speculative only, and the real situation can only be verified from the results of more detailed structural analyses of the *I* phases, using neutron diffraction to help establish the cation ordering. Powder neutron diffraction experiments are currently in progress.

I would like to thank Professor M. A. Alario, Chemistry Department, University of Madrid, for obtaining the electron diffraction patterns shown in Fig. 1 and Dr L. A. Bursill, Physics Department, University of Melbourne, for obtaining preliminary electron diffraction patterns on one of the samples. The careful analytical work of Ms C. Li (wet-chemical analyses) and Mr P. Kelly (microprobe analyses) is much appreciated. Mrs S. Foster and CNRS personnel are kindly thanked for the preparation of the manuscript.

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The Structure of Jasmundite,* $Ca_{22}(SiO_4)_8O_4S_2$

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Abstract

Crystal structure analysis of a new mineral, tentatively named jasmundite, shows that it contains a mixture of orthosilicate, oxide and sulphide ions. The crystals are tetragonal, $I\bar{4}m2$, $a = 10{\cdot}461\,(1)$, $c = 8{\cdot}813\,(1)$ Å, $d_o = 3{\cdot}03$, $d_c = 3{\cdot}23$ Mg m^{-3}; cell content $Ca_{22}(SiO_4)_8O_4S_2$; $R = 0{\cdot}07$ for 637 observed reflexions. Three of the four independent Ca^{2+} ions have irregular octahedral coordination, with four contacts to the orthosilicate groups and two to the O^{2-} or S^{2-} ions. The fourth Ca^{2+} is eight-coordinated by O atoms of the orthosilicate group. The compound is unusual; structures containing a mixture of silicate and S^{2-} ions are rare. It is related to the compound alinite, $Ca_{22}[(Si_{0{\cdot}75}Al_{0{\cdot}25})O_4]_8O_4Cl_2$, which has been reported as a constituent of specialized cement clinkers.

Introduction

A new mineral rich in Ca and Si from Ettringer Feld, a lava flow of the Bellerberg volcano near Mayen, Eifel, was described by Hentschel (1968). Semiquantitative analysis indicated that the CaO:SiO_2 ratio was approximately 2:1, and S expressed as SO_3 was about 4%. It was suggested that the new mineral might be some form of Ca_2SiO_4 containing SO_4 groups. Semi-

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Table 1. *Powder data for jasmundite*

Guinier–Hägg camera, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5407$ Å.

d_o	I_o	hkl	d_c	I_c
7·396	1	110	7·392	2
6·741	1	011	6·740	4
4·405	3	002	4·407	3
4·128	8	121	4·132	7
3·367	1	022	3·370	1
3·306	6	130	3·308	5
3·242	42	031	3·242	42
2·832	>100	222	2·832	160
		013	2·828	13
2·756	17	231	2·756	17
2·645	12	132	2·645	9
2·615	35	040	2·615	38
2·487	6	123	2·488	8
2·437	6	141	2·438	6
2·339	14	240	2·339	14
2·247	14	042	2·249	5
		033	2·247	9
2·202	9	004	2·203	14
2·151	4	332	2·152	1
2·111	6	114	2·112	3
2·068	8, bd	242	2·066	5
2·064		233	2·064	5
2·036	6	051	2·036	5
1·920	16	143	1·920	14
1·896	1	251	1·897	1
1·892	4	224	1·893	4
1·849	34	440	1·849	34
1·795	2	350	1·794	1
1·743	6	060	1·743	7
1·735	3	015	1·738	2
1·706 sh	17	442	1·705	1
1·704		053	1·704	14
1·6844	13	044	1·6850	16
1·6542	3	260	1·6540	6
1·6433	2	334	1·6429	2
1·6205	10	062	1·6212	3
		253	1·6203	11
1·6038	4	244	1·6038	3
1·5732	3	035	1·5731	4
1·5491	21	262	1·5485	24
1·5067	6	235	1·5064	7
1·4840	3	163	1·4841	4
1·4734	1	071	1·4734	2
1·4690	3	006	1·4690	5
1·4477	2	145	1·4476	2
1·4278	3	453	1·4278	4
1·4186	7 bd	271	1·4182	4
1·4168	8	444	1·4164	4
1·4029	2	552	1·4025	2
1·3914	2	354	1·3912	2
1·3782	1	462	1·3779	<1
1·3676	2, bd	064	1·3672	1
		226	1·3651	2
1·3489	2	345	1·3480	2
1·3220	1, bd	073	1·3320	1
1·3121	2	372	1·3113	2
1·3085	5	080	1·3076	5
1·2851	2	471	1·2837	2
1·2702	1	280	1·2686	1
1·2551	1	082	1·2536	1

