

# Solid solutions between ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ , and thaumasite, $\text{Ca}_3\text{SiSO}_4\text{CO}_3(\text{OH})_6\cdot 12\text{H}_2\text{O}$

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A series of solid solution phases between ettringite,  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ , and thaumasite,  $\text{Ca}_3\text{SiSO}_4\text{CO}_3(\text{OH})_6\cdot 12\text{H}_2\text{O}$ , have been prepared and analysed by X-ray powder diffraction and full pattern fitting. Solid solutions were shown to exist with both the ettringite structure (space group P31c) and the thaumasite structure (space group P6<sub>3</sub>, *c*-axis halved). A possible discontinuity was identified, characterised by a gap in the *a*-dimension of the solid solution phases produced. This discontinuity is believed to correspond to a switch between the ettringite space group and the thaumasite space group. It is suggested that any discontinuity in the solid solution is caused by differences in the hydrogen bonding of the two structures. © 2000 Kluwer Academic Publishers

## 1. Introduction

Ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) and the crystallographically related compound thaumasite ( $\text{Ca}_3\text{SiSO}_4\text{CO}_3(\text{OH})_6\cdot 12\text{H}_2\text{O}$ ) are naturally occurring minerals which also occur in hydrated cements [1–4]. The structure of ettringite was determined by Moore and Taylor [5]. It is trigonal (space group P31c) with  $a = 11.23 \text{ \AA}$ ,  $c = 21.50 \text{ \AA}$  [6]. The structure is based on columns of composition  $\text{Ca}_3[\text{Al}(\text{OH})_6\cdot 12\text{H}_2\text{O}]^{3+}$ , roughly cylindrical in cross-section, running parallel to the *c*-axis. The sulphate ions and remaining water molecules lie in the channels between these columns. Edge and Taylor determined the structure of thaumasite [7]. It is hexagonal (space group P6<sub>3</sub>) with  $a = 11.04 \text{ \AA}$  and  $c = 10.40 \text{ \AA}$ . The structure is very similar to that of ettringite but with  $\text{Si}(\text{OH})_6^{2-}$  replacing  $\text{Al}(\text{OH})_6^{3+}$  in the columns and  $2\text{SO}_4^{2-}$  plus  $2\text{CO}_3^{2-}$  replacing  $3\text{SO}_4^{2-}$  plus  $2\text{H}_2\text{O}$  in the channels. Crystallographically, the column structures are broadly similar, differing in fine structural details. The obvious difference between the two structures is in the ordered arrangement of the intercolumn material. It is this ordering which leads to the halving of the *c*-dimension of the unit cell in thaumasite.

The similarity of the structures is consistent with the formation of solid solutions between ettringite and thaumasite, although the fact that they have different space groups suggests that a discontinuity may exist in the solid solution. Some evidence for the existence of a solid solution between ettringite and thaumasite has been published [8], but it appears that no further investigation of the solid solution has been carried out.

The identification of ettringite, thaumasite and their solid solutions in cementitious systems is problematic,

since few techniques are sensitive to solid solution effects in mixtures. Full pattern fitting [9], a method of X-ray powder diffraction data analysis which employs the whole of the powder pattern, provides a means of characterising these phases in cements. Full pattern fitting is a least squares minimisation technique. A refinable model, which includes the Miller indices of the reflections present in the diffraction pattern, approximate unit cell dimensions, instrumental and sample dependent effects, is used to produce a calculated data set which is then fitted to the experimental data. Intensities, unit cell parameters,  $2\theta$  corrections and peak profile coefficients are adjusted in an iterative procedure until a good fit of observed and calculated data is achieved. This technique can now be used to refine several phases in a mixture simultaneously. An early use of this technique, in which real Portland cement systems were quantified by fitting to standard patterns for the phases present, was made by Gutteridge [10].

## 2. Experimental

Solid solutions between ettringite and thaumasite were prepared by analogy with established methods for the preparation of the ettringite and thaumasite end members [6, 11], using general purpose reagents. The Al : Si and  $\text{SO}_4^{2-} : \text{CO}_3^{2-}$  mole ratios were varied incrementally between the two compositions.

