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CAYSICHITE: A DOUBLE CRANKSHAFT CHAIN STRUCTURE

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ABSTRACT

The crystal structure of caysichite was determined and refined to R=0.06, using 959 independent reflections; the space group is $Ccm2_1$, with a 13.27(1), b 13.91(1), c 9.73(1)Å. The crystal chemical formula is $Y_4(Ca_3RE_1)(OH)(H_2O)_5[Si_8O_{20}](CO_3)_6 \cdot 2H_2O$, with two such formula units in the unit cell. Columns of yttrium, calcium and rare-earth polyhedra are parallel to [001]. The columns outline a checkered pattern of channels occupied by four-repeat double chains of silicate tetrahedra. A close tightening of the polyhedral framework is assured by carbonate groups wedged between corner-sharing polyhedra. The chains of silicate tetrahedra are shaped as double crankshafts like those chains which build up the structures of feldspars and various other framework silicates.

SOMMAIRE

La structure cristalline de la caysichite a été déterminée et affinée jusqu'au résidu R=0.06 sur 959 réflexions indépendantes, dans le groupe spatial $Ccm2_1$. La maille (a 13.27(1), b 13.91(1), c 9.73(1)Å) contient deux unités formulaires $Y_4(Ca_3TR_1)(OH)(H_2O)_5[Si_8O_{20}](CO_3)_6 \cdot 2H_2O$. La structure comporte des colonnes de polyèdres de coordination d'yttrium, de calcium et de terres rares, parallèles à [001]. Les colonnes marquent une disposition en damier de tunnels qui sont occupés par des chaînes doubles de tétraèdres de coordination du silicium. L'assemblage des polyèdres est renforcé par des groupes carbonates insérés, tels des coins, entre polyèdres à sommets communs. Les chaînes de tétraèdres de silicium ont la forme d'un vilebrequin double, en ceci semblables aux chaînes des feldspaths et autres silicates à charpente de tétraèdres.

(Traduit par la Rédaction)

INTRODUCTION

Caysichite was discovered by Hogarth *et al.* (1974) in the Evans Lou Mine, Quebec, Canada, a locality well-known for its interesting yttrium and rare-earth silicates (Hogarth 1971, 1972; Miles *et al.* 1971). In the present paper rare earths will include elements with atomic number 57-71 (La-Lu), but not yttrium. The formula proposed by Hogarth *et al.* (1974) is $(Ca,Y)_4Si_4O_{10}(CO_3)_3 \cdot 4H_2O$, with a 13.282(3), b 13.925(3), c 9.724(4)Å, space group $Ccmm$ or $Ccm2_1$, Z=4, D(calc) 3.029g cm^{-3}, D(obs) 3.03g cm^{-3}. The mineral occurs as coatings on fractures or as incrustations, and is most closely associated with hellandite, but is found also with other rare-earth minerals. Hogarth *et al.* (1974) suggested that caysichite formed by supergene alteration of hellandite.

EXPERIMENTAL

A fine specimen of caysichite was kindly given to us by Hogarth. We found a small crystal 0.05×0.03×0.18mm which did not show evidence of subparallel growth of many individuals, a feature typical of the mineral. Rotation and Weissenberg photographs confirmed the unit-cell data given by Hogarth *et al.* (1974). Cell parameters, obtained with a Philips PW 1100 single-crystal automatic diffractometer, using Mo$K\alpha$ radiation, are a 13.27(1), b 13.91(1), c 9.73(1)Å, with possible space groups $Ccmm$ (D^{17}_{2h}), $Ccm2_1$ (C^{12}_{2v}) or $Cc2m$ (C^{16}_{2v}). Intensity data from one independent octant were collected on the same diffractometer, using graphite monochromatized Mo$K\alpha$ radiation (λ=0.7107Å), scan width 1.20°, scan speed 0.04° sec^{-1}, θ–2θ scan, from 3° to 35° in θ. Among the 2169 available reflections, 1116 were skipped in the intensity data collection step, as they had $I_{top} - 2\sqrt{I_{top}} < I_{back}$, with I_{top} and I_{back} indicating peak intensity and background intensity, respectively. Lorentz and polarization factors were applied in the usual way; no absorption correction was made, owing to the small dimensions of the crystal. Of the 1053 collected reflections, 94 were considered "not observed", having observed structure factors F_{obs} less than three times the corresponding standard deviation $\sigma(F_{obs})$, estimated from counting statistics.

