

The crystal structure of cascandite, $\text{CaScSi}_3\text{O}_8(\text{OH})$

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Abstract

A new pyroxenoid mineral, cascandite, with the ideal formula $\text{CaScSi}_3\text{O}_8(\text{OH})$, is triclinic with $a = 9.791(8)\text{\AA}$, $b = 10.420(9)\text{\AA}$, $c = 7.076(6)\text{\AA}$, $\alpha = 98.91(8)^\circ$, $\beta = 102.63(8)^\circ$, $\gamma = 84.17(8)^\circ$; $Z = 4$ for the $C\bar{1}$ unit cell setting. The crystal structure of cascandite is similar to those of pectolite and serandite and is composed of two main structural units: octahedral chains and three-repeat tetrahedral chains. Cascandite, unlike pectolite and serandite, has only two octahedral cations per formula unit, and the octahedral chains are formed by two strands of edge-sharing octahedra occupied by calcium and scandium cations.

Cascandite is a member of the hydrous pyroxenoid series, whose peculiarities are related to the presence of intrachain hydrogen bonding.

Introduction

Cascandite, a new scandium silicate, was found in a geode from the granite of Baveno, Italy, together with quartz, orthoclase, albite and jervite, another new scandium silicate with ideal formula $\text{NaScSi}_2\text{O}_6$. The descriptions of these new minerals are given by Mellini *et al.* (1982). The chemical, physical and crystallographic properties indicate that cascandite is a three-repeat pyroxenoid.

The present structural study was undertaken to give a better description of the new scandium mineral and to acquire a deeper insight into the crystal chemistry of pyroxenoids.

Structure determination

A small crystal of cascandite was selected and examined first by X-ray film methods. Triclinic cell parameters (Table 1) were obtained by least squares refinement using 25 reflections centered on a Philips PW 1100 single crystal diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation. A total of 1526 non-zero reflections were measured from 3 to 30° θ , using a $\theta/2\theta$ scan and scan width 1.20° . The data were corrected for Lorentz and polarization factors. No absorption correction was made because of the small dimensions of the crystal.

Only qualitative energy dispersive analytical data were available when the structure determination was undertaken. The solution of the structure was

obtained starting from the atomic coordinates of wollastonite based on $P\bar{1}$ setting, as given by Buerger and Prewitt (1961). However the E statistics indicated a non-centrosymmetric structure, and thus we removed the symmetry constraints on the octahedral cations. We assumed that one of the six octahedral sites in the unit cell of the trial structure was vacant and the site that had been centrosymmetrically related was occupied by a scandium cation, as suggested by the preliminary analytical data. Four refinement cycles were calculated, each followed by a Fourier synthesis. The behavior of the thermal parameters and the heights of the various peaks in the Fourier maps strongly indicated that one more octahedral site had to be considered vacant and that two silicon atoms had to be shifted from their positions in the trial structure. The new structural arrangement smoothly refined to an $R_1 = \sum | |F_o| - |F_c| | / \sum |F_o| = 0.08$.

We then realized that the arrangement was indeed a centrosymmetric one, closely related to that in minerals of the pectolite-serandite series. The false indication of the absence of a symmetry center most probably resulted from not having taken into account the "unobserved" reflections. The refinement was then continued in the $P\bar{1}$ space group. The introduction of anisotropic thermal parameters for all atoms led to $R_1 = 0.042$ and $R_2 = (\sum_w | |F_o| - |F_c| |^2 / \sum_w |F_o|^2)^{1/2} = 0.046$, where w was the reciprocal of the variance on F_o as estimated from

Table 1. Unit cell parameters of cascandite, serandite and schizolite

	Cascandite CaScSi ₃ O ₈ (OH)		Serandite* Mn ₂ NaSi ₃ O ₈ (OH)	Schizolite* CaMnNaSi ₃ O ₈ (OH)
a	7.503(6) Å	9.791(8) Å	9.909(9) Å	10.059(4) Å
b	7.076(6)	10.420(9)	10.667(9)	10.880(8)
c	6.777(6)	7.076(6)	6.913(4)	6.978(6)
α	92.23(8)°	98.91(8)°	99.10(6)°	98.84(7)°
β	93.58(8)	102.63(8)	100.51(6)	100.58(5)
γ	104.49(8)	84.17(8)	82.49(7)	82.64(5)
Space group	P $\bar{1}$	C $\bar{1}$	C $\bar{1}$	C $\bar{1}$

