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The crystal structure of stellerite (1)

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Abstract. — The crystal structure of the zeolite stellerite has been studied by X-ray methods : space group *Fmmm* with $a = 13.599$, $b = 18.222$, $c = 17.863$ (Å). The framework of stellerite is topologically the same as stilbite ; its content of exchangeable cations allows the highest symmetry compatible with the framework. An explanation is given for the lower, monoclinic, symmetry of the structure of stilbite.

Structure cristalline de la stellerite.

Résumé. — La structure cristalline de la zéolite « stellerite » a été étudiée par les méthodes de diffraction des rayons X : le groupe spatial est *Fmmm* avec $a = 13{,}599$, $b = 18{,}222$, $c = 17{,}863$ (Å). La charpente de la stellerite est identique à celle de la stilbite ; son contenu en ions échangeables permet la symétrie la plus haute compatible avec la charpente. On explique en outre la symétrie inférieure rencontrée dans la stilbite monoclinique.

INTRODUCTION.

A résumé on the mineral species stellerite was given a short time ago by Galli and Passaglia (1973), when describing a new occurence of this zeolite at Villanova-Monteleone, Sardinia. Orthorhombic stellerite was known to have probably the same framework as monoclinic stilbite (Galli and Gottardi, 1966), the two minerals being similar from many aspects but with different symmetries. The aim of this research is to establish whether there is topological equivalence of the two frameworks and, if so, to ascertain the structural reasons for the existence of two different symmetries in zeolites with the same framework.

EXPERIMENTAL.

The above mentioned sample of stellerite from Sardinia (Galli and Passaglia, 1973) was used in this study. A lamellar crystal (0.32 × 0.36 × 0.80 mm) was X-rayed by Ni-filtered Cu-radiation ; intensities were collected with a two-circle (Weissenberg-type) automated diffractometer STOE STADI II. The crystal was rotated around its *a* axis and intensity data were collected for reciprocal lattice levels from $h = 0$ to $h = 8$. Altogether, 843 independent diffractions were measured, representing nearly 65 % of the possible diffraction in the Cu-Kα sphere. Of these, 10 diffractions with $I \leqslant 2\sigma(I)$ were assumed to have been not observed. The space group was confirmed as *Fmmm* ; the lattice parameters here used are $a = 13.599$ (4), $b = 18.222$ (4), $c = 17.863$ (3) (all Å, errors in brackets) as from the previous work. An absorption correction was calculated by the Alberti and Gottardi (1966) method. The unit cell content is :

$$(Ca_{7.56}Mg_{0.06}Sr_{0.02}Na_{0.34}K_{0.28})_{tot.=8.26}$$
$$[(Al_{15.86}Fe_{0.12})_{tot.=15.98}Si_{56.04}O_{144}] \cdot 56.20\ H_2O$$

REFINEMENT.

At first a least-squares refinement was carried out using as starting coordinates of Si, O and Ca those obtained by averaging the monoclinic values of the symmetrically related pairs given for stilbite by Galli (1971). The speedy convergence down to an $R \simeq 17$ % was considered as a proof that the stilbite framework is present in stellerite too. Further refinement was conducted as a combination of three dimensional electron density syntheses (to locate water molecules) and least-squares techniques.

Atomic scattering factors given by Hanson *et al.*, (1964) for neutral atoms were used throughout ; for the exchangeable cations an average curve was obtained considering all the elements detected by the chemical analysis, each with its own weight, as follows : Ca 91.5 %, Mg 0.7 %, Sr 0.2 %, Na 4.1 %, K 3.4 %.

The use of anisotropic temperature factors lead

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to a final residual R = 0.078 and a final weighted residual R = 0.082 (in both cases considering also non observed diffraction). Atomic parameters are listed in Table I, interatomic distances and angles in Tables II and III. The structure is illustrated in Fig. 1 as a projection along *b*. The pairs of atoms Si(1)-Si(2), O(1)-O(2), O(3)-O(5) and O(4)-O(6) independent in stilbite, are symmetrically related in stellerite and are indicated as Si(1), O(1), O(3) and O(4). All crystallochemical results obtained from this refinement are in good agreement with the chemical analysis so the total number of water molecules is 55.52 well in accordance with the 56.20 given by thermogravimetry, the total number of cations is 8.00 against 8.26 from the analysis. During the initial least-squares refinement the occupancy factors of W(1) and W(7) showed very strong variations; considering the values obtained up to this point, and the possible distances with nearby water molecules, in the last cycles of refinement the occupancies of W(1) and W(7) were fixed at 20 %. On the contrary no limit was set to the occupancy factors of W(5) and W(6), whose distance is only 1.33 Å and hence the sum of their occupancy factors should not exceed 100 %; the actual value is 105 %, but we left it unchanged since the surplus of occupancy is less than its standard error.