STRUCTURE DETERMINATION AND REFINEMENT

Crystal structure determination began in the centrosymmetric space group $Ccmm$. A Patterson synthesis located the heavy atom (Y,Ca,RE).

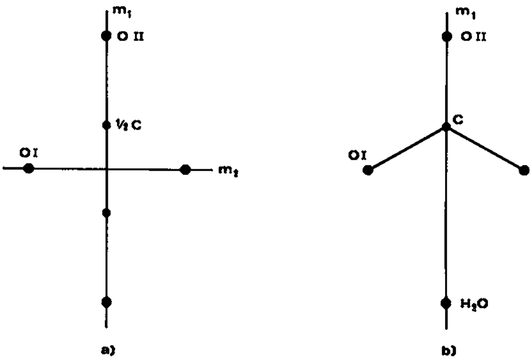

FIG. 1. a) Schematic drawing showing the apparent situation around the C(2) carbon atom in *Ccmm* space group; b) its interpretation in the *Ccm*2₁ space group.

Successive Fourier syntheses located all the atoms in the unit cell, except for hydrogen. Isotropic refinement dropped the *R* value to 0.10. The model so obtained was satisfactory in terms of the main features of the structure, as well as the coordination of silicon and (Y,Ca, RE) cations, but showed a severe problem in the location of a carbonate group. Figure 1a shows the apparent situation as indicated by the peaks in the Fourier synthesis: m_1 and m_2 indicate the traces of the reflection planes normal to *b* and *c*, respectively, in the *Ccmm* space group. There are two possible interpretations: the first interpretation assumes a disordered location of the carbonate group on both sides of the symmetry plane m_2 with a water molecule in the OII position, not linked to the carbon atom. This interpretation was discarded because when refining the model in the space group *Ccmm*, we obtained a relatively high *R* value and standard deviations too high for the atoms involved in the disorder, and unrealistic carbon to oxygen distances. The second interpretation, represented in Figure 1b, assumes an ordered distribution of carbonate groups and water molecules and requires a decrease in symmetry from *Ccmm* to *Ccm*2₁. Hogarth *et al.* (1974) observed a dome in caysichite crystals under high magnification and Mandarino (1976) correctly remarked that "if the form identified as a dome is truly a dome, the choice of the space group is narrowed to *Ccm*2₁".

The starting model in the *Ccm*2₁ space group was not far from centrosymmetric and, in the refinement, high standard deviations of various parameters together with unrealistic bond lengths and angles were obtained. All this conforms with the remarks by Rae (1974) concerning the difficulties of refining nearly centrosymmetric structures. Therefore, we used a version of ORFLS (Busing *et al.* 1962) modified by G. Ferraris (priv. comm.) according to the suggestions of Rae (1974). Two cycles with anisotropic

TABLE 1. ATOMIC POSITIONAL AND THERMAL PARAMETERS (EST. STANDARD DEVIATIONS IN PARENTHESES)