* Values for serandite and schizolite are from Ohashi and Finger (1978).

counting statistics. Observed and calculated structure factors are given in Table 2.¹

The entire refinement was carried out in the conventional $P\bar{1}$ setting of the unit cell, whereas the crystal structure will be described and discussed with reference to the C -centered cell first introduced by Narita (1973; quoted by Morimoto, 1974) and used also by Ohashi and Finger (1978) in their discussion of the three-repeat pyroxenoid crystal chemistry. Table 1 compares the C -centered unit cell parameters in this setting with the corresponding parameters given by Ohashi and Finger (1978) for the serandite and schizolite specimens studied in their paper. The transformation matrix from the conventional $P\bar{1}$ cell to the $C\bar{1}$ cell is $[101/10\bar{1}/010]$. The final atomic positional and thermal parameters for cascandite in the $C\bar{1}$ setting are given in Table 3.

Description and discussion of the structure

The crystal structure of cascandite (Fig. 1) may be described in terms of two main structural units: octahedral double chains, formed by two strands of edge-sharing octahedra, and tetrahedral single chains with a repeat period of three tetrahedra. Each octahedral chain is connected to six tetrahedral chains by corner sharing, whereas each tetrahedral chain is connected to three octahedral chains.

Cascandite is thus classified with the three-repeat pyroxenoids. It is well known that three-repeat pyroxenoids develop three distinct stacking schemes of tetrahedral and octahedral structural layers:

these different topologies appear in the structures of wollastonite, bustamite and minerals of the pectolite-serandite series. With regard to the general topological features, cascandite is closely related to the pectolite-serandite group. This is clearly shown by the comparison of Figure 1 in the present paper with Figure 3 of Ohashi and Finger (1978).

The bond lengths in the various tetrahedral and octahedral polyhedra, together with their standard deviations, are given in Table 4. Two longer M1-OC3 and M1-OC3^x distances are reported in brackets and were taken into account in calculating the valence bond balance. The mean bond lengths in M1 and M2 octahedra are given also in Table 5 together with the mean bond lengths in M1, M2 and A sites in schizolite and serandite (Ohashi and Finger, 1978). The same table compares the cation occupancies used in the present refinement with those obtained by Ohashi and Finger (1978) for schizolite and serandite. The M2 site, occupied by scandium cations, is definitely smaller than the corresponding site in the entire pectolite-schizolite-serandite series. Furthermore the difference in size between the octahedral M1 and M2 sites results in distortion of tetrahedral chains. The tetrahedral triplet, namely the C-shaped cluster of three tetrahedra which provides a nearly square arrangement of oxygens in pectolite, is slightly deformed in cascandite towards a diamond-shaped arrangement of oxygens. Moreover the A site, which in the pectolite-serandite group of minerals is occupied by sodium, appears vacant in cascandite and in this respect cascandite is unique in the entire three-repeat pyroxenoid family.

The results of the structure analysis clearly indicate the ideal formula CaScSi₃O₈(OH) for cascandite. The presence of the hydrogen atom, which was strongly suggested by the close relationship between cascandite and the minerals of the pectolite-serandite series, was confirmed by the results of the valence bond balance (Table 6) and ascertained by a difference Fourier synthesis. Apart from the peak corresponding to the hydrogen atom, two additional peaks were found in the difference map, one corresponding to the scandium position (M2 site) and the other to the position of the sodium cations (A site) in pectolite, schizolite and serandite. The chemical analysis (Mellini *et al.*, 1982) showed the presence of significant quantities of manganese and iron and indicated the presence of more than two octahedral cations in the chemical formula of cascandite. On the basis of these chemi-