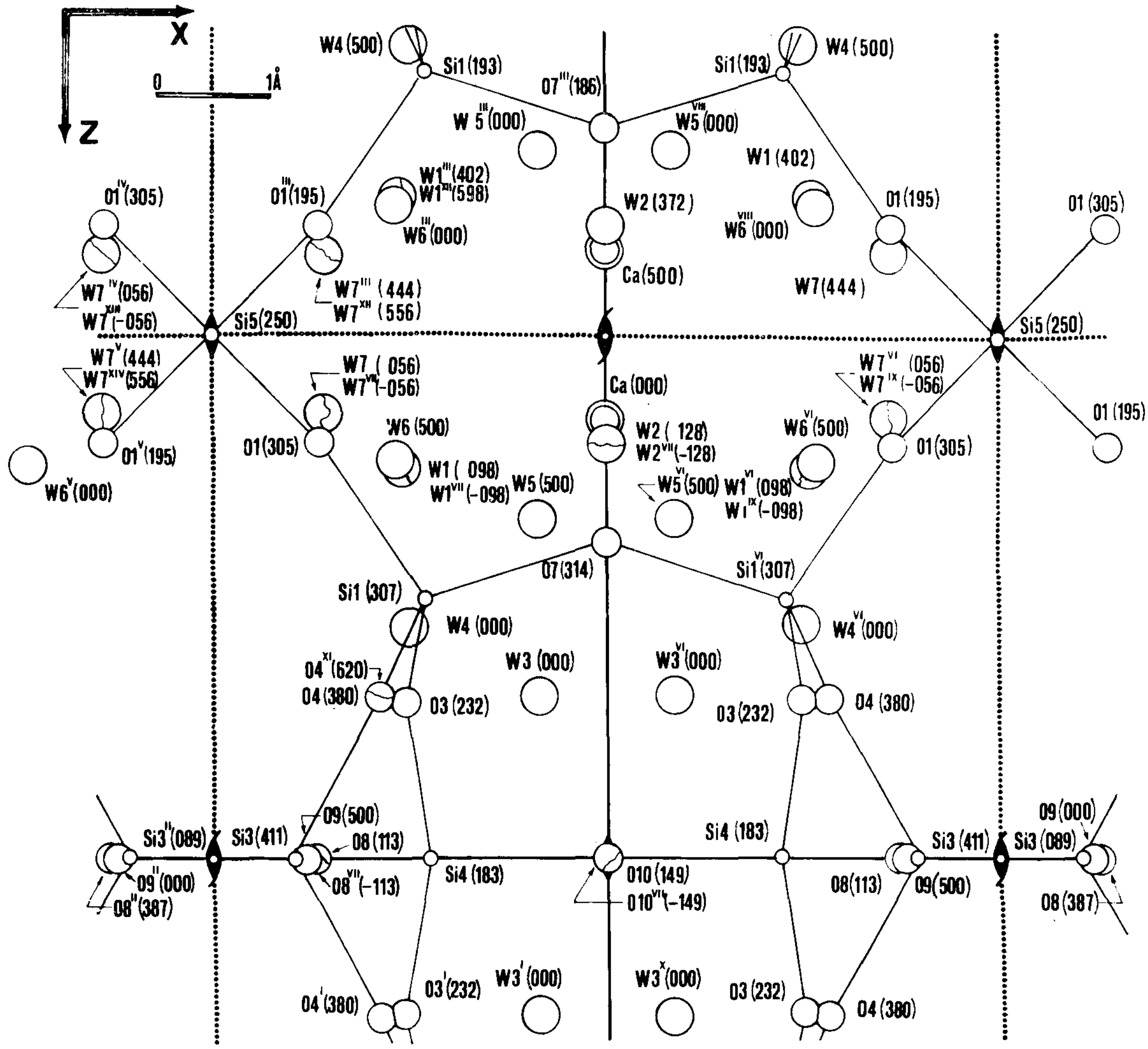

FIG. 1. — Part of the structure of stellerite projected along *b*. Codes of atoms are given as from Table II. Three digit numbers in parentheses give the height above the plane y = 0 as permillage of *b*. The part here shown is the grey area of Fig. 2.

During the refinement some tests were performed to ascertain any possible deviation from the orthorhombic symmetry within the limits of errors of the available experimental data. One point should be specially mentioned here, that is the anisotropic temperature factors of atoms located on the mirror planes. If the symmetry was not exactly orthorhombic, these atoms would lie with their gravity center at a small but definite distance from mirror planes; in such circumstances the least-squares refinement, constrained to locate

TABLE I.

Atomic coordinates, thermal parameters ($\beta_{ij} \times 10^4$) and occupancy factors, with their standard errors.