Atom	x	y	z	B*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	0.1403(1)	0.1710(1)	0.0422(0)**	0.96	91(4)	147(5)	289(10)	21(6)	-13(6)	52(7)
CaRE	0.1471(1)	0.1647(1)	0.4574(1)	1.19	117(6)	198(8)	320(13)	-40(7)	26(8)	-58(8)
Si(1)	0.3990(2)	0.1103(2)	0.0880(3)	0.30	56(14)	21(14)	91(27)	-10(12)	-41(7)	9(17)
Si(2)	0.4069(2)	0.1118(2)	0.4039(3)	0.10	18(13)	15(13)	17(24)	-7(11)	7(15)	2(16)
O(1)	0.3672(9)	0.0	0.0618(11)	0.23	85(56)	2(47)	21(91)	0	-51(64)	0
O(2)	0.3774(9)	0.0	0.4311(11)	0.80	129(65)	128(63)	133(110)	0	141(67)	0
O(3)	0.4390(6)	0.1228(6)	0.2457(8)	0.62	130(40)	72(42)	101(74)	-31(34)	-103(46)	-29(46)
O(4)	0.3092(6)	0.1808(7)	0.0559(8)	0.54	42(35)	99(45)	146(73)	0(34)	19(42)	77(48)
O(5)	0.3187(6)	0.1831(6)	0.4555(9)	0.70	106(40)	71(46)	212(80)	49(35)	-30(46)	-79(48)
O(6)	0.4953(7)	0.1382(7)	-0.0054(9)	1.19	133(42)	230(50)	224(75)	38(41)	115(51)	-77(55)
O(12)	0.1520(7)	0.2780(6)	0.2482(9)	0.89	126(45)	106(42)	255(80)	-21(38)	118(55)	5(47)
O(13)	0.3478(19)	0.0	0.7445(28)	6.50	850(200)	940(200)	1650(400)	0	-950(250)	0
O(14)	0.1698(14)	0.0	0.5297(17)	2.62	700(150)	90(75)	580(180)	0	360(130)	0
C(1)	0.0681(9)	0.1527(9)	0.7562(13)	0.89(19)						
C(2)	0.1622(12)	0.0	0.1851(18)	0.68(26)						
O(7)	0.1632(8)	0.1381(9)	0.7701(12)	2.41(20)						
O(8)	0.0226(7)	0.1597(7)	0.6407(9)	1.26(15)						
O(9)	0.0200(6)	0.1635(7)	0.8693(9)	1.09(14)						
O(10)	0.1391(11)	0.0	0.0583(14)	1.59(21)						
O(11)	0.1721(6)	0.0809(7)	0.2538(9)	0.69(13)						

* Anisotropic thermal parameters (x10^5) are of the form exp $(-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23}))$. Under column B, isotropic thermal parameters or B equivalent according to Hamilton (1959).

***z* coordinate of *Y* atom was fixed to define the origin of the polar *Ccm*2₁ space group.

thermal motion for all the atoms except those of the carbonate groups, and with the weight of each reflection assigned as $1/\sigma(F_o)^2$, led the reliability factor R to 0.06. In $Ccm2_1$ the (Y, Ca,RE) atoms have to be placed on two 8-fold general positions whereas they occupy one 16-fold general position in *Ccmm;* the cation distribution between the two crystallographically independent sites was adjusted on the basis of the chemical analysis, values of the thermal parameters and the bond-valence balance. One site is fully occupied by yttrium cations (Y site), whereas the other site is occupied by calcium and rare-earth cations with an estimated ratio Ca:RE=3:1 (CaRE site). This agrees with the mean values of the cation–oxygen distances in the polyhedra, 2.403 and 2.492Å for the Y and CaRE sites, respectively. A ΔF synthesis, calculated at this stage, did not show any troublesome peak. All the scattering factors for neutral atoms used in structure factors calculations were taken from International Tables for X-ray Crystallography (1962). Final atomic positional and thermal parameters are given in Table 1. Observed and calculated structure factors are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Description and Discussion of the Structure

The main features of the crystal structure of caysichite are illustrated in Figures 2, 3 and 4. The structure can be described as built up by double columns of alternating CaRE (calcium and rare earths) and Y polyhedra, parallel to [001]: in each column CaRE and Y polyhedra alternately share an edge and a corner, with carbonate groups wedged between two succeeding corner-sharing polyhedra. Each double column is connected to four other double columns to build up a three-dimensional framework; the connections are assured by edge-sharing in the [100] direction and by corner-sharing in the [010] direction. Further tightening of the structure in the [010] direction is assured by wedging carbonate groups between symmetry-equivalent corner-sharing Y polyhedra. The double-column connection defines a checkered pattern of channels (Fig. 2) in which run four-repeat double chains of silicon-oxygen tetrahedra.

Silicate chain

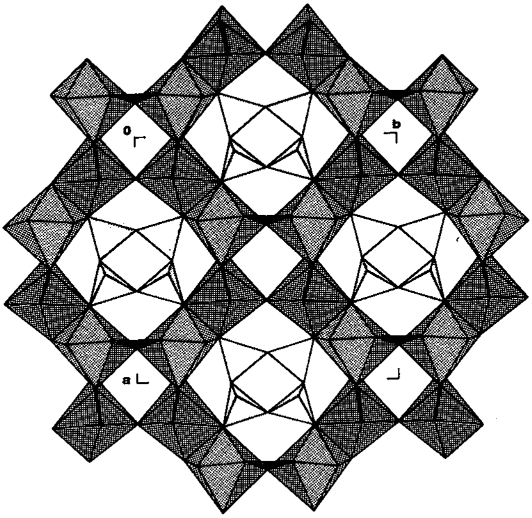

FIG. 2. Crystal structure of caysichite, projected on (001). Heavy stippling indicates Y and CaRE polyhedra, light stippling indicates Si tetrahedra, black triangles are C(2) carbonate groups and heavy lines indicate C(1) carbonate groups.

