

THE CRYSTAL STRUCTURE OF CALCIUM CATAPLEIITE

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ABSTRACT

Calcium catapleite, $\text{CaZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, the calcium-dominant analogue of catapleite, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, firstly described as hexagonal, space group $P6_3/mmc$, with a 7.32, c 10.15 Å, is actually orthorhombic, space group $Pbnn$, a 7.378(1), b 12.779(1), c 10.096(1) Å, V 951.89 Å³ and $Z = 4$. The crystals display three-fold twinning ("Drilling") about the c axis, with the three individuals rotated 120° one from the other. The crystal structure of calcium catapleite from the type locality, the Burpala massif, northern Baikal Region, Siberia, Russia, has been determined by direct methods from single-crystal X-ray-diffraction data and refined to a final $R = 0.0528$ ($wR^2 = 0.1604$) for 2167 reflections with $F_o > 6\sigma(F_o)$. It is characterized by a mixed framework of regular $[\text{ZrO}_6]$ octahedra and three-membered silicate rings $[\text{Si}_3\text{O}_9]$, very similar to the framework of catapleite. The H_2O molecules also are similarly placed in the two minerals. The Ca^{2+} cations in calcium catapleite are distributed over two distinct sites, with 0.8 and 0.2 occupancies, which contrasts with the fully disordered distribution of the Na^+ cations in catapleite.

Keywords: calcium catapleite, crystal structure, ring silicate, syenitic pegmatite, Burpala massif, Russia.

SOMMAIRE

La calcium catapléiite, $\text{CaZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, l'analogue à dominance de calcium de la catapléiite, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, a tout d'abord été décrite comme phase hexagonale, groupe spatial $P6_3/mmc$, avec a 7.32, c 10.15 Å, mais elle est en fait orthorhombique, groupe spatial $Pbnn$, a 7.378(1), b 12.779(1), c 10.096(1) Å, V 951.89 Å³ et $Z = 4$. Les cristaux font preuve de macles d'ordre trois (en allemand, "Drilling") autour de l'axe c , les trois individus montrant une rotation de 120° l'un par rapport à l'autre. La structure cristalline de la calcium catapléiite provenant de la localité-type, le massif de Burpala, dans la partie nord de la région de Baïkal, en Sibérie, Russie, a été déterminée par méthodes directes avec données obtenues en diffraction X sur monocristaux, et affinée jusqu'à un résidu R de 0.0528 ($wR^2 = 0.1604$) en utilisant 2167 réflexions pour lesquelles $F_o > 6\sigma(F_o)$. La structure contient la même trame mixte d'octaèdres réguliers de $[\text{ZrO}_6]$ et d'anneaux de tétraèdres à trois membres $[\text{Si}_3\text{O}_9]$ que la catapléiite. Les molécules de H_2O sont aussi placées de façon semblable dans les deux minéraux. Les atomes de Ca^{2+} dans la calcium catapléiite sont distribués sur deux sites, ayant des taux d'occupation 0.8 et 0.2, ce qui diffère nettement de la distribution complètement désordonnée des ions de sodium dans la catapléiite.

(Traduit par la Rédaction)

Mots-clés: calcium catapléiite, structure cristalline, silicate à anneaux, syénite pegmatitique, massif de Burpala, Russie.

INTRODUCTION

Calcium catapleite, $\text{CaZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, is a rare mineral found in hydrothermal assemblages associated with alkaline complexes. It was first discovered in syenitic pegmatites of the Burpala massif, northern Baikal Region, Siberia, Russia (Portnov 1964), and later found in the following alkaline complexes: Golden Horn in

Okanogan County, Washington, U.S.A., Strange Lake in Quebec-Labrador and Ice River, British Columbia, Canada, Norra Karr, Sweden (*cf.* Gaines *et al.* 1997), Cnoc Rhaonastil, Islay, Scotland, U.K. (Preston *et al.* 1998), and the Afrikanda complex, Kola Peninsula, Russia (Chakhmouradian & Zaitsev 2002). In this article, we provide definitive information on the crystal structure of calcium catapleite.

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At the type locality, calcium catapleite is found in aegirine–microcline pegmatite veins cross-cutting syenite along the northern and western margin zone of the Burpala massif. It occurs in the axial parts of veins (usually in cavities) as light yellow to cream-colored grains and lamellar crystals a few centimeters in size. Associated minerals include pyrophanite, pyrochlore, leucophanite, Ti-rich l avenite, loparite-(Ce), kupletskite, REE-bearing apatite, and Ca-enriched seidozerite. Some crystals of calcium catapleite are partially replaced by aegirine and Ca-rich seidozerite (Portnov 1964).