The form of the anisotropic temperature factors is exp $(-h^2\beta_{11}-k^2\beta_{22}-l^2\beta_{33}-2hk\beta_{12}-2hl\beta_{13}-2kl\beta_{23}.)$

ATOM	*x*/*a*	*y*/*b*	*z*/*c*	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	OCCUPANCY (%)
Si (1)	.3857 (2)	.3072 (1)	.3769 (1)	7 (2)	6 (1)	8 (1)	— 1 (1)	— 3 (1)	0 (1)	100
Si (3)	.3013 (3)	.4112 (1)	1/2	12 (3)	2 (1)	11 (1)	1 (1)	0	0	100
Si (4)	.3883 (3)	.1833 (1)	1/2	11 (4)	5 (1)	8 (1)	1 (1)	0	0	100
Si (5)	1/4	1/4	1/4	5 (4)	12 (1)	9 (1)	0	0	0	100
O (1)	.3175 (6)	.3046 (3)	.3018 (3)	26 (6)	21 (2)	21 (2)	6 (3)	— 17 (3)	— 5 (1)	100
O (3)	.3721 (6)	.2321 (3)	.4251 (3)	49 (6)	19 (2)	24 (2)	2 (3)	— 8 (3)	— 14 (2)	100
O (4)	.3577 (6)	.3802 (3)	.4239 (3)	41 (6)	17 (2)	26 (2)	— 2 (3)	6 (3)	8 (2)	100
O (7)	1/2	.3141 (4)	.3493 (5)	4 (1)	23 (3)	23 (3)	0	0	— 3 (2)	100
O (8)	.3135 (8)	.1129 (4)	1/2	21 (9)	16 (2)	27 (3)	10 (4)	0	0	100
O (9)	.3100 (11)	1/2	1/2	45 (12)	7 (3)	24 (4)	0	0	0	100
O (10)	1/2	.1495 (6)	1/2	25 (13)	16 (3)	19 (4)	0	0	0	100
Ca	1/2	0	.2910 (2)	73 (5)	15 (1)	18 (1)	0	0	0	100
W (1)	.395 (3)	.098 (2)	.313 (2)	4.9 (8)						20
W (2)	1/2	.128 (1)	.303 (1)	7.8 (7)						80 (4)
W (3)	.459 (2)	0	.423 (1)	3.3 (8)						37 (3)
W (4)	.376 (5)	0	.390 (3)	13.0 (24)						45 (5)
W (5)	.459 (2)	1/2	.339 (1)	4.5 (9)						43 (4)
W (6)	.368 (3)	1/2	.312 (2)	10.8 (15)						62 (5)
W (7)	.321 (5)	.056 (3)	.288 (3)	9.1 (14)						20

TABLE II.

Interatomic distances (Å) and angles (°) within the framework, with their standard errors in parentheses.

Interatomic distances and bond angles symmetrically equivalent are bracketed.

The superscripts refer to the symmetry code

	x	*y*	*z*
I	*x*	*y*	1 — *z*
II	1/2 — *x*	1/2 — *y*	1 — *z*
III	*x*	1/2 — *y*	1/2 — *z*
IV	1/2 — *x*	*y*	1/2 — *z*
V	1/2 — *x*	1/2 — *y*	*z*
VI	1 — *x*	*y*	*z*
VII	*x*	— *y*	*z*
VIII	1 — *x*	1/2 — *y*	1/2 — *z*
IX	1 — *x*	— *y*	*z*
X	1 — *x*	*y*	1 — *z*
XI	*x*	1 — *y*	*z*
XII	*x*	1/2 + *y*	1/2 — *z*
XIII	1/2 — *x*	— *y*	1/2 — *z*
XIV	1/2 — *x*	1/2 + *y*	*z*

Si (1) *tetrahedron*

Si (1)-O (1)	1.63 (1) Å
Si (1)-O (3)	1.63 (1)
Si (1)-O (4)	1.62 (1)
Si (1)-O (7)	1.64 (1)
Average	1.63
O (1)-O (3)	2.68 (1)
O (1)-O (4)	2.64 (1)
O (1)-O (7)	2.63 (1)
O (3)-O (4)	2.71 (1)
O (3)-O (7)	2.66 (1)
O (4)-O (7)	2.64 (1)
O (1)-Si (1)-O (3)	110.3 (3)°
O (1)-Si (1)-O (4)	108.5 (4)
O (1)-Si (1)-O (7)	107.1 (4)
O (3)-Si (1)-O (4)	112.9 (3)
O (3)-Si (1)-O (7)	109.4 (4)
O (4)-Si (1)-O (7)	108.4 (4)

Si (4) *tetrahedron*

Si (4)-O (3)	1.62 (1)
Si (4)-O (3)$^{\mathrm{I}}$	
Si (4)-O (8)	1.64 (1)
Si (4)-O (10)	1.64 (1)
Average	1.63
O (3)-O (3)$^{\mathrm{I}}$	2.67 (1)
O (3)-O (8)	2.67 (1)
O (3)$^{\mathrm{I}}$-O (8)	
O (3)-O (10)	2.66 (1)
O (3)$^{\mathrm{I}}$-O (10)	
O (8)-O (10)	2.62 (1)
O (3)-Si (4)-O (3)$^{\mathrm{I}}$	111.2 (5)
O (3)-Si (4)-O (8)	110.2 (3)
O (3)$^{\mathrm{I}}$-Si (4)-O (8)	
O (3)-Si (4)-O (10)	109.4 (4)
O (3)$^{\mathrm{I}}$-Si (4)-O (10)	
O (8)-Si (4)-O (10)	106.3 (5)