¹ To receive a copy of Table 2, order Document AM-82-200 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Atomic positional coordinates and anisotropic temperature factors ($\times 10^4$) in the form: $\exp -(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23})$. The coordinates of the H and A sites were obtained from the difference Fourier synthesis.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M1	0.0027(1)	0.6629(1)	0.9128(1)	37(1)	24(1)	36(2)	3(1)	13(1)	10(1)
M2	-0.0019(1)	0.6421(1)	0.4062(1)	10(1)	13(1)	10(1)	-4(1)	0(1)	4(1)
Si1	0.2163(1)	0.0402(1)	0.0886(2)	19(1)	20(1)	27(2)	-1(1)	4(1)	8(1)
Si2	0.2102(1)	0.0666(1)	0.5229(2)	18(1)	18(1)	26(2)	-2(1)	3(1)	10(1)
Si3	0.2055(1)	0.8366(1)	0.7399(2)	20(1)	18(1)	28(2)	-6(1)	2(1)	6(1)
OA1	0.1160(3)	0.4490(3)	0.8729(5)	19(3)	26(3)	42(6)	-4(2)	1(3)	10(3)
OA2	0.1176(3)	0.4462(3)	0.4203(5)	18(3)	25(3)	40(6)	-3(2)	2(4)	8(3)
OA3	0.1279(4)	0.6930(4)	0.2416(5)	24(3)	38(3)	47(6)	-6(3)	3(4)	13(4)
OB1	0.1295(4)	0.1568(3)	-0.0262(5)	46(4)	25(3)	52(7)	10(3)	16(4)	19(4)
OB2	0.1479(4)	0.2006(3)	0.6291(5)	40(4)	22(3)	49(6)	2(3)	15(4)	3(3)
OB3	0.1113(4)	0.7139(3)	0.6736(5)	26(3)	24(3)	43(6)	-9(2)	-2(4)	8(3)
OC1	0.1571(4)	0.0538(4)	0.2871(5)	23(3)	38(3)	36(6)	-2(2)	6(3)	10(3)
OC2	0.1507(4)	0.9458(3)	0.5940(5)	33(4)	27(3)	66(7)	-9(3)	5(4)	22(4)
OC3	0.1815(4)	0.8981(3)	0.9601(5)	36(4)	29(3)	37(6)	-11(3)	9(4)	1(3)
H	0.13	0.18	0.86						
A	0.03	0.89	0.28						

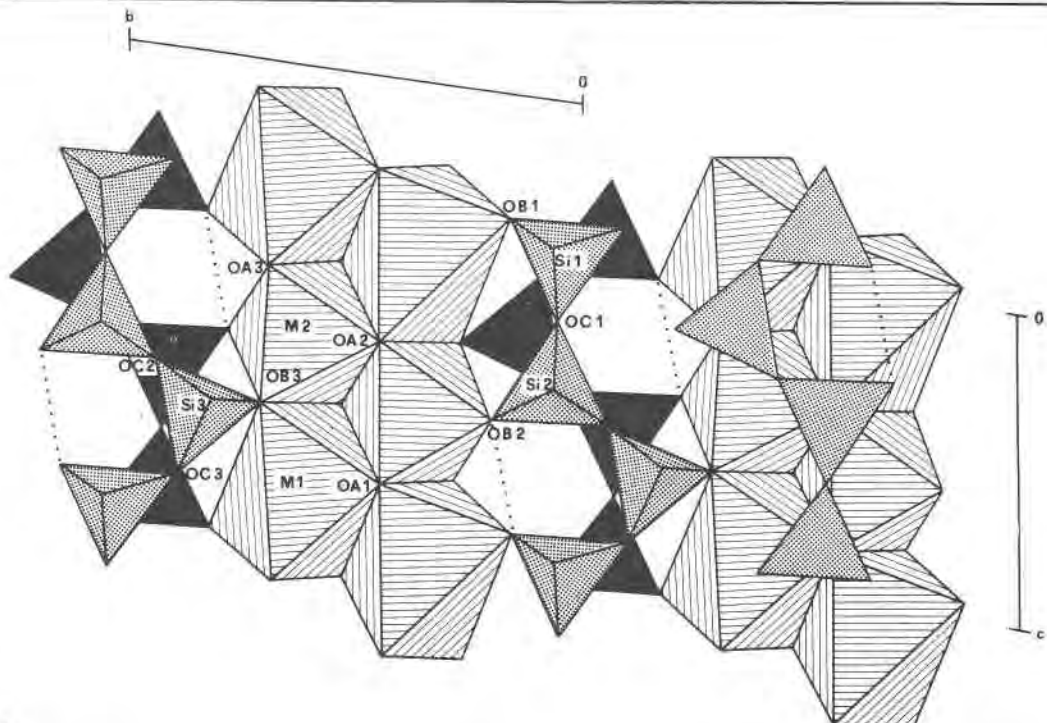


Fig. 1. Crystal structure of cascandite as projected along a^* onto (100) plane. Dotted lines indicate hydrogen bonds.