REVIEW OF PREVIOUS INVESTIGATIONS

The crystal structure of catapleite $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ was described by Brunowsky (1936) in the space group $P6_3/mmc$, a 7.40, c 10.05 Å. As reported by Vlasov (1966), both optically uniaxial and biaxial crystals exist, and different crystallographic systems (monoclinic, hexagonal, orthorhombic) have been given by various authors, even before the development of the X-ray studies. Through measurements on catapleite crystals at ordinary and elevated temperatures, Br ogger (1890) established the existence of two modifications: monoclinic (pseudo-hexagonal) at ordinary temperature and hexagonal at 140°C (Vlasov 1966). The structure of the monoclinic modification has been determined and refined by Chao *et al.* (1973) in the space group $I2/c$, a 12.779, b 7.419, c 20.157 Å, β 90.41°, and by Ilyushin *et al.* (1981) in the space group $B2/b$, with a 23.917(2), b 20.148(2), c 7.432(1) Å, γ 147.46(1)°. The setting of Chao *et al.* (1973), metrically almost orthorhombic and pseudo-hexagonal ($a \approx b\sqrt{3}$), may be obtained from that of Ilyushin *et al.* (1981) through the transformation matrix [110/001/010]. The monoclinic structure, as described by Ilyushin *et al.* (1981), and the hexagonal one, as described by Brunowsky (1936) are essentially the same: they contain a mixed framework built up of $[\text{ZrO}_6]$ octahedra and $[\text{Si}_3\text{O}_9]$ rings of tetrahedra; however, the sites occupied by Na atoms and H_2O molecules are exchanged in the monoclinic model with respect to the hexagonal one.

The synthetic analogue of catapleite was obtained in the hydrothermal system ZrO_2 – SiO_2 – Na_2O – H_2O ($P = 700$ bars, $300^\circ < T < 700^\circ\text{C}$) by Baussy *et al.* (1974), who indicated a hexagonal cell, space group $P6_3/mmc$, with a 7.388(2), c 10.068(3) Å. In an investigation of the thermal behavior of the synthetic analogue of catapleite (Ilyushin & Dem'yanets 1988), the reversible phase-transition from the monoclinic modification to the hexagonal one was established to occur at $T = 155^\circ\text{C}$ (the reverse transformation occurs at 145°C).

Calcium catapleite, $\text{CaZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, was considered to be an end member of a solid-solution series with catapleite, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, and consequently was originally described as presenting "the crystal lattice of catapleite" (Portnov 1964), which, at the time, according to the indication of Brunowsky (1936), was assumed

to be hexagonal, space group $P6_3/mmc$. However, the subsequent structural investigations carried out on catapleite with modern X-ray methods (Chao *et al.* 1973, Ilyushin *et al.* 1981) did not confirm that indication and suggested that the hexagonal symmetry of catapleite as claimed could be not correct (Piatenko *et al.* 1999), probably the result of an involuntary omission of a set of very weak reflections and of pervasive polysynthetic twinning [a careful study of the multiple twinning in catapleite was made by Chen & Chao (1974)].

For these reasons, the crystallographic data normally reported for calcium catapleite, indicating that it is hexagonal, space group $P6_3/mmc$, a 7.32, c 10.15 Å (cell parameters calculated by analogy with catapleite in ICDD 13–371), are not reliable. This lack of reliable data concerning the metrics and the symmetry of calcium catapleite, as well as our interest in deriving its actual structural arrangement and defining the difference between it and that of catapleite, stimulated us to carry out a characterization by XRD using some fragments kindly provided to us by N.V. Vladykin, taken from Portnov's holotype specimen.

EXPERIMENTAL

Chemical analyses were carried out by means of a Camebax MBX electron microprobe equipped with a LINK 10000 energy-dispersion X-ray spectrometer, operating at 10 kV and 10 nA. The electron beam was rastered over an area of $10 \times 10 \mu\text{m}^2$ to minimize damage to the sample. We used the following standards: albite (Na), orthoclase (K), amphibole (Ca, Si), and wadeite (Zr). The results obtained (Table 1) are very close, at least for the main constituents, to the data published by Portnov (1964). Results of our analysis correspond to the following empirical formula, calculated on

