

The crystal structure of cesanite, $\text{Ca}_{1+x}\text{Na}_{4-x}(\text{SO}_4)_3(\text{OH})_x \cdot (1-x)\text{H}_2\text{O}$, a sulphate isotypic to apatite

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ABSTRACT. Cesanite, $\text{Ca}_{1+x}\text{Na}_{4-x}(\text{SO}_4)_3(\text{OH})_x \cdot (1-x)\text{H}_2\text{O}$, is hexagonal, space group $P6_3/m$, $a = 9.446(1)$ and $c = 6.895(1)$ Å, $Z = 2$. The crystal structure refinement, carried out by utilizing 457 independent reflections (final $R = 0.021$), shows that cesanite is isotypic to hydroxyapatite. The P atom of apatite is completely replaced in cesanite by an S atom; the two independent Ca sites of apatite are occupied respectively by Na and Na + Ca, the charge balance being by partial substitution of H_2O for OH^- although the occupancy of the $(\text{H}_2\text{O}, \text{OH}^-)$ sites is not complete. The relationship between the water vacancies and the structural features of the (Ca, Na) polyhedron is discussed. A new general formula for the apatite-wilkeite-ellestadite series is proposed.

CESANITE, whose general chemical formula is $\text{Ca}_{1+x}\text{Na}_{4-x}(\text{SO}_4)_3(\text{OH})_x \cdot (1-x)\text{H}_2\text{O}$, has been found in core samples of the Cesano I geothermal well (Cesano area, Latium, Italy).

Cavarretta *et al.* (1981) recognized cesanite as a new mineral, describing its morphological, chemical, physical, and paragenetic properties; part of the identification procedure was supported by preliminary results of the crystallographic investigation described here, for which the same authors provided the sample.

Experimental. A Philips PW 1100 single-crystal diffractometer was used to collect the X-ray diffraction data. Table I presents the experimental details. Three standard reflections, monitored at three-hour intervals, showed less than 1.9% intensity variation during the data collection. Intensities were corrected for absorption following the method of North *et al.* (1968). A program for structure refinement based on Busing *et al.* (1962), with the scattering curves for neutral atoms given by the *International Tables for X-ray Crystallography* (1974), was used. Unit cell dimensions were measured using the routine LAT available in the PW 1100 software. The program ORTEP (Johnson, 1965) for drawing of figures was employed.

TABLE I. *Crystal and diffraction data*

Space group	$P6_3/m$
a (Å)	9.446(1)
c (Å)	6.895(1)
V (Å ³)	56.404
Z	2
Crystal dimensions (mm)	$0.35 \times 0.41 \times 0.18$
Radiation (Å)	$\text{Mo-K}\alpha$, $\lambda = 0.71069$
Monochromator	graphite
μ (cm ⁻¹)	15.8
Scan mode	θ - 2θ
Scan width (°)	2.00
Scan speed (°s ⁻¹)	0.07
θ range (°)	2-30
Maximum (sin θ/λ)	0.703
Measured reflections	1753
Independent reflections	561
Observed reflections (with $I \geq 5\sigma I$)	457
R_{sym}^*	0.026
R_{obs}	0.021
R_{all}	0.029

* $R_{\text{sym}} = \sum_{hkl} \sum_{i=1}^N \left| \bar{I}(hkl) - I(hkl)_i \right| / \sum_{hkl} \sum_{i=1}^N I(hkl)_i$ where $I(hkl)_i$ is the i th measurement of reflection hkl and $\bar{I}(hkl)$ is the mean value of the N equivalent reflections.

Structure determination and refinement. The unit cell dimensions of cesanite, $a = 9.446$ and $c = 6.895$ Å, compare very well with those computed by Cavarretta *et al.* (1981) from the powder diffraction pattern; moreover they are very similar to those reported by Sudarsanan and Young (1969) for Holly Springs hydroxyapatite ($a = 9.424$, $c = 6.879$ Å, $P6_3/m$).

This observation, together with the chemical formula $\text{Ca}_{1.53}\text{Sr}_{0.3}\text{Na}_{3.42}\text{K}_{0.02}[(\text{Cl}_{0.06}\text{F}_{0.06}\text{OH}_{0.44})(\text{S}_{2.99}\text{O}_{12})] \cdot 0.44\text{H}_2\text{O}$ found by Cavarretta

et al. (1981), suggested that cesanite and hydroxyapatite are isostructural minerals.

In order to test this hypothesis a refinement of the crystal structure of cesanite in the space group $P6_3/m$, compatible with the observed systematic absences, was undertaken, starting with the atomic coordinates of Holly Springs hydroxyapatite. The atomic scattering factors of S and (Ca,Na) were used respectively for the P and Ca sites of hydroxyapatite; only the O atomic scattering factor was used for the OH^- site, the amounts of F and Cl given by the chemical analysis being very small. The occupancies were refined together with the positional and thermal parameters of all non-hydrogen atoms. Convergence was reached after three cycles of anisotropic least-squares refinement, the conventional R factor at this stage being $R = 0.041$ for the 457 observed reflections.