A slurry of calcium oxide in 10% w/w sucrose solution was mixed with a slurry containing varying amounts of sodium aluminate, sodium silicate, sodium sulphate and sodium carbonate in distilled water. With the exception of the ettringite end member, in which the reaction occurs immediately upon mixing, the mixtures were sealed in polythene bottles and stored at 4°C for

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six months. The samples were agitated for eight hours per day throughout the reaction time.

The solids produced were isolated by suction filtration, washed with distilled water followed by acetone, and dried at room temperature. X-ray powder diffraction data was collected using a Philips PW1050 diffractometer with Cu  $K_{\alpha}$  radiation, driven by a Hiltonbrooks control system. Data was collected over the  $5^{\circ}$ – $75^{\circ}$   $2\theta$  range, using a step size of  $0.04^{\circ}$  and a count time of 10s per step. Full pattern fitting was performed using the BESTFIT program developed by Adam [12], with the ICDD standard patterns [13] for ettringite and thaumasite used to provide Miller indices of reflections and approximate unit cell parameters.

### 3. Results

Sections of the X-ray powder diffraction patterns of the ettringite and thaumasite end members and several of their solid solutions are shown in Fig. 1. Samples prepared with Al : Si mole ratios of between 90 : 10 and 30 : 70 produced two ettringite/thaumasite-type phases. Samples prepared with an Al : Si mole ratio of 20 : 80 and lower produced a single thaumasite-type phase. Most samples also produced a very small amount of calcite,  $\text{CaCO}_3$ .

The unit cell parameters produced by full pattern fitting for these phases are shown in Fig. 2. The unit cell parameters of all of the intermediate solid solution phases produced deviate significantly from those of the

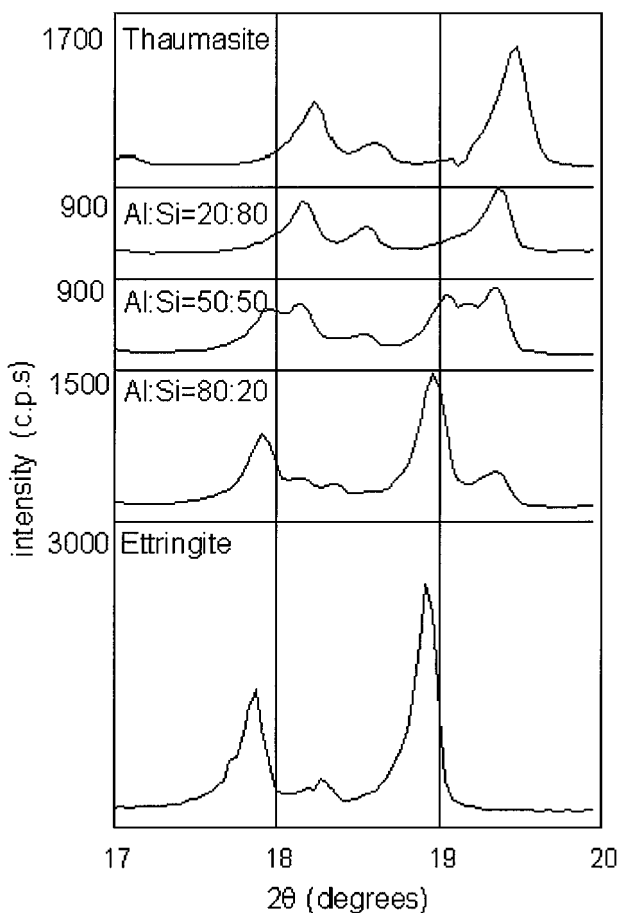


Figure 1 XRPD patterns of ettringite-thaumasite solid solutions. The Al : Si mole ratios used in preparation are shown for the solid solutions.

ettringite and thaumasite end members. Amongst the two-phase systems, both phases (referred to as phases 1 and 2) are apparently solid solutions of ettringite and thaumasite, but the unit cell parameters of phase 1 vary much more than those of phase 2. Phase 1 has unit cell parameters larger than phase 2.