Si (3) *tetrahedron*

Si (3)-O (4)	1.66 (1)
Si (3)-O (4)$^{\mathrm{I}}$	
Si (3)-O (8)$^{\mathrm{II}}$	1.62 (1)
Si (3)-O (9)	1.62 (1)
Average	1.64
O (4)-O (4)$^{\mathrm{I}}$	2.72 (1)
O (4)-O (8)$^{\mathrm{II}}$	2.70 (1)
O (4)$^{\mathrm{I}}$-O (8)$^{\mathrm{II}}$	
O (4)-O (9)	2.65 (1)
O (4)$^{\mathrm{I}}$-O (9)	
O (8)$^{\mathrm{II}}$-O (9)	2.66 (1)
O (4)-Si (3)-O (4)$^{\mathrm{I}}$	109.9 (5)
O (4)-Si (3)-O (8)$^{\mathrm{II}}$	110.6 (3)
O (4)$^{\mathrm{I}}$-Si (3)-O (8)$^{\mathrm{II}}$	
O (4)-Si (3)-O (9)	107.8 (4)
O (4)$^{\mathrm{I}}$-Si (3)-O (9)	
O (8)$^{\mathrm{II}}$-Si (3)-O (9)	109.9 (6)

Si (5) *tetrahedron*

Si (5)-O (1)	1.64 (1)
Si (5)-O (1)$^{\mathrm{III}}$	
Si (5)-O (1)$^{\mathrm{IV}}$	
Si (5)-O (1)$^{\mathrm{V}}$	
Average	1.64
O (1)-O (1)$^{\mathrm{III}}$	2.72 (1)
O (1)$^{\mathrm{IV}}$-O (1)$^{\mathrm{V}}$	
O (1)-O (1)$^{\mathrm{IV}}$	2.61 (1)
O (1)$^{\mathrm{III}}$-O (1)$^{\mathrm{V}}$	
O (1)-O (1)$^{\mathrm{V}}$	2.71 (1)
O (1)$^{\mathrm{III}}$-O (1)$^{\mathrm{IV}}$	
O (1)-Si (5)-O (1)$^{\mathrm{III}}$	111.9 (5)
O (1)$^{\mathrm{IV}}$-Si (5)-O (1)$^{\mathrm{V}}$	
O (1)-Si (5)-O (1)$^{\mathrm{IV}}$	105.3 (4)
O (1)$^{\mathrm{III}}$-Si (5)-O (1)$^{\mathrm{V}}$	
O (1)-Si (5)-O (1)$^{\mathrm{V}}$	111.3 (4)
O (1)$^{\mathrm{III}}$-Si (5)-O (1)$^{\mathrm{IV}}$	

Si (1)-O (7)-Si (1)$^{\mathrm{VI}}$	143.7 (6)°
Si (1)-O (4)-Si (3)	144.4 (4)
Si (1)-O (3)-Si (4)	151.9 (4)
Si (1)-O (1)-Si (5)	143.1 (4)
Si (3)$^{\mathrm{II}}$-O (8)-Si (4)	144.2 (6)

TABLE III.

Cation, oxygen and water molecule distances (Å) less than 3.30.