It was thus possible to show that cesanite has the same structure as hydroxyapatite (fig. 1). The

P atom of hydroxyapatite is completely replaced in cesanite by an S atom; the two independent Ca sites of apatite are occupied in cesanite by Na and Ca in considerably different proportions. The $M(1)$ site, with multiplicity 4 (and 6 + 3 coordination), is almost completely occupied by Na; the $M(2)$ site, with multiplicity 6 (and 7 coordination), is filled by Ca and Na in approximately equal amounts. The charge balance is ensured by partial substitution of H_2O for OH^- .

The $(\text{H}_2\text{O}, \text{OH}^-)$ oxygen in cesanite lies on the mirror plane at $z = 0.25$; this position is occupied in Holly Springs hydroxyapatite by a small amount of fluorine, being the hydroxyl at $z = 0.195$ with statistical distribution on either side of the mirror plane. Furthermore, the refinement of the occupancy factor showed that the $(\text{H}_2\text{O}, \text{OH}^-)$ site in cesanite was only about 94% occupied. A difference Fourier map, computed at this stage of the refinement procedure, showed no other sites occupied by OH^- , H_2O , F^- , or Cl^- . Therefore it could be

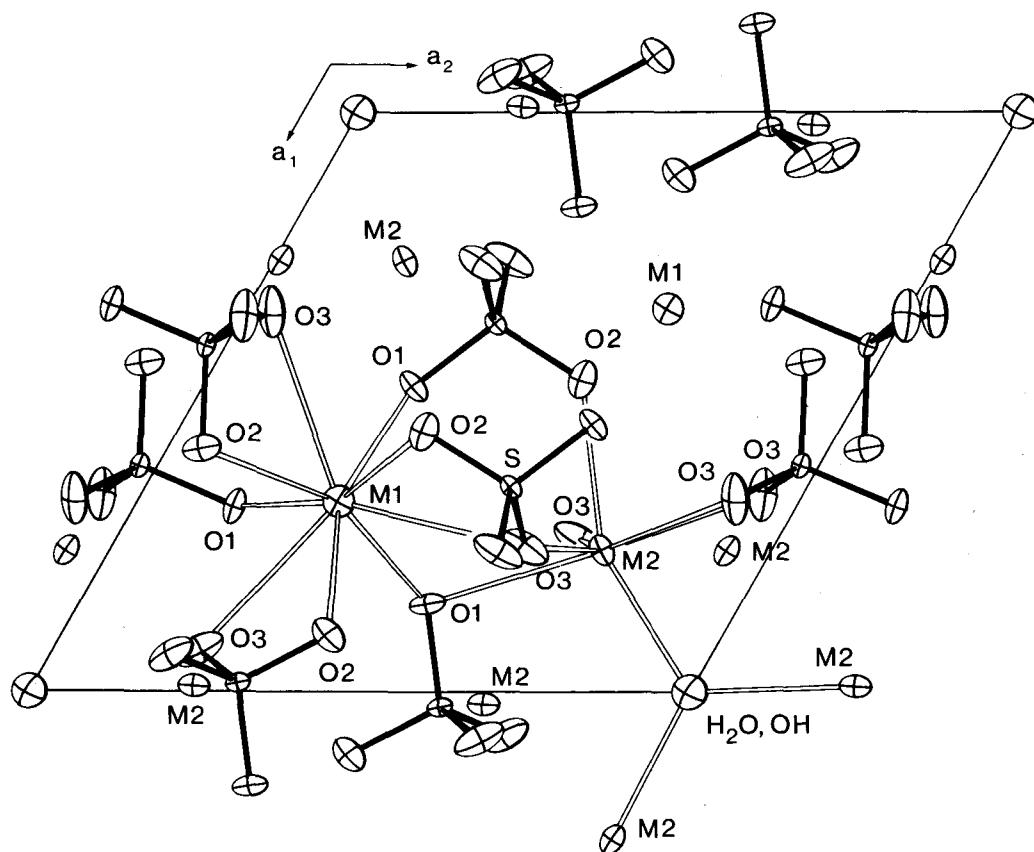


FIG. 1. ORTEP plot (Johnson, 1965) of the crystal structure of cesanite. The section plane is nearly parallel to (110). The $M(1)$ site is occupied by Na, the $M(2)$ site by Na + Ca.

concluded that the sum of these atoms is less than unity in the cesanite formula.

The difference Fourier map clearly revealed an electron density residue, approximately 0.5 Å away from the $M(2)$ position; this residue was interpreted as a split position, $M(2)'$, of the $M(2)$ cation.