Notes: bd = broad, sh = shoulder. d_o, I_o measured with microdensitometer. Mean of two films, one with internal standard, one with external standard photographed on same film: the differences were barely significant. Indices assigned from calculated intensities: d_c based on cell from least-squares fit: $a = 10{\cdot}461$, $c = 8{\cdot}813 \pm 0{\cdot}001$ Å.

quantitative analyses made in conjunction with the present study with an analytical transmission electron microscope (CORA) and microprobe confirmed the presence of S, and showed that the CaO/SiO_2 ratio was between 2·25 and 2·91. As the quantity of sample available was too small for a full chemical analysis, the cell content was determined by crystal structure analysis. The crystal data are given in the *Abstract* [also $\omega = 1{\cdot}75$, $\varepsilon = 1{\cdot}728$ (Hentschel, 1968)], and indexed powder data in Table 1.

Crystal structure analysis subsequently suggested that the S might be present as S^{2-}. A crystal in contact with lead acetate paper was treated with dilute HCl; a smell of H_2S was noticed, and the lead acetate paper was stained brown.

Dr Hentschel, who kindly provided our sample, has suggested the name jasmundite for this mineral, after Professor Dr Karl Jasmund, Director of the Mineralogical–Petrographic Institute of the University of Cologne, in recognition of his work on these rocks. The mineral and name have been submitted to the International Mineralogical Association Commission on New Minerals and Mineral Names.

Experimental

The crystals did not appear tetragonal when viewed under the optical microscope. Neither (*hk*0) nor (00*l*) planes were apparent; instead, development of the (101) face gave the impression that the crystals might be rhombohedral. Because of this unexpected morphology, setting the crystal about a symmetry axis proved difficult, but when this was achieved the tetragonal symmetry was revealed. The crystal selected for intensity measurements was a typical triangular plate, with the longest edge about 0·5 mm.

Intensities were collected on a Hilger & Watts Y190 automatic linear diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The crystal was rotated about **c**, and reflexions in one half of reciprocal space up to $l = 10$ were measured. This gave 2363 reflexions not systematically absent. The data were not of high accuracy, partly due to the peculiar morphology of the crystal. An empirical absorption correction (North, Phillips & Mathews, 1968) and layer scaling were later applied. Agreement between equivalent reflexions was fair after correction for absorption, and after averaging these, 862 reflexions remained, of which 709 were observed and 153 unobserved.

Calculations were made on a Honeywell computer, mainly with programs supplied by Dr F. R. Ahmed and collaborators of the National Research Council of Canada, and adapted for use on this machine by Dr R. A. Howie of the Department of Chemistry, University of Aberdeen. Scattering-factor curves for Ca^{2+}, Si, O^{2-} and S^{2-} were taken from *International Tables for X-ray Crystallography* (1962); for O attached to Si, values for O^- (Ahmed & Dent Glasser, 1970) were used.

Structure determination

Approximate positions for 20 Ca, 8 Si and 32 O atoms in the space group $I\bar{4}m2$ were determined from a Patterson synthesis. The initial positions were refined by least squares (block-diagonal) with the entire data and isotropic temperature factors. An electron-density map then revealed the positions of O^{2-} and the remaining Ca^{2+} ions, and a Ca atom that had originally been placed at the origin was replaced by a S atom. The structure was refined by least squares with isotropic temperature factors with a weighting scheme $w = \{1 + [(|F_o| - P_2)/P_1]^2\}^{-1}$ with P_1 and P_2 adjusted by trial and error to give a reasonable distribution of $\sum w\Delta^2/n$. Reflexions for which $\Delta F/F_o > 0{\cdot}30$ were omitted from the least-squares calculations. R refined to 0·09 for 610 of the 709 observed reflexions.

On the assumption that the S was present as sulphate, the electron-density and difference maps were searched in the region about the origin. No peaks were found, and all attempts to place four O atoms in a suitable tetrahedron failed; refinement gave either improbably high temperature factors or occupancy factors that tended to zero. It was concluded that the S

Table 2. *Final fractional coordinates and isotropic temperature factors* (Å^2)

E.s.d.'s in least significant digits are given in parentheses.

	x	y	z	B_{iso}
Ca(1)	0·2437 (2)	0	0·1960 (2)	1·13 (2)
Ca(2)	0·2583 (2)	0	0·7911 (2)	1·14 (3)
Ca(3)	$\frac{1}{2}$	0	0·0032 (4)	0·79 (2)
Ca(4)	$\frac{1}{2}$	$\frac{1}{2}$	0	0·55 (3)
Si	0·2116 (2)	0·2116 (2)	$\frac{1}{2}$	0·46 (2)
O(1)	0·1446 (5)	0·1457 (5)	0·3523 (3)	0·78 (5)
O(2)	0·3648 (3)	0·1795 (3)	0·5062 (7)	0·68 (5)
O(3)	0	$\frac{1}{2}$	$\frac{1}{4}$	2·4 (4)
O(4)	0	$\frac{1}{2}$	$\frac{3}{4}$	0·7 (2)
S	0	0	0	1·36 (5)

Table 3. *Interatomic distances* (Å) *and angles* (°)

Figures in parentheses correspond to the e.s.d. of the least significant digit. O(3), O(4) denote oxide ions.