Ca-W (1)	2.32 (4)
Ca-W (1)$^{\mathrm{VI}}$	
Ca-W (1)$^{\mathrm{VII}}$	
Ca-W (1)$^{\mathrm{IX}}$	
Ca-W (2)	2.34 (2)
Ca-W (2)$^{\mathrm{VII}}$	
Ca-W (3)	2.42 (2)
Ca-W (3)$^{\mathrm{VI}}$	
Ca-W (4)	2.44 (5)
Ca-W (4)$^{\mathrm{VI}}$	
Ca-W (5)$^{\mathrm{III}}$	2.39 (2)
Ca-W (5)$^{\mathrm{VIII}}$	
Ca-W (6)$^{\mathrm{III}}$	2.56 (4)
Ca-W (6)$^{\mathrm{VIII}}$	
Ca-W (7)	2.64 (6)
Ca-W (7)$^{\mathrm{VI}}$	
Ca-W (7)$^{\mathrm{VII}}$	
Ca-W (7)$^{\mathrm{IX}}$	
W (1)-O (1)$^{\mathrm{III}}$	2.91 (4)
W (1)-O (3)	3.17 (4)
W (1)-W (1)$^{\mathrm{VI}}$	2.85 (9)
W (1)-W (2)	1.54 (4)
W (1)-W (3)	2.80 (4)
W (1)-W (4)	2.27 (5)
W (1)-W (6)$^{\mathrm{III}}$	2.88 (4)
W (1)-W (7)	1.34 (6)
W (1)-W (7)$^{\mathrm{VII}}$	3.02 (7)
W (2)-O (7)$^{\mathrm{III}}$	2.92 (2)
W (2)-W (1)	1.54 (4)
W (2)-W (1)$^{\mathrm{VI}}$	
W (2)-W (3)	3.21 (2)
W (2)-W (3)$^{\mathrm{VI}}$	
W (2)-W (4)	3.27 (4)
W (2)-W (4)$^{\mathrm{VI}}$	
W (2)-W (7)	2.77 (6)
W (2)-W (7)$^{\mathrm{VI}}$	
W (3)-O (8)	3.17 (2)
W (3)-O (8)$^{\mathrm{VII}}$	
W (3)-O (10)	3.10 (2)
W (3)-O (10)$^{\mathrm{VII}}$	
W (3)-W (1)	2.80 (4)
W (3)-W (1)$^{\mathrm{VII}}$	
W (3)-W (2)	3.21 (2)
W (3)-W (2)$^{\mathrm{VII}}$	
W (3)-W (3)$^{\mathrm{I}}$	2.76 (5)
W (3)-W (3)$^{\mathrm{VI}}$	1.10 (6)
W (3)-W (3)$^{\mathrm{X}}$	2.97 (5)
W (3)-W (4)	1.28 (6)
W (3)-W (4)$^{\mathrm{VI}}$	2.31 (8)
W (3)-W (7)	3.22 (6)
W (3)-W (7)$^{\mathrm{VII}}$	
W (4)-O (8)	2.97 (4)
W (4)-O (8)$^{\mathrm{VII}}$	
W (4)-O (9)$^{\mathrm{II}}$	3.20 (6)
W (4)-W (1)	2.27 (5)
W (4)-W (1)$^{\mathrm{VII}}$	
W (4)-W (2)	3.27 (4)
W (4)-W (2)$^{\mathrm{VII}}$	
W (4)-W (3)	1.28 (6)
W (4)-W (3)$^{\mathrm{VI}}$	2.31 (8)
W (4)-W (7)	2.22 (7)
W (4)-W (7)$^{\mathrm{VII}}$	
W (5)-O (4)	2.99 (2)
W (5)-O (4)$^{\mathrm{XI}}$	
W (5)-W (5)$^{\mathrm{VI}}$	1.11 (6)
W (5)-W (6)	1.33 (4)
W (5)-W (6)$^{\mathrm{VI}}$	2.40 (6)
W (5)-W (7)$^{\mathrm{III}}$	3.11 (6)
W (5)-W (7)$^{\mathrm{XII}}$	
W (6)-O (4)	2.97 (2)
W (6)-O (4)$^{\mathrm{XI}}$	
W (6)-W (1)$^{\mathrm{III}}$	2.88 (4)
W (6)-W (1)$^{\mathrm{XII}}$	
W (6)-W (5)	1.33 (4)
W (6)-W (5)$^{\mathrm{VI}}$	2.40 (6)
W (6)-W (7)$^{\mathrm{III}}$	2.15 (6)
W (6)-W (7)$^{\mathrm{XII}}$	
W (6)-W (7)$^{\mathrm{V}}$	2.81 (7)
W (6)-W (7)$^{\mathrm{XIV}}$	
W (7)-O (1)$^{\mathrm{III}}$	3.00 (5)
W (7)-O (1)$^{\mathrm{V}}$	3.17 (6)
W (7)-W (1)	1.34 (6)
W (7)-W (1)$^{\mathrm{VII}}$	3.02 (7)
W (7)-W (2)	2.77 (6)
W (7)-W (3)	3.22 (6)
W (7)-W (4)	2.22 (7)
W (7)-W (5)$^{\mathrm{III}}$	3.11 (6)
W (7)-W (6)$^{\mathrm{III}}$	2.15 (6)
W (7)-W (6)$^{\mathrm{V}}$	2.81 (7)
W (7)-W (7)$^{\mathrm{IV}}$	2.36 (12)
W (7)-W (7)$^{\mathrm{VII}}$	2.05 (11)
W (7)-W (7)$^{\mathrm{XIII}}$	3.13 (11)

these atoms exactly on the mirror planes, would lead to strong (and false) anisotropic oscillations in the directions normal to these planes. Now a careful analysis of the anisotropic parameters of these atoms (Table IV) shows that oscillations normal to the mirror planes are, on the average, no larger than in other directions, and this is a confirmation of the orthorhombic symmetry.

Another test is based on the arrangement of water molecules, which in stilbite has definitely no orthorhombic symmetry. In stellerite this asymmetry is balanced by the statistical occupancy of the sites in which they appear in stilbite and of the symmetrically equivalent orthorhombic sites. To confirm the statistical orthorhombic distribution of the water molecules in stellerite, we reduced the symmetry *Fmmm* of stellerite to the monoclinic space group *F2/m*. The passage from *Fmmm* to *F2/m* was obained by splitting up those atoms that are single in the orthorhombic space group into doubles in the monoclinic space group, excluding of course, those that do not split for reasons of symmetry. This refinement converged indicating the presence of water molecules in both the symmetrically related sites, with an occupancy factor difference less that the value of their standard deviations. Obviously, this confirms the orthorhombic symmetry of stellerite.