An interesting feature of the caysichite structure is the presence of so-called double crankshaft chains (Figure 4). These chains, cross-linked in different ways, give rise to the frameworks of feldspars, paracelsian, isostructural danburite, hurlbutite, phillipsite, isostructural harmotome, gismondine and phase A, a synthetic compound with composition $BaAlSi_2O_6$-(Cl,OH) (Solov'eva *et al.* 1972).

The repeat distance down a chain is largely dependent on the contracted or extended form assumed by the chain. Thus whereas the repeat distance ranges in feldspars from 8.183Å in anorthite to 8.603Å in sanidine (Smith 1974) and is 8.58Å in paracelsian (Bakakin 1963), an indication that in these minerals the chains are in a relatively contracted form, the repeat distance in phillipsite, harmotome, gismondine and phase A is 10Å, corresponding to a chain in the extended form. A similar value was found in caysichite (*c* 9.73Å), where the chains are isolated; they run in the large channels and are connected to the four double columns of CaRE and Y polyhedra delimiting the channels.

In the conventional classification of silicates, caysichite belongs to the chain silicates, in the subgroup characterized by four-repeat double chains of silicon–oxygen tetrahedra together with narsarsukite (Pyatenko & Pudovkina 1960; Peacor & Buerger 1962). According to the code developed by Smith & Rinaldi (1962) the chains in caysichite can be described as connected four-membered rings of the type *UUDD* projecting one over the other, whereas those in narsarsukite can be described as a similar connection of rings of type *UDUD*.

TABLE 2. BOND LENGTHS (Å), ANGLES (°), AND EDGE LENGTHS (Å) IN THE SILICATE CHAINS (EST. STANDARD DEVIATIONS IN PARENTHESES)

Si(1)-O(1)	1.610(5)	Si(2)-O(2)	1.626(5)
-O(2)	1.631(8)	-O(3)	1.606(8)
-O(3)	1.576(8)	-O(5)	1.615(9)
-O(4)	1.617(9)	-O(6)vii	1.610(9)
mean	1.608	mean	1.614
O(1)-Si(1)-O(3)	109.5(5)	O(2)-Si(2)-O(3)	108.2(5)
O(1)-Si(1)-O(4)	111.5(5)	O(2)-Si(2)-O(5)	111.0(5)
O(1)-Si(1)-O(6)	110.3(5)	O(2)-Si(2)-O(6)vii	108.8(6)
O(3)-Si(1)-O(4)	111.5(5)	O(3)-Si(2)-O(5)	115.7(5)
O(3)-Si(1)-O(6)	104.1(5)	O(3)-Si(2)-O(6)vii	107.1(5)
O(4)-Si(1)-O(6)	109.7(5)	O(5)-Si(2)-O(6)vii	105.7(5)
O(1)-O(3)	2.647(12)	O(2)-O(3)	2.618(12)
O(1)-O(4)	2.633(10)	O(2)-O(5)vii	2.671(10)
O(1)-O(6)	2.648(12)	O(2)-O(6)iv	2.632(12)
O(3)-O(4)	2.651(11)	O(3)-O(5)	2.727(12)
O(3)-O(6)	2.562(12)	O(3)-O(6)	2.562(12)
O(4)-O(6)	2.612(12)	O(5)-O(6)vii	2.571(12)
Si(1)-O(3)-Si(2)	143.6(5)	Si(1)-O(1)-Si(1)iii	144.6(5)
Si(1)-O(6)-Si(2)ix	152.9(5)	Si(2)-O(2)-Si(2)iii	145.9(5)

In tables 2, 3 and 5 the atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

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

With regards to the bond lengths in silicon–oxygen tetrahedra (Table 2), it is worth noting that whereas the length of Si(1)–O(4) non-bridging bond (1.576Å) is significantly shorter than those of bridging bonds in the same tetrahedron, the length of Si(2)–O(5) non-bridging bond (1.615Å) does not differ significantly from those of the bridging bonds in the Si(2) tetrahedron. The atoms O(4) and O(5) have different surroundings (Table 3): both are linked to Y and CaRE cations, but whereas the Y–O(4) and Y–O(5) distances are similar, 2.249Å and 2.265Å respectively, the CaRE–O(4) bond length (2.421Å) is much larger than that of the CaRE–O(5) bond (2.293Å).