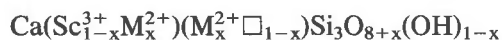
Table 4. Bond distances (Å), with the corresponding standard deviations, in the various coordination polyhedra

M1 - OB1 ^{vii}	2.312(4)	Si1 - OC1	1.614(4)
- OB3	2.336(4)	- OA1 ^{viii}	1.617(4)
- OA3 ⁱ	2.370(4)	- OB1	1.628(4)
- OA1	2.391(4)	- OC3 ^v	1.639(4)
- OA2 ^{vii}	2.542(3)	average value	1.624
- OA1 ^{vi}	2.570(4)	Si2 - OB2	1.610(4)
average value	2.420	- OC1	1.624(4)
M1 - OC3 ^x	3.055(4)	- OC2 ^{iv}	1.628(4)
- OC3	3.090(4)	- OA2 ^{viii}	1.642(4)
		average value	1.626
M2 - OB3	2.044(3)	Si3 - OB3	1.604(4)
- OA3	2.057(4)	- OA3 ^{ix}	1.609(4)
- OB2 ^{vii}	2.070(4)	- OC2	1.627(4)
- OA1 ^{vii}	2.173(4)	- OC3	1.647(4)
- OA2 ^{vii}	2.192(4)	average value	1.622
- OA2	2.253(3)		
average value	2.131		

In this table, as well as in the text, the following symmetry code was used:

i	x	y	1+z	vi	-x	1-y	2-z
ii	x	1+y	z	vii	-x	1-y	1-z
iii	x	1+y	1+z	viii	1/2-x	1/2-y	1-z
iv	x	-1+y	z	ix	1/2-x	3/2-y	1-z
v	x	-1+y	-1+z	x	1/2-x	3/2-y	2-z

cal data, the peak at the M2 site was interpreted to be due to a limited replacement of scandium by the heavier iron or manganese cations, which is consistent with the relatively low thermal parameters of the M2 cation. The peak at the A site was interpreted to be due to a limited insertion of iron or manganese cations in that site. The crystal chemical formula which reconciles the chemical and structural data is:



with $\text{M}^{2+} = (\text{Fe}^{2+}, \text{Mn}^{2+})$ and $x \approx 0.1-0.2$. The substitutions summarized in the formula are probably coupled to preserve local charge balance.

Hydrogen bonding and pyroxenoid series

Takéuchi (1976) recognized two series of octahedral bands in pyroxenoid minerals. His *w-p* series corresponds to anhydrous pyroxenoids and the *p-p* series to hydrous pyroxenoids (Takéuchi and Koto,

1977). The two pyroxenoid series differ in the following respects: (1) the tetrahedral triplets occur on the same octahedron in the *w-p* series, whereas they occur on a tetrahedral void in the *p-p* series; (2) the tetrahedral-octahedral linkage at the basal oxygens of tetrahedra is parallel in the *w-p* series, namely the upper triangular faces of octahedra are pointing in the same direction as the central tetrahedron in the triplet, whereas it is antiparallel in the *p-p* series; (3) the tetrahedral chains present a marked shrinkage due to kinking of the chains in the hydrous pyroxenoids relative to those in anhydrous ones. This last feature was interpreted by Liebau (1980) to be a result of the reduction of repulsive forces between SiO_4 tetrahedra that was caused by an increase of the average electronegativity of cations where cationic hydrogen is present, with subsequent formation of intrachain hydrogen bonds.