- For samples prepared with Al : Si mole ratios down to 50 : 50, both unit cell dimensions of phase 1 gradually decrease with increasing Si content (Region A in Fig. 2).
- There is a very sudden drop in the  $c$ -dimension of phase 1 between the samples prepared with Al : Si mole ratios of 50 : 50 and 40 : 60 (Region B).
- The  $a$ -dimension of phase 1 drops sharply between the samples prepared with Al : Si mole ratios of 40 : 60 and 30 : 70 (Region C).
- The unit cell dimensions of phase 2 in samples prepared with Al : Si mole ratios down to 30 : 70 are generally slightly larger than those of thaumasite and approach those of the thaumasite end member with increasing Si content (Region D).
- For samples prepared with 80 mole-% Si and above, the unit cell dimensions of the single phase present gradually decrease towards those of the thaumasite end member with increasing Si content (Region E).

A comparison of the  $a$ - and  $c$ -dimensions of ettringite, thaumasite and their solid solutions, shown in Fig. 3, provides further information. This figure suggests a discontinuity in the solid solution, identifiable as a gap in  $a$ -values between  $a \sim 11.11 \text{ \AA}$  and  $a \sim 11.17 \text{ \AA}$ .

### 4. Discussion

Solid solution between ettringite and thaumasite involves the replacement of aluminium by silicon and the partial replacement of sulphate by carbonate. In addition, incorporation of silicon requires an increase in the total sulphate plus carbonate in order to account for the discrepancy in oxidation state. The solid solution is complex and crystallographically involves a change in space group. It is possible that this is a three-way solid solution, in which the Al : Si and  $\text{SO}_4^{2-} : \text{CO}_3^{2-}$  mole ratios are independently variable, or that there is a certain ratio of sulphate : carbonate which must be present for any given Al : Si ratio.

Fig. 4 shows the crystallographic arrangement of the column structures of the ettringite and thaumasite end members. The fine structural differences between ettringite and thaumasite are highlighted by a comparison of the bond lengths in these columns, as determined by Rietveld refinement [14, 15], outlined in Table I. The most noticeable difference between these columns occurs in the Ca-O bond lengths. In the ettringite structure, the Ca-O bonds are generally shorter when the O atom is part of an  $\text{OH}^-$  group than when it is part of a water molecule. However, no such distinction can be made between the Ca-O bond lengths in thaumasite. This effect is clearly revealed when a comparison is made between the average lengths of the two classes of Ca-O bonds in the two structures.