No order in the (Si, Al) distribution has been detected, the average (Si, Al)-O distances in the different tetrahedra being always near to 1.64 Å (see Table II) (1).

DESCRIPTION OF THE STRUCTURE OF STELLERITE AND COMPARISON WITH THE STRUCTURE OF MONOCLINIC STELLERITE.

First of all let us consider the relationships between the lattice crystallography of the two minerals, as explained in Fig. 2 ; they may be summarized as follows :

$$\mathbf{a}_m = \mathbf{a}_{or} \quad \mathbf{b}_m = \mathbf{b}_{or} \quad \mathbf{c}_m = 1/2\ \mathbf{c}_{or} - 1/2\ \mathbf{a}_{or}$$

$$\mathbf{c}_{or} = 2\ \mathbf{c}_m + \mathbf{a}_m.$$

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(1) The structure factors are collected in Table V which is available from the authors.

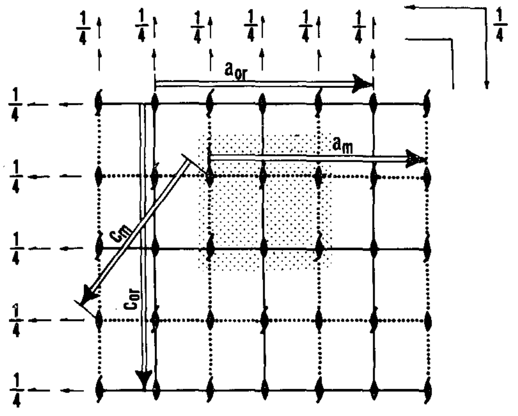

Fig. 2. — Symmetry elements in orthorhombic stellerite. In monoclinic stilbite only rotation- and screw-diads normal to the drawing remain, along with the mirror and glide-planes parallel to the drawing. Arrows show the shape of the orthorhombic (or) and of the monoclinic (m) cells. The grey area is the part of the structure projeted in Fig. 1.

The origin of the monoclinic cell, as choosen by Galli (1971), is shifted by $1/4\, a_{or} + 1/4\, c_{or}$ from the origin of the orthorhombic cell, which must be at the intersection of the mirror planes. If one applies the above transformation to the unit cell data of monoclinic stilbite (Galli, 1971), one obtains a pseudo-orthorhombic cell of space group $F2/m$ with :

$$a = 13{\cdot}64\ \text{Å} \quad ; \quad b = 18{\cdot}24\ \text{Å} \quad ; \quad c = 17{\cdot}70\ \text{Å} \quad ; \quad \beta = 91^\circ\ 05'.$$

Fig. 3 compares the framework and the cations of stellerite with those of stilbite, the drawings of the two structures being superposed as well as is permitted by the different symmetries. Although the symmetry elements are not drawn in Fig. 3, their position can be easily deduced by comparison with Fig. 2. The inspection of the figures reveals a close resemblance of the two figures, the displacement from the exactly orthorhombic position being less than 0.2 Å for Si atoms and less than 0.4 Å for the O atoms. The deviation of the stilbite framework from the higher symmetry can be interpreted as a clock-wise rotation around some binary diads (as shown by the curved arrows in Fig. 3).

The deviation from orthorhombic symmetry by rotation of part of the framework is due to the presence of the Na ions. In fact, exchangeable cation positions in stilbite are of two kinds : because of its higher charge, Ca^{++} is surrounded by water molecules only, i. e. is wholly solvated, and is placed in a widening of the main channel ; because of its lower charge, Na^+ is not wholly solvated and coordinates also some oxygen atoms of the framework and is placed in a narrowing of the main channel, under or over the tetrahedron centered by Si(5). The presence of cations near to Si(5) is well in accordance with Galli's idea that this tetrahedron is the probable location of aluminium. Fig. 4 has been drawn to explain the situation in the stilbite channels ; Na^+ ions are dispersed in four nearby positions, each having an occupancy factor of 25 %, but, on the average, there is one Na^+ ion at $y/b = 0$ or 1/2, over or under the Si(5) tetrahedron, and these Na^+ ions shift the Ca^{++} ions away from the mirror planes. The asymmetry in the cation distribution causes the asymmetry of the framework, i. e. of the whole structure. In stellerite there are no Na^+ ions either over under Si(5) and the Ca^{++} ions remain on the mirror planes and there is no deviation from the orthorhombic symmetry.

Table IV.

Analysis of the anisotropic thermal parameters.

Root mean square thermal vibrations (Å) along the ellipsoid axes and angles between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid.

