_2SiO_4 is formed in two orientations because it is equally possible for $(1\bar{3}0)$ of the modified hemimorphite to become (001) of β-Zn_2SiO_4.

Figure 2C shows the arrangement of atoms within a single lamella parallel to (130) in hemimorphite. It is much closer to that occurring in a single sheet from a structure of the $BaAl_2O_4$ type (Fig. 2B) than to that in a sheet from tridymite or cristobalite (Fig. 2A). This is part of the evidence that β-Zn_2SiO_4 has a structure more nearly resembling that of $BaAl_2O_4$. Figures 2B and 2C are drawn in the observed relative orientations. It is apparent that considerable portions of the β-Zn_2SiO_4 sheets exist already in those of the hemimorphite and that relatively small atomic movements would suffice to convert one structure into the other. This explains the observation that the *c*-axis of hemimorphite becomes the *b*-axis of β-Zn_2SiO_4.

The similarity between the two structures is particularly close as regards the oxygen atoms, and especially as regards those which form the bases of the tetrahedra (Figs. 2B and C). Some of the zinc and silicon atoms are also in the same positions, but others must move through the oxygen layer to form new tetrahedra on the opposite side. The zinc and silicon atoms are therefore probably more mobile than the oxygens during this transformation. Considerable movements of oxygen must nevertheless occur. Figure 3 shows that there are four lamellae parallel to (130) in hemimorphite in approximately the same distance as three lamellae parallel to (001) in β-Zn_2SiO_4. The lamellae in hemimorphite are divided into strips, whereas those in β-Zn_2SiO_4 are complete (Fig. 2); there are also more oxygen atoms between the lamellae in β-Zn_2SiO_4 (Fig. 3). One lamella in four must be destroyed to complete the structures of and between the other three.

In Fig. 3, there are outlined in the two structures pseudo repeat units of approximately equal volume. The corresponding true repeat units are considerably larger. As a first approximation it may be assumed that the material in the pseudo repeat unit of modified hemimorphite is converted into the material in the corresponding unit of β-Zn_2SiO_4. The hemimorphite unit contains $Zn_{16}Si_8O_{36}H_8$, while that of β-Zn_2SiO_4 contains $Zn_{18}Si_9O_{36}$. The number of oxygen atoms remains the same, but the numbers of zinc and silicon atoms increase. This suggests that the mechanism is of the "inhomogeneous" type suggested for the dehydrations of tremolite (Freeman and Taylor, 1959) and brucite (Ball and Taylor, 1961). On this hypothesis, donor and acceptor regions develop in the crystal. The donor regions are destroyed and become pores. Their zinc and silicon atoms migrate into the acceptor regions, while protons move in the opposite direction; their oxygen atoms go into the water that is formed. The stoichiometry of this process is shown below:

$$\begin{array}{lll} \text{Donor regions:} & Zn_4Si_2O_9H_2 & \rightarrow 9H_2O \\ & \begin{matrix}4Zn^{2+}\\ 2Si^{4+}\end{matrix} \downarrow\uparrow\ 16\ H^+ & \\ \text{Acceptor regions:} & 8Zn_4Si_2O_9H_2 & \rightarrow 18\ \beta\text{-}Zn_2SiO_4 \end{array}$$

This stoichiometry is possibly only approximate, as there may be some movement of oxygen from donor into acceptor regions.

The transformation of β-Zn_2SiO_4 *into willemite*

Detailed discussion of this process would demand studies using untwinned β-Zn_2SiO_4 as starting material, and only two aspects will be briefly considered. Firstly, there is no significant change in density. The process therefore involves only a rearrangement of atoms in which no division into donor and acceptor regions need be postulated. Secondly, there is evidence that, as in the previous transformation, the orientation relationship is determined by a tendency for the oxygen packing to change as little as possible. To within 15°, the $(11\bar{2}0)$ plane of the willemite is formed parallel to the (001) plane of the β-Zn_2SiO_4 (Fig. 1). In willemite, there are sheets of oxygen parallel to $(11\bar{2}0)$ (Bragg and Zachariasen, 1930). These are possibly formed from the sheets parallel to (001) in β-Zn_2SiO_4. If the structures are compared in any of the observed relative orientations, it is found that the arrangement of oxygen atoms within the sheets in willemite is very similar to tht suggested here for the sheets in β-Zn_2SiO_4. This provides further evidence for the structure proposed for the latter compound.

These considerations do not explain the 15° difference in angle between (001) of β-Zn_2SiO_4 and $(11\bar{2}0)$ of willemite. Discussion of this problem is postponed until studies using untwinned β-Zn_2SiO_4 have been made.

Comparison with some other oriented transformations

The atomic or ionic movements postulated for the two processes considered here may be compared with those known or believed to occur in topotactic or oriented reactions of some other silicates at 700–1200° C. With calcium or manganese silicates, where the cation is relatively large, there is a strong tendency for the entire cation-oxygen framework to persist relatively unchanged while movements of silicon occur (Taylor, 1960; Dent Glasser and Glasser, 1961). With smaller cations, as Mg^{2+} or Fe^{2+}, the oxygen packing seems to be relatively unaffected, though less so than with the calcium silicates, while movements both of silicon and of the other cations occur (Freeman and Taylor, 1959; Gay and Le Maitre, 1961). Zinc is comparable in size to Mg^{2+} and Fe^{2+}, but is more electronegative and shows a greater tendency to fourfold coordination. The present results suggest that it behaves in much the same way as these other small cations, though it possibly promotes greater mobility of the oxygen atoms.

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