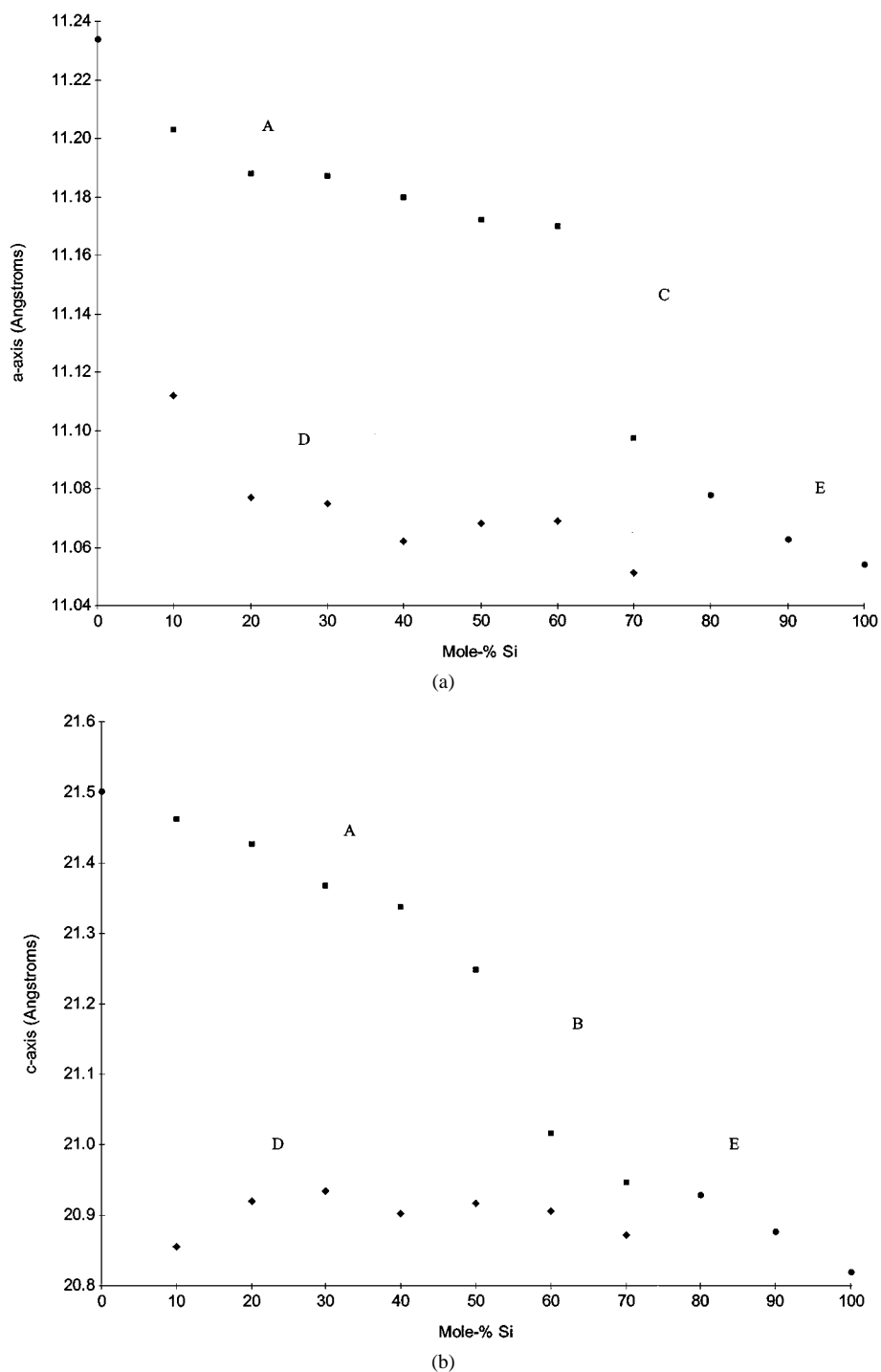


Figure 2 Unit cell parameters of ettringite-thaumasite solid solution series. (a) Unit cell *a*-dimension (b) Unit cell *c*-dimension. Legend: circle-single phase system; square-phase 1 of each 2 phase system; diamond-phase 2 of each 2 phase system. Note: The *c*-axis of the thaumasite-type phases is doubled to aid comparison. Letters A to E identify regions of these plots that are referred to in the text. The horizontal axis shows the mole-% Si of the total Al + Si used in preparation.

There is also evidence that the extent of hydrogen bonding between the O atoms of the OH<sup>-</sup> groups and the surrounding water molecules is different in ettringite and thaumasite. The average distance between the O of OH<sup>-</sup> and the O of water is longer in ettringite than in thaumasite (Table I), indicating stronger hydrogen bonding in the latter mineral.

Finally, it is possible to calculate the approximate diameters of the columns both within phases with ettringite structures and those with thaumasite structures. This has been done for a number of these compounds (Table II) using the atomic co-ordinates (as determined

by Rietveld refinement) of the water molecules that form their edges. All three of the compounds with the ettringite structure (space group P31c) examined have very similar column diameters, at around 8.08 Å. In contrast, the two phases with the thaumasite structure (P6<sub>3</sub>, *c*-axis halved) have column diameters of about 7.76 Å. There is little change in the diameter of the columns when Al or Si are replaced by atoms of larger ionic radii but the same oxidation state (e.g. Al(III) {0.51 Å} by Fe(III) {0.74 Å}, or Si(IV) {0.42 Å} by Mn(IV) {0.60 Å} [16]). This suggests that each of the two space groups tolerate little or no change in