	R.m.s.	$U_i a$ (°)	$U_i b$ (°)	$U_i c$ (°)
Si (1)….	.07	26	76	68
	.10	77	166	85
	.12	113	90	23
Si (3)….	.06	98	8	90
	.11	172	98	90
	.13	90	90	0
Si (4)….	.09	112	22	90
	.10	158	112	90
	.11	90	90	0
Si (5)….	.07	0	90	90
	.12	90	90	0
	.14	90	0	90
O (1)…..	.09	38	91	52
	.17	74	152	112
	.24	123	118	47
O (3)…..	.11	82	43	48
	.20	153	67	104
	.25	116	124	45
O (4)…..	.14	71	38	122
	.20	150	62	80
	.23	67	66	34
O (7)…..	.06	0	90	90
	.18	90	127	143
	.20	90	37	127
O (8)…..	.10	143	53	90
	.19	127	143	90
	.21	90	90	0
O (9)…..	.11	90	0	90
	.20	90	90	0
	.21	0	90	90
O (10)….	.15	0	90	90
	.16	90	0	90
	.17	90	90	0
Ca…….	.16	90	0	90
	.17	90	90	0
	.26	0	90	90

Coordination of water molecules around Ca^{++} is explained sufficiently in Fig. 5 : it may appear complicated, but it is not the, most probable

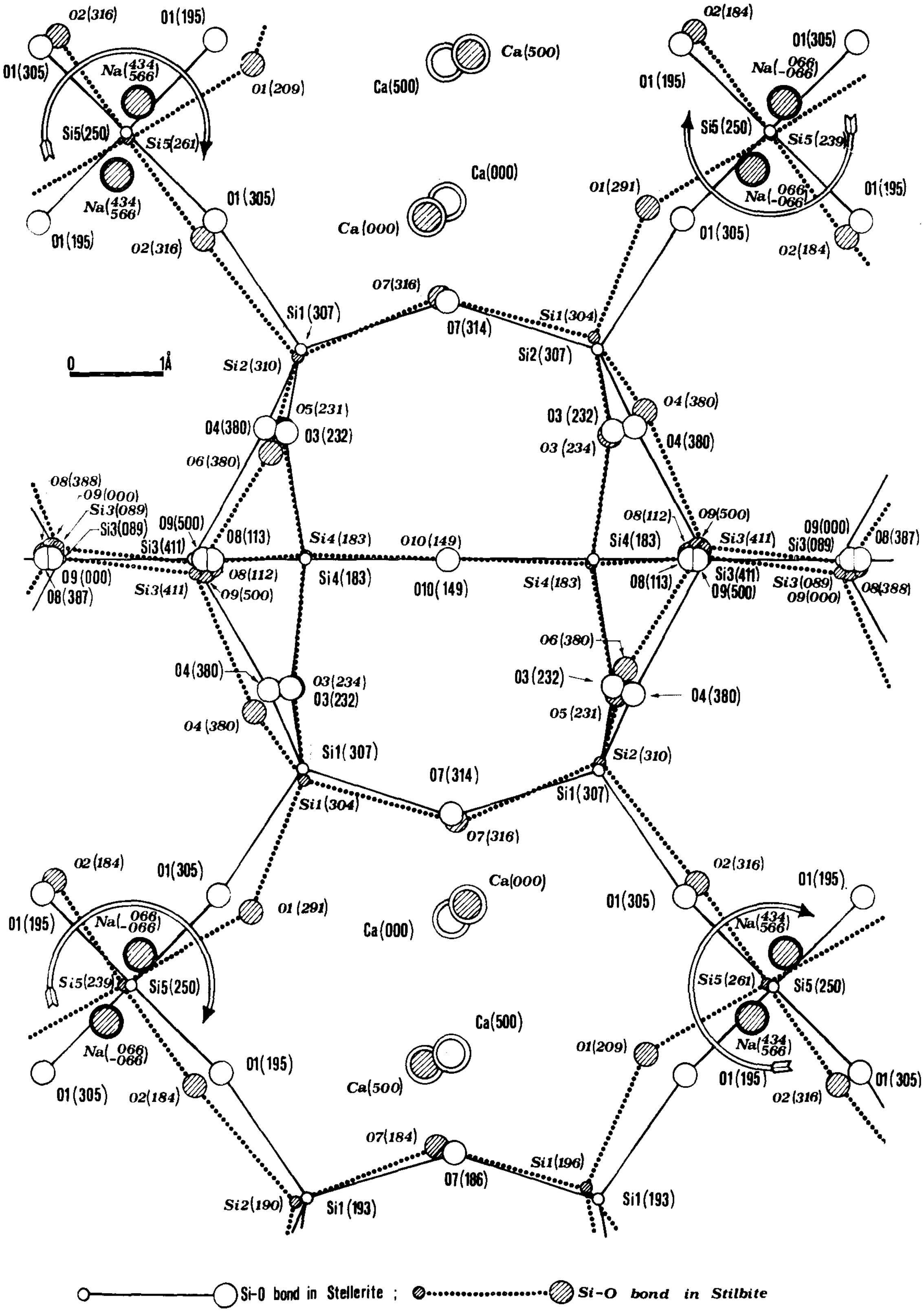

FIG. 3. — Comparison of the framework and the exchangeable extraframework cations of stellerite with those of stilbite. Symmetry elements are not shown, but can easily be recognized with the help of Fig. 2.