CaRE, Y polyhedra and carbonate groups

The Y cation is coordinated with two oxygen atoms of the silicate chain, five oxygen atoms of the carbonate groups and a water molecule, with Y–O distances ranging from 2.249Å to 2.680Å (Table 3). The cations in the CaRE site are coordinated with two oxygen atoms of the silicate chain, three oxygen atoms of the carbonate groups, a water molecule and an oxygen atom which corresponds, as will be explained in the following section, either to a water molecule or a hydroxyl anion with equal occupancies: CaRE–O distances range from 2.293Å to

TABLE 3. BOND AND EDGE LENGTHS (Å) FOR *Y* AND Ca*RE* POLYHEDRA, AND BOND LENGTHS (Å) AND ANGLES FOR CARBONATE GROUPS

		Y polyhedron			
Y-O(4)	2.249(8)	O(7)ix-O(9)ix	2.153	O(7)ii-O(5)vi	3.071
-O(5)vi	2.265(9)	O(10)-O(11)	2.252	O(4)-O(12)	3.111
-O(9)ii	2.322(9)	O(9)vii-O(8)viii	2.702	O(9)ii-O(5)vi	3.137
-O(8)viii	2.375(9)	O(4)-O(5)vi	2.723	O(10)-O(8)viii	3.193
-O(10)	2.382(8)	O(11)-O(12)	2.754	O(10)-O(9)ii	3.326
-O(11)	2.446(8)	O(12)-O(5)vi	2.924	O(4)-O(10)	3.379
-O(12)	2.505(9)	O(4)-O(11)	2.991	O(10)-O(7)ii	3.393
-O(7)ix	2.680(16)	O(11)-O(8)viii	3.015	O(4)-O(7)ii	3.423
		O(12)-O(8)viii	3.031	O(5)vi-O(8)viii	3.922
		CaRE polyhedron			
CaRE-O(5)	2.293(8)	O(7)-O(8)	2.279	O(5)-O(11)	3.111
-O(11)	2.324(8)	O(8)-O(9)viii	2.702	O(8)-O(14)	3.145
-O(9)viii	2.373(9)	O(5)-O(4)v	2.723	O(8)-O(4)v	3.251
-O(14)	2.418(6)	O(11)-O(12)	2.754	O(5)-O(12)	3.274
-O(4)v	2.421(9)	O(11)-O(14)	2.916	O(5)-O(14)	3.303
-O(8)	2.433(17)	O(11)-O(9)viii	3.013	O(7)-O(14)v	3.305
-O(12)	2.572(9)	O(12)-O(9)viii	3.019	O(14)-O(9)viii	3.734
-O(7)	3.100(14)	O(7)-O(14)	3.044	O(5)-O(7)	3.764
		O(12)-O(4)v	3.091	O(4)v-O(9)viii	3.972
		Carbonate groups			
C(1)-O(7)	1.286(14)	O(7)-C(1)-O(8)	125.2(5)		
-O(8)	1.280(16)	O(7)-C(1)-O(9)	114.1(6)		
-O(9)	1.280(16)	O(8)-C(1)-O(9)	120.7(5)		
C(2)-O(11)x2	1.315(15)	O(10)-C(2)-O(11)	121.1(6)		
-O(10)	1.270(14)	O(11)-C(2)-O(11)iii	117.6(5)		