TABLE 1. CHEMICAL COMPOSITION OF CALCIUM CATAPLEITE FROM THE BURPALA MASSIF, RUSSIA

	1	2
Na_2O wt.%	0.32	0.38 (0.15–0.44)
K_2O	0.10	0.05 (0.00–0.08)
CaO	13.82	13.59 (13.32–13.74)
REE_2O_3	0.28	b.d.l.
Fe_2O_3	0.36	b.d.l.
Al_2O_3	0.60	b.d.l.
SiO_2	44.49	44.99 (44.51–45.39)
TiO_2	0.06	b.d.l.
ZrO_2	31.00	31.03 (30.58–31.33)
H_2O^*	9.15	9.01*
H_2O^-	0.18	-
Total	100.36	99.05

NOTE: 1: wet-chemical data (Portnov 1964), 2: our electron-microprobe data for the sample under study (average values from four analyses); b.d.l.: below the detection limit; *: calculated so as to give 2 H_2O molecules per formula unit.

the basis of 11 O atoms: $(\text{Ca}_{0.97}\text{Na}_{0.05})_{\Sigma 1.02}\text{Zr}_{1.01}\text{Si}_{2.99}\text{O}_9 \cdot 2\text{H}_2\text{O}$.

A crystal fragment (dimensions $0.2 \times 0.1 \times 0.1 \text{ mm}^3$) was mounted on a Nonius Kappa CCD diffractometer, equipped with a MoK α X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operating at 55 kV and 30 mA. The intensity data were collected with a crystal-to-detector distance of 25 mm. As a first step, 20 ϕ -rotation images with frame-widths of 1° were collected for the initial orientation matrix and cell setting. A total of 334 frames, using frame-widths of 2° and exposure of 60 s, were collected, corresponding to 93.8% of the reciprocal space. The reflections were collected up to a resolution of 0.50 \AA ($\theta_{\text{max}} = 45.29^\circ$) in ca. 6.5 hours.

On the basis of the structural information available for catapleite and related structures, we carefully examined the frames for a possible doubling of the c parameter. Unexpectedly, whereas the c parameter was found to be ca. 10 \AA , we found the a parameter to be doubled (ca. 14.8 instead of ca. 7.4 \AA). The extraction of the data was therefore carried out assuming a hexagonal cell ($a \approx 14.8$, $c \approx 10.0 \text{ \AA}$; it will be denoted H2 in the following). The three-dimensional data were reduced using the DENZO-SMN program from Nonius, which is based on the HKL package (Otwinowski & Minor 1997). A semi-empirical absorption correction was accomplished in DENZO-SMN using the redundancy of data measurements. A total of 71220 reflections were extracted from the collected images. The value of R_{int} , computed on squared structural amplitudes by merging equivalent reflections in the $P6_3/mmc$ space group after absorption correction, was 6.3%. A set of 30128 independent reflections was obtained.

At this stage, a careful inspection of the intensities of the reflections in the hexagonal cell revealed that all reflections with both h and k even were, on average, about ten times more intense than the other reflections, thus pointing to a subcell H1 with a halved a axis. The whole diffraction-pattern, presented in Figure 1, has been interpreted as resulting from a triple twin (in German, "Drilling") of an orthorhombic cell O, with $a \approx 7.4 \text{ \AA}$, $b \approx \sqrt{3}a$, $c \approx 10.1 \text{ \AA}$, with rotation axis $[001]_{\pm 120^\circ}$. This type of reticular merohedral twinning may also be described as a multiple twin with twin axes $[110]_{180^\circ}$ and $[310]_{180^\circ}$; the latter two twin laws were already observed, together with four others, by Chen & Chao (1973) in crystals of catapleite. The relationships among the various reciprocal lattices are illustrated in Figure 1. The reflections in the orthorhombic setting are of two types, namely those that correspond to the reciprocal lattice points of the hexagonal H1 cell (*subcell* reflections, with $h_{\text{O}} + k_{\text{O}} = 2n$, indicated with large circles in Fig. 1), and those that are not present in the H1 diffraction pattern (*characteristic* reflections, with $h_{\text{O}} + k_{\text{O}} = 2n + 1$, indicated with small circles in Fig. 1). The *subcell* reflections are common to the three orthorhombic individuals, whereas the *characteristic* reflections are not. To test the "Drilling" hypothesis, we

selected a few rather strong *characteristic* reflections ($n = 10$, with 2θ angles ranging between 15 and 40°) and measured their intensities in the three individuals; the ratios of the intensities was found to be constant, indicating that the volume proportions of the three individuals were 50, 40 and 10%. Of course, the structure determination and refinement were carried out by selecting the largest individual, for which the hkl indices were adequately converted from the hexagonal H2 setting; moreover, a different scale-factor was assigned to the common *subcell* reflections, to place them on the same scale as the *characteristic* non-superimposed reflections.