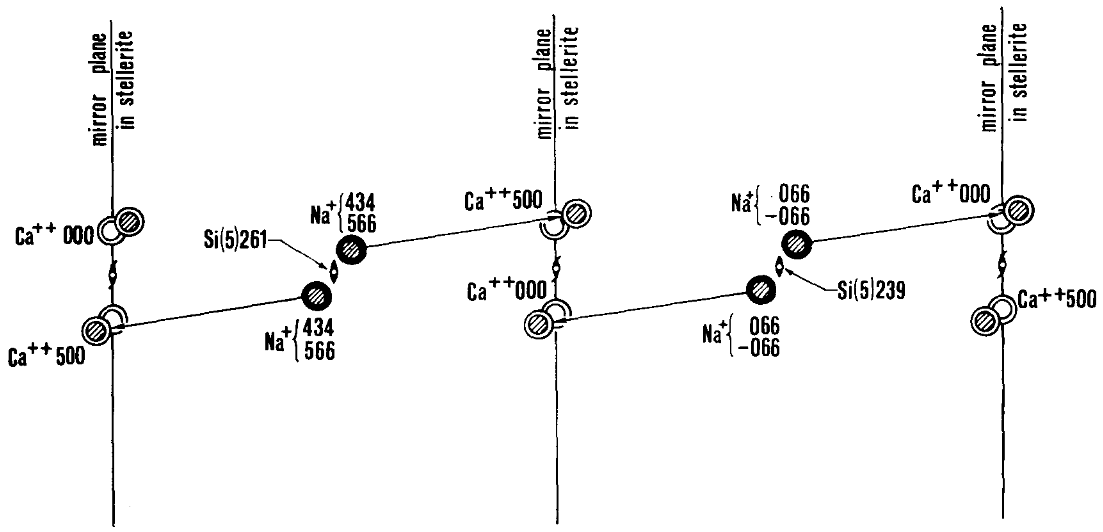

FIG. 4. — Repulsive forces between exchangeable cations in stilbite, and shifting of some cations out of the mirror planes. The positions of some cations are here represented in projection along *b*. Three digit numbers give the height over the plane y = 0 as permillage of *b*.

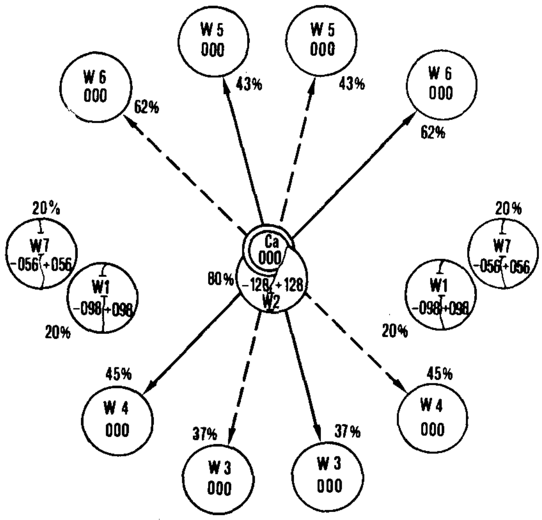

FIG. 5. — Coordination of water molecules around Ca^{++} as a projection along *b*. W is a code for water molecules as in Table II. Numbers inside the circles give the height over (or under) the projection plane as permillage of *b*. Numbers outside the circles give the occupancy factor as percent. W (3), W (4), W (5), W (6) are occupied at levels near at 50 %, so that usually four out of the eight positions are occupied at one time, for instance those joined by the continuous bar (or those joined by the dashed bar). W (2) is occupied in the 80 % of the cases : when both atoms, over and under Ca^{++}, are present, W (1) is absent; but when W (2) is present only over Ca^{++}, but not under, two W (1) may be present under the plane y = 0, and vice versa. W (7) may not be present if the nearest W (6) is occupied; and the same holds for W (1) and W (4); but remember that W (1) and W (7) are occupied only in 20 % of the cases. On the whole, the most probable pattern is an octahedral coordination given by the two W (2) and by four molecules lying in the plane y = 0.

coordination being simply an octahedron. Many rather short water-water distances are easily explained by considering the different patterns around Ca^{++} made possible by the low occupancies of some sites of water molecules.

Finally, one point concerning water sites should be emphasized : the electron density map shows badly defined peaks in the positions corresponding to W(1) and W(7), refined both with an occupancy factor of 20 %. This can be explained with a scheme of the following kind : whether W(4) and/or W(6) are occupied or not, their influence will be felt by W(1) and/or W(7), which thus tend to give a blurried picture of movement in the electron density map. W(7) occupies a site in the structure which matches quite closely the Na^+ site in stilbite.

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