Estimated standard deviations in parentheses

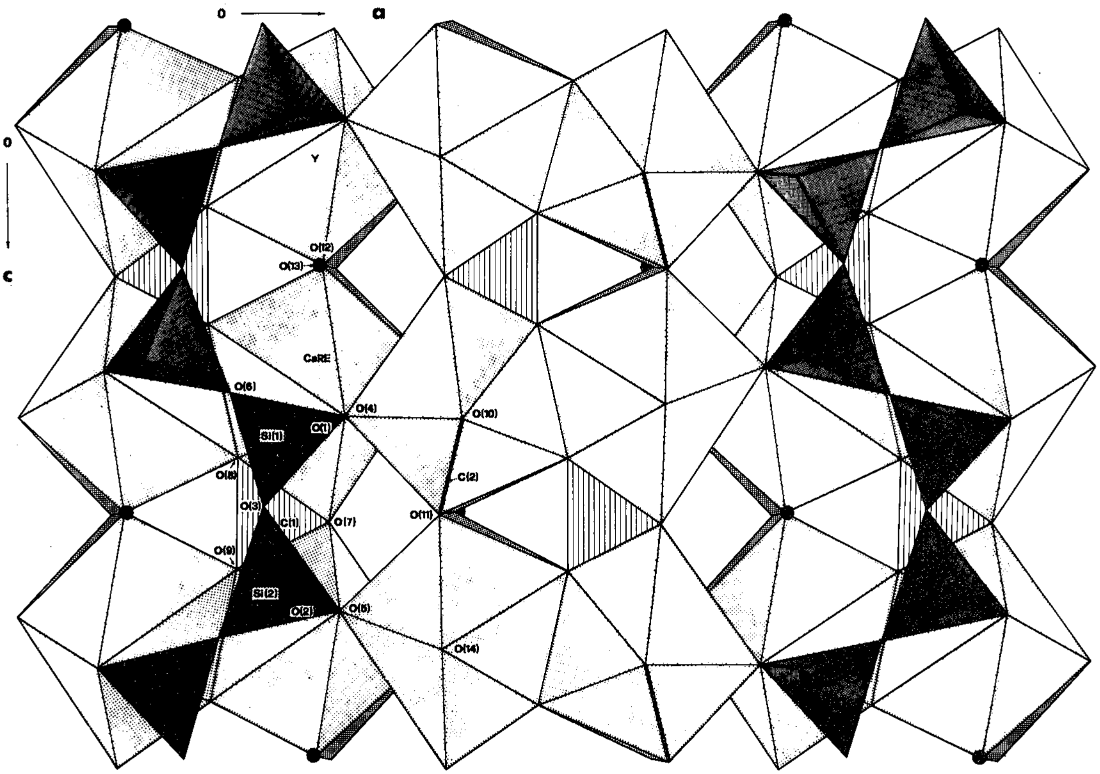

FIG. 3. Projection on (010). The atoms marked Si(1), Si(2), C(2), O(1), O(2), O(3), O(4), O(5), O(6), O(10), O(11), O(13) and O(14) are obtained from those of the fundamental asymmetric unit (Table 1) by the operation of the screw axis at $y = \frac{1}{4}$ and $x = \frac{1}{4}$ (symmetry operation v of footnote in Table 2). The atoms O(10), O(14), O(1) and O(2) lie on the mirror plane at $y = \frac{1}{2}$.

2.572Å. One more oxygen atom of the C(1) carbonate group, namely O(7), occurs at a distance of 3.100Å from the CaRE site. However, as it lies within the maximum bonding distance for Ca–O bonds (Donnay & Allmann 1970) we consider it as interacting with the CaRE cation. Both Y and CaRE polyhedra are so-called Δ-dodecahedra. The CaRE polyhedron is larger than the Y polyhedron and more distorted.

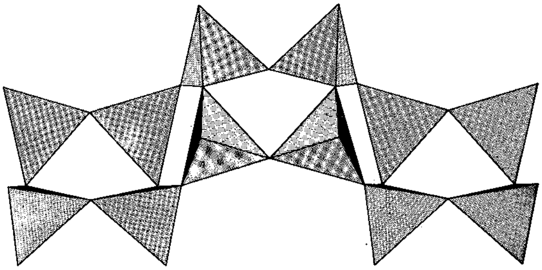

FIG. 4. The four-repeat double chain of silicon tetrahedra of caysichite, projected on (110).

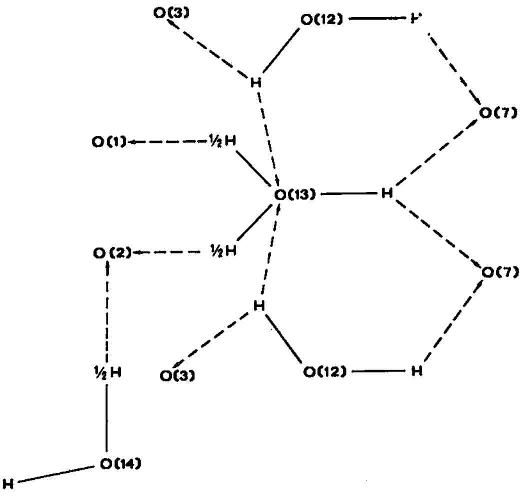

FIG. 5. Schematic drawing of the hydrogen-bond system in caysichite.