The orthorhombic unit-cell has $a 7.378(1)$, $b 12.779(1)$, $c 10.096(1) \text{ \AA}$, space-group symmetry $Pbnn$, determined on the basis of the systematic absences. The non-standard space-group was adopted to keep the correspondence with the H1 and H2 settings.

Eventually, a set of 21775 reflections was obtained in the orthorhombic unit-cell. The set was reduced to 4002 independent squared amplitudes ($R_{\text{int}} = 9.81\%$). Only those reflections with $F_{\text{O}} > 6\sigma(F_{\text{O}})$ were considered as observed, and used in the least-square refinement. A higher-than-usual cutoff was chosen to overcome minor inaccuracies due to the treatment of twinned data. The structure of calcium catapleite was solved through direct methods using the SIR-92 program (Altomare *et al.* 1994) and refined with the SHELXL-97 software package (Sheldrick 1997).

In total, the positions of one Zr, two Ca, two Si, and six O atoms, one of which belonging to a H_2O molecule, were determined and refined. In the last cycles of least-square refinement (the final index of reliability $R1$ was 0.053 for 2167 observed reflections), the positions of the H atoms belonging to the H_2O molecule were found in the difference-Fourier map, and refined with loose metrical constraints on the relevant O-H distances through the DFIX option of SHELX-97. Further details concerning the collection of the single-crystal X-ray data and the structure refinement are given in Table 2.

The atom coordinates and site occupancies, displacement parameters, selected interatomic distances, and bond-valence sums (Brese & O'Keeffe 1991, Ferraris & Ivaldi 1988) are reported in Tables 3a, 3b, 4, and 5, respectively. A table of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. The crystal structure of calcium catapleite is shown in Figure 2.

Finally, for comparative purposes, the structure of calcium catapleite was also refined in the hexagonal H1 subcell [space group $P6_3/mmc$, $a 7.378(1)$, $c 10.096(1) \text{ \AA}$], using only those reflections common to the three twin individuals. In this case, the final R factor was found to be 4.68% for 704 unique reflections. Despite its slightly higher index of reliability, the orthorhombic model is definitely preferable, as it takes into account those reflections omitted in the refinement of

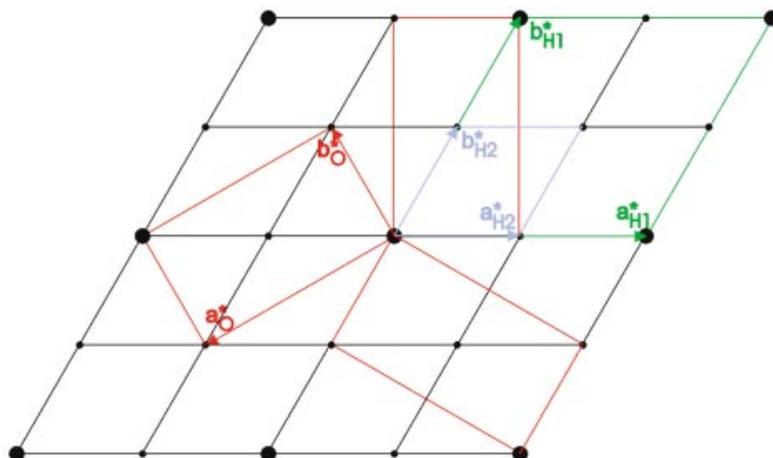


FIG. 1. Drawing of the reciprocal lattices of the hexagonal cell with $a = 7.4 \text{ \AA}$ (H1, in green), the hexagonal cell with $a = 14.8 \text{ \AA}$ (H2, in blue), and the orthorhombic cell (O, in red) of the "Drilling".