(*A*) Si–O tetrahedra

Si–O(1) ×2	1·631 (4)	Si–O(2) ×2	1·638 (5)
O(1)–Si–O(1)	105·9 (3)	O(1)–Si–O(2)	107·4 (3)
O(1)–Si–O(2)	111·1 (3)	O(2)–Si–O(2)	113·7 (3)

(*B*) Calcium–anion polyhedra (idealized angles in square brackets)

(*a*) Ca(1)

Ca(1)–O(1) ×2	2·301 (5)	Ca(1)–O(4)	2·723 (1)
Ca(1)–O(2) ×2	2·413 (6)	Ca(1)–S	3·079 (1)

O–Ca(1)–O,S	71·8 (2)–109·8 (1)	[90]
O–Ca(1)–O,S	155·9 (1)–168·6 (2)	[180]

(*b*) Ca(2)

Ca(2)–O(1) ×2	2·296 (5)	Ca(2)–O(3)	2·554 (2)
Ca(2)–O(2) ×2	2·370 (6)	Ca(2)–S	3·270 (2)

O–Ca(2)–O,S	73·3 (2)–115·5 (1)	[90]
O–Ca(2)–O,S	153·9 (1)–161·6 (2)	[180]

(*c*) Ca(3)

Ca(3)–O(2) ×4	2·352 (4)	Ca(3)–O(4)	2·175 (4)
Ca(3)–O(3)	2·231 (4)		

O–Ca(3)–O	73·9 (2)–105·9 (2)	[90]
O–Ca(3)–O	176·0 (2)–180·0 (1)	[180]

(*d*) Ca(4)

Ca(4)–O(1) ×8	2·511 (5)

O–Ca(4)–O	62·5 (2)– 74·7 (2)	[70·53]
O–Ca(4)–O	105·6 (2)–117·6 (2)	[109·5]
O–Ca(4)–O	179·5 (2)	[180]

is present not as a sulphate group but as a S^{2-} ion, and this was subsequently confirmed by a qualitative chemical test.

At this stage absorption corrections and layer scaling were applied, and R refined to 0·07 for 637 observed reflexions.* The final coordinates are given in Table 2. The temperature factors vary more than one would wish, probably as a result of the rather poor data. Bond lengths and angles (Table 3) are all reasonable.

With slight adjustments the structure also fits space groups $I\bar{4}2m$ and $I4/mmm$, and it was refined in these too, giving $R = 0{\cdot}08$ and 0·09 respectively. The original choice of $I\bar{4}m2$ thus appears to be correct.

Description of the structure

Fig. 1 shows an overall view of the structure.

The Si atoms are tetrahedrally coordinated by O(1) and O(2): bond lengths and angles are normal. Both O atoms are also in contact with three Ca^{2+} atoms, giving them approximately tetrahedral environments.

Ca(1), Ca(2) and Ca(3) all have irregular octahedral coordination, with O–Ca–O,S angles ranging from 71·8 to 115·5° and from 159 to 180°, compared with 90 and 180° respectively in a regular octahedron. Fig. 2 shows the relationship of these octahedra. Ca(1) and Ca(2) are each coordinated by two O(1) and two O(2) atoms of the silicate tetrahedra, one O^{2-} ion [O(4) and O(3) respectively] and one S^{2-} ion (Fig. 2*a*). These octahedra share the S–O(2)–O(2) face to form pairs, and the pairs form fourfold clusters (eight octahedra in