CaRE and Y polyhedra in caysichite correspond well to the Ca and Y polyhedra in kainosite (Rumanova *et al.* 1967), a mineral similar to caysichite in chemical composition but differing from it structurally: it is characterized by isolated four-membered rings of silicon–oxygen tetrahedra. As pointed out by Rumanova *et al.* (1967), polyhedra of this kind are typical of many calcium minerals, (*e.g.*, anhydrite, grossular, scheelite and hydroboracite) and zirconium and yttrium minerals (*e.g.*, zircon and xenotime). They also occur in the crystal structures of various calcium arsenates, *e.g.*, in pharmacolite (Ferraris 1969) and weilite (Ferraris & Chiari 1970).

Bond lengths and angles within carbonate groups are given in Table 3.

BOND-VALENCE BALANCE AND HYDROGEN BONDING

Table 4 gives the bond valences calculated according to Donnay & Allmann (1970). The valence sums of the bonds joining each oxygen, Σc_v, were obtained assuming a ratio RE:Ca=1:3 in the CaRE site. According to the chemical data of Hogarth *et al.* (1974), sixteen water molecules are present in the unit cell. The O(12), in general position, and O(13) and O(14) in special position on symmetry planes normal to [010], were first assumed to be water molecules on the basis of the bond valence sums.

Taking account of all the O · · · O distances less than 3.15Å (Table 5) involving at least one of the oxygen atoms O(12), O(13) and O(14) and excluding all those distances corresponding to the edge of a coordination polyhedron, the hydrogen-bonding scheme represented in Figure 5 appeared likely. The O(12) water molecule is donor in a relatively strong hydrogen bond with O(7) and in a bifurcated hydrogen bond with O(3) oxygen atom and O(13) water molecule. This molecule lies on a mirror plane normal to [010]. One of its hydrogen atoms is involved in a bifurcated bond with two O(7) oxygen atoms symmetrically disposed on both sides of the mirror plane. Two possible sites can be suggested for the other hydrogen atom corresponding to hydrogen bonding O(13) · · · O(1) or O(13) · · · O(2); we assumed a disordered distribution of the hydrogen atom between the two possible sites, corresponding to different orientations of the O(13) water molecule on the mirror plane.

If such a scheme is taken into account and the bond valence sums are corrected for the hydrogen bonding by the procedure of Donnay & Allmann (1970), the heavy undersaturation of oxygen atom O(7) is removed (see Table 4, column $\Sigma c'_v$). Moreover, the bond valence sums

TABLE 4. BOND VALENCE BALANCE (V.U.) CALCULATED FOLLOWING DONNAY & ALLMANN (1970)

	Y	CaRE	Si(1)	Si(2)	C(1)	C(2)	Σc_v	Anion chemistry	$\Sigma c'_v$	
O(1)			0.997x2*				1.99	$O^=$	2.03	(a)
O(2)				0.977x2			1.95	$O^=$	2.05	(b)
O(3)			0.957	1.016			1.97	$O^=$	2.04	(c)
O(4)	0.480	0.315	1.065				1.86	$O^=$	1.86	
O(5)	0.467	0.376		0.999			1.84	$O^=$	1.84	
O(6)			0.984	1.008			1.99	$O^=$	1.99	
O(7)	0.214	0.040			1.322		1.58	$O^=$	1.82	(d)
O(8)	0.392	0.305			1.338		2.03	$O^=$	2.03	
O(9)	0.426	0.333			1.341		2.10	$O^=$	2.10	
O(10)	0.387x2					1.438	2.21	$O^=$	2.21	
O(11)	0.350	0.359				2x1.283*	1.99	$O^=$	1.99	
O(12)	0.316	0.249					0.56	H_2O	0.21	(e)
O(13)							0.0	H_2O	-0.07	(f)
O(14)		0.312x2					0.62	$(H_2O)_{0.5}(OH^-)_{0.5}$	0.56	(g)
Σa_v	3.03	2.29	4.00	4.00	4.00	4.00				
L max	3.05	3.20	2.13	2.13	1.70	1.70				
L mean	2.40	2.49	1.61	1.61	1.28	1.30				
p	3.69	3.51	3.10	3.10	3.05	3.25				

Σa_v : sum of bond valences reaching the cation.
Σc_v : sum of bond valences reaching the anion.
$\Sigma c'_v$: sum of bond valences reaching the anion, corrected for the proposed hydrogen bonding system.