It is becoming more and more evident, as new examples are studied and more data are collected about the exact hydrogen locations in these structures, that the various features which characterize the hydrous pyroxenoid series are related to the presence of the intrachain hydrogen bonding. Ohashi and Finger (1978), in their attempt to explain the two series of pyroxenoids, first emphasized the role of alkali cations in the *p-p* series as the cause for the antiparallel stacking of octahedral-tetrahedral layers. However, they were compelled by the occurrence of a similar feature in alkali-free babingtonite to conclude that hydrogen should have a role at least as important as that of alkali cations. More recently, they stated the central role of hydrogen bonding in conditioning the antiparallel linkage at the apical oxygens of tetrahedra: "in santaclaraite, OB1 and OB4, bridged by the hydrogen atom, are

Table 5. Mean bond lengths in the M1, M2 and A coordination polyhedra in cascandite, schizolite and serandite

	Cascandite	Schizolite	Serandite
M1-O	2.420 A	2.376 A	2.286 A
M2-O	2.131	2.263	2.235
A -O		2.556	2.505
M1	Ca	$\text{Ca}_{0.87}\text{Mn}_{0.13}$	$\text{Ca}_{0.34}\text{Mn}_{0.66}$
M2	Sc	$\text{Ca}_{0.36}\text{Mn}_{0.64}$	Mn
A		Na	Na

Table 6. Valence bond balance: the calculations were made following the method of Donnay and Allman (1970). The values in parentheses are the valence bond sums corrected for the hydrogen bond contribution, which was estimated by the procedure of Donnay and Allman (1970) from the distance between the hydrogen bonded atoms.

	M1	M2	Si1	Si2	Si3	Total	
OA1	0.33 0.25	0.47	1.01			2.06	
OA2	0.26	0.45 0.40		0.97		2.08	
OA3	0.35	0.57			1.03	1.95	
OB1	0.38		0.99			1.37	(1.11)
OB2		0.55		1.03		1.58	(1.84)
OB3	0.37	0.58			1.04	1.99	
OC1			1.02	1.00		2.02	
OC2				1.00	0.99	1.99	
OC3	0.07 0.06		0.97		0.95	2.05	

too close to become an edge of the Mn octahedron. Thus the octahedral module, relative to the tetrahedral module, is arranged in such a way that these two oxygens do not coordinate to the same octahedral cation." (Ohashi and Finger, 1981).

The OB2. . . OB1¹ distance in cascandite, 2.603 Å, is similar to the corresponding distance in babingtonite, 2.581 Å, (Araki and Zoltai, 1972), and is longer than the corresponding distances in santaclaraite, 2.491 Å, (Ohashi and Finger, 1981), pectolite, 2.482 Å, (Takéuchi and Kudoh, 1977), serandite, 2.453 Å, (Takéuchi *et al.*, 1976), nambulite, 2.464 Å, (Narita *et al.*, 1975), and lithium-hydro-rhodonite, 2.449 Å, (Murakami *et al.*, 1977).

In cascandite, as in santaclaraite, the hydrogen is ordered. Only one hydrogen peak was found in the difference Fourier synthesis, and it is located closer to OB1 than to OB2. On the other hand, the shape of the peak found by Takéuchi and Kudoh (1977) in their study of Magnet Cove pectolite, was interpreted to be due to a random distribution of hydrogen between two positions corresponding to the hydrogen bonds O(3)-H . . . O(4) or O(3) . . . H-O(4). The occurrence of the first configuration is higher than the other, in accord with the somewhat higher valence bond sum of 1.52 v.u. for O(4), relative to 1.48 v.u. for O(3) (Takéuchi and Kudoh, 1977).

The ordered hydrogen bonding in cascandite and santaclaraite is consistent with the marked difference in the valence bond sums for OB1 (1.38 v.u.) and OB2 (1.59 v.u.) in cascandite and for OB1 (1.36 v.u.) and OB4 (1.55 v.u.) in santaclaraite. A similar difference was observed in babingtonite, where valence bond sums of 1.40 v.u. for O(1) and 1.62 v.u. for O(11) indicate the presence of ordered hydrogen bonds.

In santaclaraite the high valence bond sums of OB4 is related to the short M4-OB4 bond lengths, the shortest bond lengths in the M4 octahedron and Si4 tetrahedron, respectively. In cascandite and babingtonite, the marked difference in the valence bond sums for the two hydrogen-bonded oxygen atoms is related to the ordering of divalent and trivalent cations in the octahedral bands. This ordering thus appears to be an additional feature dependent on hydrogen bonding in the *w-p* series of pyroxenoids.

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