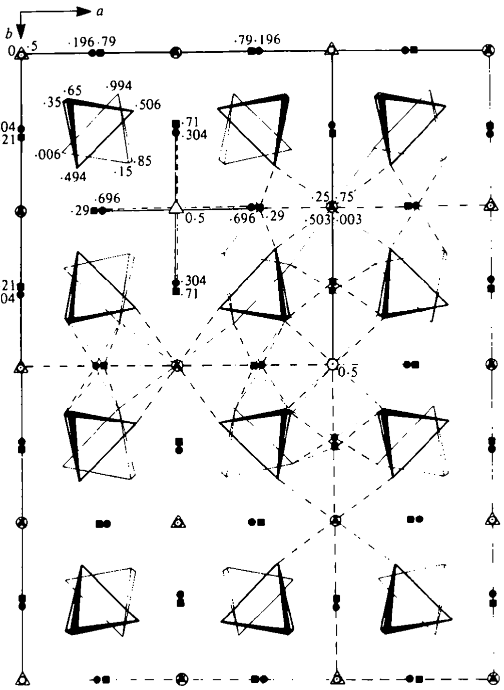

Fig. 1. Structure of jasmundite projected down **c**; heights are in z/c. O(1) and O(2) are at the corners of the silicate tetrahe .ra. Some S and Ca(4) are omitted to show the coordination of the atoms beneath more clearly. The coordination of Ca(3) at height 0·503 is shown alone in the lower right-hand corner. ● Ca(1), ■ Ca(2), ▲ Ca(3), ○ Ca(4), △ S, ⊗ O(3,4).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35877 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

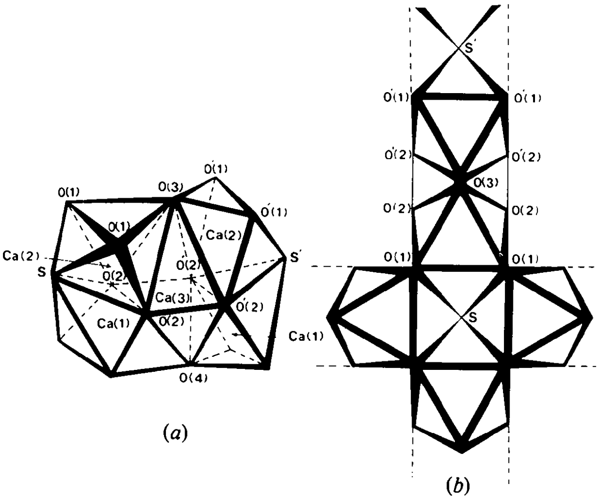

Fig. 2. (*a*) Side view (along **a** or **b**) of two pairs of Ca(1)–Ca(2) octahedra, showing how the Ca(3) octahedron fits between them, sharing a face with each adjacent octahedron. (*b*) Top view (down **c**) of a cluster of four pairs of Ca(1)–Ca(2) octahedra centred on a S atom. The upper part of the diagram shows the complete top view of (*a*).

all) related by the fourfold inversion axis centred on the S atom, and sharing S—O(1) edges (Fig. 2*b*). Each pair is further associated with three other Ca(1)–Ca(2) pairs through the $\bar{4}$ axes centred on the oxide ions O(3) and O(4); Fig. 2(*a*) shows two of these. Ca(3) is located between two pairs, in a distorted octahedron consisting of the O(2)–O(2) edges of the pairs and the O(3) and O(4) ions. The Ca(3) octahedron thus shares a face with each of the four adjacent octahedra. Ca(4), in contrast, is eight-coordinated, by O(1). The structure obeys Pauling's electrostatic valency rule reasonably well.

Comparison with other structures

The combination of sulphide and silicate ions in the same structure is interesting and unusual, although not unknown; it is generally supposed to occur in ultramarine. The structure analysis seems to have established it in the present case, and the occurrence of the mineral in conjunction with sulphide-bearing species such as pyrites is consistent with this.

$Ca_2SiO_3Cl_2$ (Golovastikov & Kazak, 1977) has a cell similar to that of jasmundite: a = 10·698, c = 9·345 Å, $I4$, Z = 8. However, its structure is quite different, the Ca^{2+} atoms being coordinated by four O atoms and three Cl^- ions forming a seven-cornered polyhedron, and the silicate tetrahedra sharing corners to form rings between the Ca layers.

The structure of jasmundite is closely related to that of alinite, $Ca_{22}(Si_{0.75}Al_{0.25})_8O_{36}Cl_2$ (Ilyukhin, Nevosky, Bickbau & Howie, 1977), which is described in the space group $I\bar{4}2m$. In alinite partial occupancy of the Si position by Al is required for charge balance. In jasmundite, with S instead of Cl, there is no such requirement. The origin in jasmundite is shifted by $c/2$ from that given for alinite.

Alinite has been reported to occur in specialized chloride-containing cement clinkers. It therefore seemed possible that jasmundite might also prove to occur in cement clinker. Sulphate, derived either from the raw materials or from the fuel, normally occurs in clinker kilns, and under suitably reducing conditions sufficient sulphide might be present for jasmundite to form. Although we have examined several such samples without detecting jasmundite, the possibility of its formation may well be of interest to cement technology.

We thank Dr E. Lachowski of this department for the CORA analyses, and Mr G. Taylor of the Department of Geology, University of Aberdeen, for the microprobe analyses, and the late Mr B. G. Cooksley for collecting the intensities.

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