* x2 following the bond valence implies two bonds per anion.
* x2 preceding the bond valence implies two bonds per cation.

(a) : it receives 0.5x0.08 from O(13).
(b) : it receives 0.5x0.08 from O(13) and 0.5x0.12 from O(14).
(c) : it receives 0.07 from O(12).
(d) : it receives 0.20 from O(12) and 0.5x0.07 from O(13).
(e) : it gives 0.20 to O(7), 0.08 to O(13) and 0.07 to O(3).
(f) : it receives 0.08 from O(12) and gives 0.07 to O(7), 0.5x0.08 to O(1) and 0.5x0.08 to O(2).
(g) : it gives 0.5x0.12 to O(2).

clearly indicate that O(12) and O(13) are water molecules; with regards to O(14), an equal occupancy of this site by water molecules and hydroxyl anions is inferred, which assures charge balance in the structural chemical formula. The O(14) atom is 2.92Å away from O(2), indicative of a possible hydrogen bond. The O(14) position may be occupied by a water molecule or a hydroxyl anion; as "the negative charge on the OH^- ion obviously makes the ion a poor proton donor" (Hamilton & Ibers 1968), we assumed that the hydrogen atom involved in the O(14)· · · O(2) hydrogen bond has occupancy 0.50 and its presence corresponds to a location of a water molecule in the O(14) site.

The two kinds of substitutions, calcium-rare earths and water molecule-hydroxyl ion, which take place in the structure, are obviously related to each other, as follows: if a water molecule is located in the O(14) site, both cations linked to it are likely to be calcium cations, whereas if a hydroxyl anion is located in that site then one of the two cations is a trivalent rare-earth cation. With such a coupled substitution a satisfactory local balance of charges is obtained.

CONCLUSION

A structural investigation and the chemical data of Hogarth *et al.* (1974) for caysichite lead to the chemical formula: $Y_4(Ca_3RE_1)(OH)(H_2O)_5[Si_8O_{20}](CO_3)_6 \cdot 2H_2O$ with $Z=2$. The structural results are in fair agreement with the observations made by Hogarth *et al.* (1974) on the basis of their thermal and infrared studies. They indicated a three-step weight loss in the thermogravimetric analysis, the first stage (290-580°C) representing dehydration, the two subsequent stages (580-895°C and 895-1120°C) representing a two-step decarbonation. In fact the weight loss in the first stage was 8.3%, corresponding to fifteen water molecules. Moreover, static heating studies showed that nearly one third of the water content was lost between 290 and 350°C; this corresponds, in our view, to the loss of the O(13) water molecules not bound to any cations and only engaged in relatively weak hydrogen bonds. A two-step decarbonation process is in keeping with our results, which indicate the presence, in the crystal structure of caysichite, of two crystallographically distinct carbonate groups, as was also inferred by Hogarth *et al.* (1974) from the analysis of the infrared spectrum: the weight loss in two subsequent steps (10.6% and 5.3%) clearly corresponds to the expulsion of CO_2 from the eight C(1) sites and from the four C(2) sites, respectively.

TABLE 5. DISTANCES (Å) AND ANGLES (°) INVOLVED IN THE HYDROGEN BONDING SYSTEM

0(13)-0(7)	3.13(2)	0(13)-0(12)v-0(7)	64.7(5)
0(13)-0(12)v	3.09(1)	0(3)vii-0(12)v-0(7)	128.4(4)
0(13)-0(1)i	3.10(2)	0(1)i-0(13)-0(7)	88.8(7)
0(13)-0(2)	3.08(2)	0(2)-0(13)-0(7)	100.7(7)
0(12)v-0(3)vii	3.15(1)		
0(7)-0(12)v	2.73(1)		
0(2)-0(14)	2.92(2)		

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