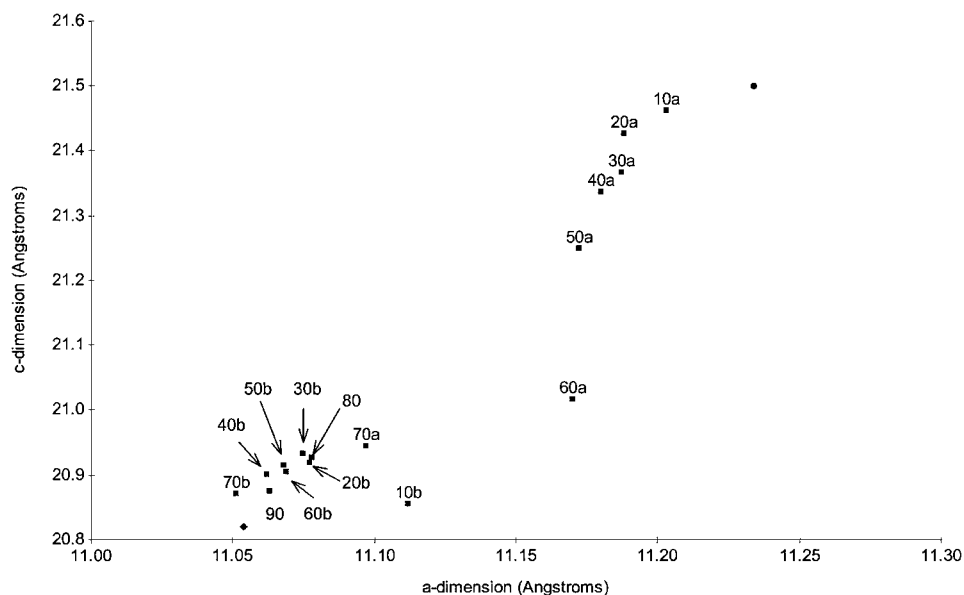


Figure 3 Comparison of unit cell dimensions for ettringite-thaumasite solid solutions. Legend: circle-*ettringite*; diamond-*thaumasite*; square-solid solution phases. Notes: Solid solution phases are labelled according to the mole-% Si (of total Al + Si) used in the preparation. a and b indicate two phases present in the same sample. The *c*-axis of the thaumasite-type phases is doubled to aid comparison.

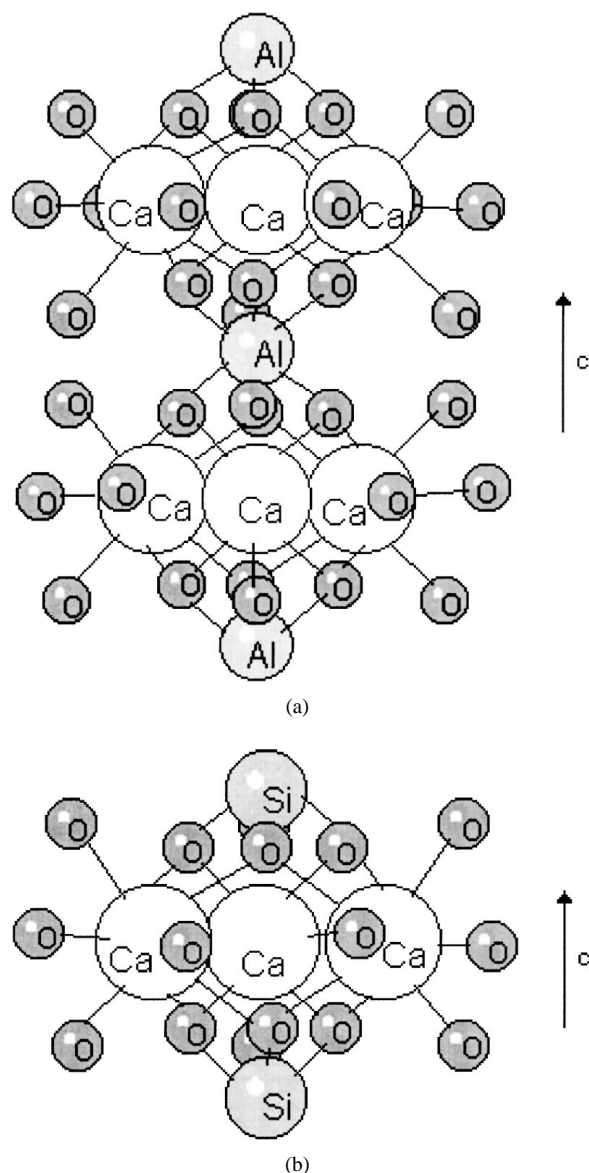


Figure 4 Column structures of ettringite and thaumasite. (a) Ettringite (b) Thaumasite.

the diameter of the columns, possibly as such changes cause concomitant alterations in the degree of hydrogen bonding achievable.