The coordination of the $M(2)'$ site differs from that of $M(2)$ mainly because of a significant increase in its distance from the water molecule (2.86 and 2.35 Å respectively), with a consequent change in the coordination from 7 to 6+1. However, the electron microprobe analysis, performed on the same crystal used for X-ray data collection, ruled out the presence of any cation, apart from Na^+ and Ca^{2+} , capable of occupying such a position.

The question arises as to why the (Ca,Na) site is farther from the $(\text{H}_2\text{O},\text{OH}^-)$ position in some unit cells than in others. This may happen because the latter site is not fully occupied; it is conceivable

that when a water molecule, which belongs to three different (Ca,Na) coordination polyhedra, is missing, the (Ca,Na) cations shift from $M(2)$ to $M(2)'$, moving farther away from the vacant H_2O position in order to rearrange the bonds to a 6-fold coordination.

The refinement of the structure proceeded on the basis of this hypothesis, using scattering factors which accounted for 50% Ca and 50% Na in the $M(2)'$ site, the initial occupancy of it being set at 10%. A few least squares cycles were run, refining the parameters of $M(2)$ and $M(2)'$ sites separately in order to avoid correlation effects among the variables. Convergence was reached at a conventional R factor of 0.021 for the 457 observed reflections; accordingly the standard deviations of the positional parameters were halved. The atomic coordinates and temperature factors are summarized in Tables II and III; bond lengths and

TABLE II. Atomic coordinates, multiplicity (m), site population ($s.p.$), and equivalent isotropic temperature factor

Site	m	$s.p.$	x	y	z	$B_H(\text{Å}^2)$
S	3	S 1.00	0.3644(1)	0.3905(1)	0.25	0.86
$M(1)$	2	Na 0.96, Ca 0.04	0.3333	0.6667	-0.0040(2)	1.57
$M(2)$	3	Na 0.47, Ca 0.41	0.9902(1)	0.2441(1)	0.25	0.98
$M(2)'$	3	Na 0.06, Ca 0.06	0.3124(7)	0.0206(7)	0.25	1.69
O(1)	3	O 1.00	0.4721(2)	0.3198(2)	0.25	1.54
O(2)	3	O 1.00	0.4604(3)	0.5692(2)	0.25	2.84
O(3)	6	O 1.00	0.2581(2)	0.3365(2)	0.0785(2)	2.48
$\text{H}_2\text{O},\text{OH}^-$	1	O 0.94	0.0	0.0	0.25	3.98

Standard deviations of atomic coordinates in parentheses. Equivalent isotropic temperature factors after Hamilton (1959). The temperature factor of $M(2)'$ was refined isotropically.

TABLE III. Analysis of the anisotropic thermal parameters

Site	r.m.s.	aU_i	bU_i	cU_i	Site	r.m.s.	aU_i	bU_i	cU_i
S	0.091(1)	160	40	90	O(2)	0.124(3)	81	159	90
	0.098(1)	90	90	0		0.183(3)	9	111	90
	0.121(1)	110	130	90		0.243(3)	90	90	180
$M(1)$	0.123(3)	90	90	180	O(3)	0.104(3)	117	91	148
	0.149(4)	—	—	90		0.133(2)	27	126	115
	0.149(4)	—	—	90		0.256(2)	91	144	71
$M(2)$	0.097(2)	160	80	90	$\text{H}_2\text{O},\text{OH}^-$	0.163(4)	—	—	90
	0.105(2)	90	90	0		0.163(4)	—	—	90
	0.131(2)	70	70	90		0.314(7)	90	90	180
O(1)	0.095(4)	160	40	90					
	0.149(3)	90	90	0					
	0.166(3)	110	130	90					

Root mean square thermal vibration along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid. Standard deviations of r.m.s. in parentheses.

angles are compared with those of hydroxyapatite in Table IV, while observed and calculated structure factors are deposited with the library of the Department of Mineralogy, British Museum (Natural History).

The number of electrons obtained from the refinement is 13.30 for $M(2)$ and 1.87 for $M(2)'$ site. Assuming the same Na/Ca ratio for both sites, with the constraint that $(\text{Na} + \text{Ca})_{M(2)} + (\text{Na} + \text{Ca})_{M(2)'} = 1$, the following site populations were deduced: $(0.471\text{Na} + 0.407\text{Ca})$ for $M(2)$ and $(0.065\text{Na} + 0.057\text{Ca})$ for $M(2)'$.