TABLE 2. INFORMATION ON DATA COLLECTION AND REFINEMENT FOR CALCIUM CATAPLEIITE

Chemical formula	CaZrSi ₃ O ₉ ·2H ₂ O
Unit-formula weight	393.59
Radiation and wavelength (Å)	MoK α ; 0.71069
μ (mm ⁻¹)	2.12
Diffractometer, monochromator	Nonius CCD, graphite
Space group	<i>Pbnn</i>
Z	4
Unit-cell dimensions (Å)	a 7.378(1), b 12.779(1), c 10.096(1)
Unit-cell volume (Å ³)	951.89
$F(000)$	768.0
D_{calc} (g/cm ³)	2.746
Crystal size (mm ³)	0.2 × 0.1 × 0.1
Index ranges	$-12 \leq h \leq 14$, $-14 \leq k \leq 14$, $-19 \leq l \leq 20$
Standard reflection	Every 100 reflections
No. collected reflections	21775
No. reflections with $I > 3\sigma(I)$	2167, $R_{int} = 0.0981$
Refinement method	full-matrix least-squares on F^2
Weights	$1/[\sigma^2(F_o^2) + (0.0376P)^2 + (8.10P)]$, $P = [\max(F_o, 2) + 2(F_c)^2]/3$
$R(F)$, $wR(F^2)$, GooF	0.0528, 0.1601, 1.025
Number of refined parameters	91
Largest residues ($e/\text{\AA}^3$)	1.54, -5.51

Numbers in parentheses are estimated standard deviations referred to the last digit.

the hexagonal model, and properly describes the Ca distribution in calcium catapleite, as will be discussed in the next section and is illustrated in Figure 3.

DISCUSSION

The topology of calcium catapleite corresponds to that already described for catapleite (Ilyushin *et al.* 1981). The latter authors refined the structure of catapleite in a non-standard space group (*B2/b*) and unconventional monoclinic setting with a very large

obtuse angle $\gamma = 147^\circ$. As stated above, their unit cell can be transformed into a nearly metrical orthorhombic cell that matches our unit cell, apart from the doubled c parameter.

In common with catapleite, the most specific feature of calcium catapleite is a mixed framework of regular $[\text{ZrO}_6]$ octahedra and three-membered $[\text{Si}_3\text{O}_9]$ silicate rings. This kind of mixed framework is also displayed in the isotopic pairs of Ti- and Zr-minerals and analogous synthetic compounds: wadeite, $\text{K}_2\text{Zr}[\text{Si}_3\text{O}_9]$ (Henshaw 1955), the synthetic Ti-dominant analogue of wadeite (Choisnet *et al.* 1973), bazirite $\text{BaZr}[\text{Si}_3\text{O}_9]$ (Hawthorne 1987), benitoite $\text{BaTi}[\text{Si}_3\text{O}_9]$ (Fischer 1969), pabstite $\text{Ba}(\text{Sn}, \text{Ti})[\text{Si}_3\text{O}_9]$ (Hawthorne 1987), and the synthetic Ca-dominant analogue of pabstite $\text{CaSn}[\text{Si}_3\text{O}_9]$ (benitoite structure-type; Nekrasov 1973).

The three-membered $[\text{Si}_3\text{O}_9]$ rings in calcium catapleite are built up of two crystallographically independent $[\text{SiO}_4]$ tetrahedra, one lying on the twofold axis parallel to \mathbf{b} , the other on a general position. The calcium cations and the H_2O molecule are located in tunnels formed by the framework of tetrahedra and octahedra and running parallel to $[100]$, $[110]$ and $[10]$. The relevant bond-distances are presented in Table 4. The H_2O molecule O(6) is connected through weak hydrogen bonds to O(1) ($-x + 3/2, y, -z + 3/2$) [O(6)...O(1) distance 3.07 Å] and possibly to O(2) ($-x + 1, y + 1/2, z$) and O(5) ($-x + 1, -y + 1, -z + 2$) with a bifurcated hydrogen bond [O(6)...O(2) and O(6)...O(5) distances 3.18 and 3.20 Å, respectively].

It is worthy of note that a complex of tetrahedra in the form of a three-membered ring is quite rare in minerals. It almost exclusively occurs in the structures of cyclosilicates, as in walstromite $\text{BaCa}_2[\text{Si}_3\text{O}_9]$ (Dent