If this argument is extended to the replacement of Si(IV) by Al(III), as occurs in the thaumasite-*ettringite* solid solution, it would predict that only two structural types would exist. One, the thaumasite-type, would have a column diameter approximating to 7.76 Å and a space group of P6<sub>3</sub>, while the other, the *ettringite*-type, would have a column diameter close to 8.08 Å and a space group of P31c. Unfortunately, the extra reflections that are present in the *ettringite* diffraction pattern, when compared with that of thaumasite, are weak and become weaker with increasing carbonate content [14]. This means that differentiation of these two structural types, on the basis of systematic absences is problematic.

A plot allowing a comparison of the unit cell parameters for the solid solutions synthesised is shown in Fig. 3. This shows the *c*-dimension plotted against the *a*-dimension, assuming that all structures have the P31c space group (i.e. the *c*-dimension of the thaumasite-type phases has been doubled to simplify comparison on a single diagram). It is apparent that this provides supporting evidence for the presence of two distinct structural types. The thaumasite-type forms a cluster with *a*-dimensions between ~11.05 and ~11.11 Å, whilst the *ettringite*-type have *a*-dimensions between ~11.17 and 11.23 Å. The presence of a gap in the *a*-dimension between ~11.11 and ~11.17 Å into which no phases fall, strongly indicates that there is not a continuum between these structural types. Furthermore, the vast majority of the mixtures prepared formed two phases, with one of a thaumasite-type, the other an *ettringite*-type, thus supporting the hypothesis that compositions with intermediate structures are not favoured.

Interestingly, as evident from the data presented in Table II, the *a*-dimension is much more sensitive to the carbonate content of the phases than to the diameter

TABLE I Comparison of interatomic distances in ettringite and thaumasite

	Ettringite		Thaumasite	
	Bond	Length (Å)	Bond	Length (Å)
Bonds between Al/Si and O	Al(1)-O(1)	1.98(9)	Si(1)-O(7)	1.78(4)
	Al(1)-O(2)	1.98(10)	Si(1)-O(8)	1.82(4)
	Al(2)-O(3)	1.98(15)		
	Al(2)-O(4)	1.98(13)		
Bonds between Ca and O of OH <sup>-</sup>	Ca(1)-O(1)	2.37(12)	Ca(1)-O(7)	2.57(5)
	Ca(1)-O(1)	2.56(12)	Ca(1)-O(7)	2.54(4)
	Ca(1)-O(3)	2.48(14)	Ca(1)-O(8)	2.39(5)
	Ca(1)-O(3)	2.43(12)	Ca(1)-O(8)	2.51(4)
	Ca(2)-O(2)	2.49(13)		
	Ca(2)-O(2)	2.44(11)		
	Ca(2)-O(4)	2.40(15)		
	Ca(2)-O(4)	2.47(11)		
	Average	2.37(12)	Average	2.50
Bonds between Ca and O of H <sub>2</sub> O	Ca(1)-O(6)	2.53(14)	Ca(1)-O(1)	2.53(21)
	Ca(1)-O(8)	2.49(13)	Ca(1)-O(2)	2.53(27)
	Ca(1)-O(10)	2.59(15)	Ca(1)-O(3)	2.53(5)
	Ca(1)-O(12)	2.72(6)	Ca(1)-O(4)	2.53(5)
	Ca(2)-O(5)	2.35(14)		
	Ca(2)-O(7)	2.77(12)		
	Ca(2)-O(9)	2.64(11)		
	Ca(2)-O(11)	2.91(7)		
	Average	2.63	Average	2.50
Distances between O of OH <sup>-</sup> and O of H <sub>2</sub> O	O(1)-O(5)	3.22	O(7)-O(1)	2.95
	O(1)-O(6)	3.55	O(7)-O(1)	3.05
	O(1)-O(6)	3.31	O(7)-O(1)	3.36
	O(1)-O(10)	2.99	O(7)-O(1)	3.35
	O(1)-O(12)	3.16	O(7)-O(1)	2.91
	O(2)-O(5)	3.48	O(8)-O(1)	3.06
	O(2)-O(5)	3.37	O(8)-O(1)	3.01
	O(2)-O(6)	3.14	O(8)-O(1)	2.95
	O(2)-O(9)	3.11	O(8)-O(1)	3.36
	O(2)-O(11)	3.20	O(8)-O(1)	3.24
	O(3)-O(7)	3.04		
	O(3)-O(8)	3.47		
	O(3)-O(8)	3.45		
	O(3)-O(10)	2.93		
	O(3)-O(12)	3.11		
	O(4)-O(7)	3.39		
	O(4)-O(8)	3.29		
	O(4)-O(9)	3.07		
	O(4)-O(11)	3.03		
		Average	3.23	Average