The refinement also confirms that the $(\text{H}_2\text{O}, \text{OH}^-)$ position is only 94.3% occupied. Even if the lack of water molecules (0.06 mol. per f.u.) in the coordination polyhedron is less than the assumed population of the $M(2)'$ site (0.12 at. per f.u.), it seems reasonable to suggest, although only qualitatively, that the shift of the cation from the

TABLE IV. Comparison between interatomic distances (\AA) and bond angles ($^\circ$) in cesanite (standard deviations in parentheses) and hydroxyapatite

Cesanite		Hydroxyapatite*	
Atoms	Distances	Atoms	Distances
S-O(1)	1.471(2)	P-O(1)	1.538(2)
-O(2)	1.463(2)	-O(2)	1.539(2)
-O(3) \times 2	1.467(2)	-O(3) \times 2	1.531(2)
Average	1.467	Average	1.535
$M(1)$ -O(1) \times 3	2.457(2)	Ca(1)-O(1) \times 3	2.405(2)
-O(2) \times 3	2.542(2)	-O(2) \times 3	2.454(2)
-O(3) \times 3	2.887(2)	-O(3) \times 3	2.802(2)
Average	2.629	Average	2.554
$M(2)$ -O(1)	2.606(2)	Ca(2)-O(1)	2.709(2)
-O(2)	2.433(2)	-O(2)	2.356(2)
-O(3) \times 2	2.521(2)	-O(3) \times 2	2.510(2)
-O(3)' \times 2	2.378(2)	-O(3)' \times 2	2.345(2)
-H ₂ O, OH ⁻	2.352(2)	-H ₂ O, OH ⁻	2.388(2)
Average	2.452	Average	2.452
$M(2)'$ -O(1)	2.449(2)		
-O(2)	2.027(2)		
-O(3) \times 2	2.719(2)		
-O(3)' \times 2	2.314(2)		
-H ₂ O, OH ⁻	2.859(2)		
Average	2.486		
Atoms	Angles	Atoms	Angles
O(1)-S-O(2)	110.69(12)	O(1)-P-O(2)	111.09(13)
O(1)-S-O(3) \times 2	110.53(07)	O(1)-P-O(3) \times 2	111.42(09)
O(2)-S-O(3) \times 2	108.81(08)	O(2)-P-O(3) \times 2	107.48(11)
O(3)-S-O(3)'	107.38(12)	O(3)-P-O(3)'	107.76(10)

* Distances and angles for hydroxyapatite are computed from the atomic coordinates given by Sudarsanan and Young (1969) for the specimen X-23-4.

$M(2)$ to $M(2)'$ site is the result of this deficiency. In fact it must be taken into account that: if F and Cl scattering factors are included in the refinement of the occupancy of the $(\text{H}_2\text{O}, \text{OH}^-)$ site, its actual vacancy would slightly increase, giving better agreement with the $M(2)'$ site population; the occupancy values found for split sites so close as $M(2)$ and $M(2)'$, each hosting different atomic species, are intrinsically imprecise.

Conclusions. If the bond lengths of cesanite are compared with those of hydroxyapatite (Table IV), the following observations can be made:

1. The S-P substitution shortens the T-O tetrahedral bond lengths by the expected amount (from 1.535 to 1.467 \AA for the T-O mean distance). The tetrahedral bond lengths and angles in cesanite fit perfectly the linear relationship found in sulphate tetrahedral oxyanions by Louisnathan *et al.* (1977).

2. Most of the Ca atoms are ordered in the $M(2)$ site, i.e. in the polyhedron with lower coordination; in this polyhedron the mean $M(2)$ -O distance is unaffected.

3. The volume decrease of the tetrahedron is, in cesanite, accompanied by a volume increase of the $M(1)$ polyhedron, thus explaining the small differences in the cell dimensions between cesanite and hydroxyapatite. They can therefore hardly be distinguished on the basis of lattice parameters.

The results of this crystallographic analysis indicate that the chemical formula of the examined cesanite is $\text{Ca}_{1.49}\text{Na}_{3.51}(\text{SO}_4)_3(\text{OH})_{0.49} \cdot 0.45\text{H}_2\text{O}$ which compares well with that calculated from the chemical analysis.

The crystal structure determination confirms that cesanite has to be considered one member of the apatite-wilkeite-ellestadite series, where $(\text{PO}_4)^{3-}$ is entirely substituted by $(\text{SO}_4)^{2-}$, the charge balance being made up by partial substitution of Na^+ for Ca^{2+} and H_2O for $(\text{OH}, \text{Cl}^-, \text{F}^-)$. The general formula of this series, proposed by Harada *et al.* (1971) and modified by Cavarretta *et al.* (1981), is more properly expressed as $\text{Ca}_{5-w}\text{Na}_w(\text{Si}_y\text{S}_z\text{P}_{3-y-z})\text{O}_{12}(\text{F}, \text{Cl}, \text{OH})_x \cdot n\text{H}_2\text{O}$ where $w = 1 - x - y + z$ and $n \leq 1 - x$.

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