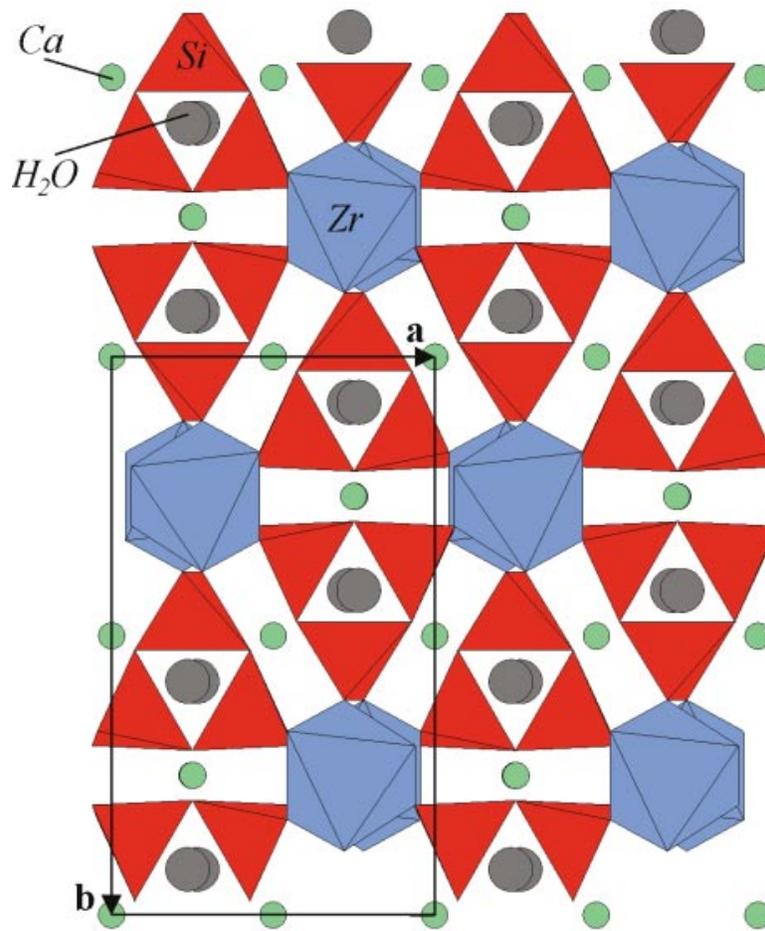


FIG. 2. Projection of the crystal structure of calcium catapleite on (001), drawn with the program ATOMS (Dowty 1995).

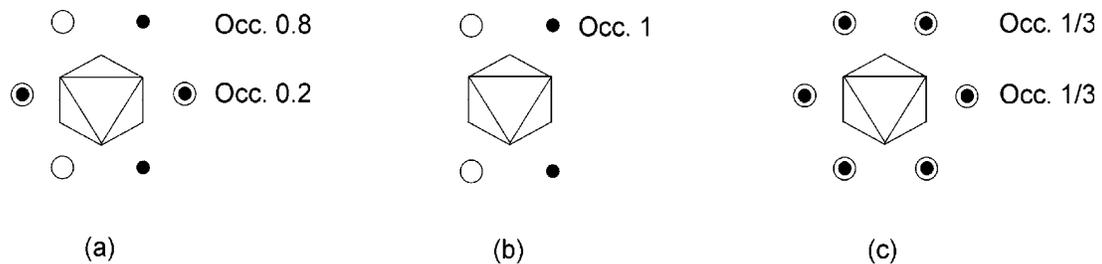


FIG. 3. Positions of the calcium cations in calcium catapleite, with an indication of the corresponding occupancies, around the columns of $[ZrO_6]$ octahedra running along c . (a) Actual distribution in calcium catapleite, (b) ordered distribution in calcium catapleite, and (c) fully disordered distribution of calcium cations, corresponding to the actual distribution of sodium cations in catapleite (Ilyushin *et al.* 1981) and to the distribution found in the refinement carried out in the hexagonal H1 subcell of calcium catapleite.

TABLE 3a. FRACTIONAL COORDINATES OF ATOMS, WYCKOFF SITE-MULTIPLICITIES AND OCCUPANCY COEFFICIENTS FOR CALCIUM CATAPLEIITE

Atom	x	y	z	Wyckoff multiplicity	SOF
Zr	0.7442(1)	0.2500	0.0000	0.5	1.0
Si(1)	0.4545(1)	0.3467(1)	0.7488(1)	1	1.0
Si(2)	0.2500	0.5528(1)	0.7500	0.5	1.0
Ca(1)	0.5000	0.5000	0.0000	0.5	0.776(4)
Ca(2)	0.7485(7)	0.7500	0.0000	0.5	0.224(4)
O(1)	0.4285(4)	0.4746(2)	0.7374(3)	1	1.0
O(2)	0.2500	0.2949(4)	0.7500	0.5	1.0
O(3)	0.2803(5)	0.6148(3)	0.8839(3)	1	1.0
O(4)	0.5602(6)	0.3030(3)	0.6250(3)	1	1.0
O(5)	0.5434(6)	0.3293(5)	0.8904(3)	1	1.0
O(6)	0.7630(6)	0.5827(4)	0.9143(5)	1	1.0
H(1)	0.885(6)	0.555(8)	0.892(7)	1	1.0
H(2)	0.768(9)	0.581(7)	0.013(1)	1	1.0

Numbers in parentheses are estimated standard deviations referred to the last digit. SOF: site-occupancy factor.