TABLE II Approximate diameters of column structures

Space Group	Phase	Diameter of Column (Å)	Unit Cell Parameters (Å)		Refs
			<i>a</i>	<i>c</i>	
P31c	Ettringite: Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O	8.07	11.234	21.501	14
	CO <sub>3</sub> -ettringite: Ca <sub>3</sub> Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O	8.07	10.847	21.257	14
	Fe-ettringite: Ca <sub>6</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O	8.11	11.173	22.019	14
P6 <sub>3</sub>	Thaumasite: Ca <sub>3</sub> SiSO <sub>4</sub> CO <sub>3</sub> (OH) <sub>6</sub> ·12H <sub>2</sub> O	7.76	11.054	10.410	15
	Jouravskite: Ca <sub>3</sub> MnSO <sub>4</sub> CO <sub>3</sub> (OH) <sub>6</sub> ·12H <sub>2</sub> O	7.75	11.06	10.60	17

of their columns. The presence of a gap in the  $a$ -dimensions of the members of the ettringite-thaumasite solid solution series (as illustrated by Fig. 3) suggests that a three-way solid solution (with the Al : Si and  $\text{SO}_4^{2-} : \text{CO}_3^{2-}$  ratios being independently variable) does not occur. If it were to occur, variation of the  $\text{SO}_4^{2-} : \text{CO}_3^{2-}$  ratio at a given Al : Si ratio would fill the gap.

## 5. Conclusions

The solid solution between ettringite and thaumasite has been investigated in depth for the first time. Solid solutions have been shown to exist with the ettringite structure (space group P31c) and the thaumasite structure (space group P6<sub>3</sub>,  $c$ -axis halved).

A probable discontinuity in the solid solution, characterised by the gap in the  $a$ -dimensions between  $a \sim 11.11 \text{ \AA}$  and  $a \sim 11.17 \text{ \AA}$ , has been identified. It seems likely that this gap represents a range of compositions in the solid solution series which are unstable, and is believed to correspond to a switch between the ettringite structure and the thaumasite structure. Solid solution phases with a  $c$ -dimension in the range 21–21.2  $\text{\AA}$  can be characterised as thaumasite-type if the  $a$ -dimension is less than  $\sim 11.11 \text{ \AA}$  or as ettringite-type if the  $a$ -dimension is greater than  $\sim 11.17 \text{ \AA}$ .

A comparison of the crystal structures of ettringite and thaumasite, as discussed above, provided a possible explanation for any gap which may exist in the solid solution between ettringite and thaumasite. This comparison highlighted differences in the hydrogen bonding of the two structures and showed that, within each space group, there can be little or no change in the diameter of the column structures with varying Al : Si ratio. Any variation in the  $a$ -dimension would therefore appear to be due to changes in the  $\text{SO}_4^{2-} : \text{CO}_3^{2-}$  ratio.

This work provides clear evidence of the existence of a solid solution between ettringite and thaumasite, and shows that solid solutions exist with both structures. A possible discontinuity has been identified and

explained in terms of the differing crystallography of the two structures. Further work is required in order to determine any range of compositions which are unstable, and to investigate the possibility of a three-way solid solution.

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