TABLE 3b. DISPLACEMENT PARAMETERS FOR CALCIUM CATAPLEIITE

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq} /U _{iso}
Zr	0.0098(2)	0.0113(2)	0.0066(2)	0.0001(1)	0	0	0.0092(1)
Si(1)	0.0119(3)	0.0154(4)	0.0087(3)	-0.0007(4)	0.0002(4)	0.0024(3)	0.0119(2)
Si(2)	0.0150(5)	0.0108(5)	0.0086(4)	0	-0.0018(6)	0	0.0115(2)
Ca(1)	0.0188(6)	0.0134(5)	0.0147(5)	-0.0025(5)	-0.0046(5)	0.0043(4)	0.0157(3)
Ca(2)	0.0106(14)	0.0213(18)	0.0116(14)	0.0044(14)	0	0	0.0145(8)
O(1)	0.0160(11)	0.0147(10)	0.0229(15)	0.0036(11)	0.0021(11)	0.0010(9)	0.0179(5)
O(2)	0.0121(14)	0.0181(16)	0.0354(23)	0	-0.0017(19)	0	0.0219(8)
O(3)	0.0259(16)	0.0266(15)	0.0159(12)	-0.0106(12)	0.0039(11)	-0.0016(12)	0.0228(7)
O(4)	0.0393(21)	0.0317(19)	0.0165(14)	-0.0035(14)	-0.0098(14)	-0.0107(16)	0.0292(8)
O(5)	0.0290(16)	0.0297(16)	0.0115(11)	-0.0039(11)	0.0066(12)	0.0148(14)	0.0234(7)
O(6)	0.0300(21)	0.0390(22)	0.0455(24)	-0.0024(20)	-0.0090(19)	0.0069(19)	0.0382(9)
H(1)							0.09(3)*
H(2)							0.04(2)*

Numbers in parentheses are estimated standard deviations referred to the last digit. * U_{iso} values.

Glasser & Glasser 1968), margarosanite PbCa₂[Si₃O₉] (Freed & Peacor 1969) and the high-temperature polymorph (T > 1125°C) of CaSiO₃ (α-CaSiO₃, pseudowollastonite; Yang & Prewitt 1999), in α'-CaSiO₃, which forms at high pressure (Ilyukhin *et al.* 1979), and in synthetic compounds of the benitoite structure-type: BaTiGe₃O₉ (Robbins 1960); TlTiGe₃O₉, CsBX₃O₉ (B = Ti, Sb; X = Si, Ge) (Choisnet *et al.* 1973), in metafluorberillates, with the general formula Me⁺Me²⁺

(BeF₃)₃ (Me⁺ = Rb, NH₄, Tl; Me²⁺ = Mg, Ni, Co, Zn) (Favre *et al.* 1969), in NaBaNd[Si₃O₉] (Malinovskii *et al.* 1984) and in (NH₄)₂ZrGe₃O₉ (Liu *et al.* 2003), with the wadeite structure-type. Only very rarely do silicate three-membered rings occur in more condensed silicate anions, as in the sheet silicate zussmanite (Lopes-Vieira & Zussman 1969). They never occur in framework silicates (zeolites and zeolite-like materials).

The relatively low stability of three-membered silicate rings reflects the large deviations of the Si–O–Si angles ($\approx 130^\circ$) from 147° , which is typical of a ring of tetrahedra with low energy (Chakoumakos *et al.* 1981). The structure of calcium catapleiite does not represent an exception in this sense: the values of the bond angles Si(1)–O(2)–Si(1) ($-x + 1/2, y, -z + 3/2$) and Si(1)–O(1)–Si(2) are 132.59° and 133.19° , respectively, similar to values found in the other silicates with three-membered rings. As the Si–O–Si angles narrow, the higher repulsion between the Si atoms and the decreasing *s*-character of the bridging oxygen (O_{br}) orbitals (decreasing π -bond strengths) are factors leading to longer Si– O_{br} bonds (Gibbs *et al.* 1972) and lower stability of the ring. According to Chakoumakos *et al.* (1981), the *s*-component in the hybrid orbitals of the bridging oxygen can be estimated simply on the basis of the equation $d(\text{Si}-O_{br}) = -3.5 \times 10^{-3} \delta + 1.78$, where δ is the percent fractional *s*-character. This *s*-component in calcium catapleiite is 36.1%, which is significantly lower than in the silicates with four- or six-membered silicate rings (close to 47%) (Pushcharovsky 1986).

The main difference between the structures of catapleiite and calcium catapleiite lies in the occupancy

of the larger, [8]-coordinated cationic sites. In catapleiite, Na is statistically distributed among five different sites (four with multiplicity 4 and one with multiplicity 8), all of which present a 1/2 occupancy. The investigations of the thermal behavior of catapleiite (Ilyushin & Dem'yanets 1988) indicate that there is no variation in the distribution of Na among these sites at higher T; "the transition to the more symmetrical hexagonal phase leads to symmetrization of the framework and to equalization of the bond lengths" for the various Na atoms; thus the transition (at 155°C) is of the *displacement* kind and "the distances through which the Na atoms move are much smaller than the interatomic distances" (Ilyushin & Dem'yanets 1988). In calcium catapleiite, cations Ca(1) and Ca(2) are distributed between two sites, both with multiplicity 4, with largely different occupancies, 0.8 and 0.2, respectively, as schematically represented in Figure 3a. This figure shows the positions of the calcium cations, with an indication of the corresponding occupancies, around the columns of $[\text{ZrO}_6]$ octahedra running along *c*. The actual distribution is compared to a perfectly ordered distribution [Fig. 3b: occupancies 1.0 and 0.0 at Ca(1) and Ca(2) sites, respectively] and with a distribution (Fig. 3c) corresponding to that in catapleiite, with occupancy 1/2 instead of 1/2 owing to the different cationic charge. In the case of occupancy 1/2 in both Ca(1) and Ca(2) sites, the orthorhombic symmetry of calcium catapleiite would be preserved. We may presume that in the case of calcium catapleiite, a phase transformation of the *order-disorder* type will take place at high temperature, made possible by Ca diffusion along the tunnels of the framework; however, we cannot reliably foresee which would be the final step in the transformation, namely whether it will correspond to the equalization of the occupancies in the Ca(1) and Ca(2) sites with preservation of the orthorhombic symmetry, or to that described in Figure 3c, with transition to a hexagonal form (space group $P6_3/mmc$) with unit-cell H1. It would be very interesting to carry out a high-temperature investigation to monitor the transformation path and to define the transition tem-

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF CALCIUM CATAPLEIITE

Ca(1) – O(6)	2.373(5) × 2	Si(1) – O(4)	1.576(4)
– O(5)	2.467(3) × 2	– O(5)	1.589(3)
– O(3)	2.481(4) × 2	– O(1)	1.648(3)
– O(1)	2.723(3) × 2	– O(2)	1.649(2)
<Ca(1) – O>	2.511	<Si(1) – O>	1.616
Ca(2) – O(6)	2.310(5) × 2	Si(2) – O(3)	1.582(3) × 2
– O(2)	2.588(1) × 2	– O(1)	1.658(3) × 2
– O(5)	2.625(6) × 2	<Si(2) – O>	1.620
– O(4)	2.710(6) × 2		
<Ca(2) – O>	2.561		
Zr – O(4)	2.033(4) × 2		
– O(3)	2.096(3) × 2		
– O(5)	2.109(3) × 2		
<Zr – O>	2.079		

TABLE 5. BOND-VALENCE SUMS (*v.u.*) FOR CALCIUM CATAPLEIITE

	Zr	Ca(1)*	Ca(2)*	Si(1)	Si(2)	ΣH^v	Σ_v
O(1)		0.101 ⁺²¹		0.935	0.912 ⁺²¹	+0.12	1.960
O(2)			0.042 ⁺²⁺²¹	0.937 ⁺²⁺		+0.05	2.008
O(3)	0.651 ⁺²¹	0.193 ⁺²¹			1.120 ⁺²¹		1.964
O(4)	0.771 ⁺²¹		0.030 ⁺²¹	1.139			1.940
O(5)	0.628 ⁺²¹	0.201 ⁺²¹	0.038 ⁺²¹	1.099		+0.05	2.016
O(6)		0.259 ⁺²¹	0.086 ⁺²¹			-0.22	0.125
Σ_v	4.100	1.508	0.392	4.110	4.064		

* The bond strength was calculated considering the partial occupancy of Ca sites resulting from the structural refinement.

perature and the structural arrangement of the high-temperature form.

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