

The crystal structure of chiavennite

VITTORIO TAZZOLI¹, M. CHIARA DOMENEGHETTI², FIORENZO MAZZI¹
and ELIO CANNILLO²

¹ Dipartimento di Scienze della Terra, Università di Pavia,
Via Abbiategrasso 209, 27100 Pavia, Italy

² CNR, Centro di Studio per la Cristallografia e la Cristallografia
Via Abbiategrasso 209, 27100, Pavia, Italy

Abstract: Chiavennite, $\text{CaMn}(\text{BeOH})_2\text{Si}_5\text{O}_{13}\cdot 2\text{H}_2\text{O}$, is orthorhombic, space group $Pnab$, $a = 8.729(5)$, $b = 31.326(11)$, $c = 4.903(2)$, $Z = 4$. The structure was determined by direct methods, using 1976 independent reflections, measured with an automated X-ray single crystal diffractometer. The anisotropic least-squares refinement led to a final discrepancy index $R = 0.041$ for the 999 observed reflections with $I \geq 5\sigma(I)$. Chiavennite has an interrupted framework of four-connected $[\text{SiO}_4]$ and three-connected $[\text{BeO}_4]$ tetrahedra, which consists of zig-zag chains combined with a 4.8^2 2D net. The framework density $\text{FD} = 20.9 \text{ T}/1000 \text{ \AA}^3$ classifies chiavennite as a zeolite. Nine-membered rings of tetrahedra form one-dimensional system of channels parallel to $[001]$ with free diameters of $3.3 \times 4.3 \text{ \AA}$. The extra-framework cations are Mn, in 6-fold coordination (octahedron, four O + two OH) and Ca, in 8-fold coordination (square antiprism, four O + two OH + two H_2O). Ca and H_2O are located in the channels.

Key-words: chiavennite, crystal-structure, zeolite, interrupted framework.

Introduction

Chiavennite, $\text{CaMn}(\text{BeOH})_2\text{Si}_5\text{O}_{13}\cdot 2\text{H}_2\text{O}$, has been found in the alpine pegmatites crossing the Chiavenna ultramafics in the Retic Alps of Italy and in the syenite pegmatites of the Oslo Region, Norway. It was recognized as a new mineral independently by Bondi *et al.* (1983) and Raade *et al.* (1983), who described its morphological, chemical, physical and paragenetic properties.

Recently, a boron-bearing chiavennite has been found in proterozoic lithium-pegmatites of Utö, Stockholm, Sweden (Langhof & Holtstam, 1994).

A preliminary description of the crystal structure of chiavennite was made by Domeneghetti *et al.* (1981) in the non-centrosymmetric space group $Pca2_1$ and the refined atomic positions were made available to the Atlas of zeolite struc-

ture types (Meier & Olson, 1992). In that paper the structure is described in the non standard space group $P2_1ab$ to ensure the cell parameter condition $c < a < b$.

The single crystals used for these studies and for the present work come from the Italian occurrence.

Experimental

X-ray diffraction data were collected with a Philips PW 1100 four circle automated diffractometer, using the graphite monochromatized $\text{MoK}\alpha$ radiation. Table 1 reports the experimental details. Three standard reflections, monitored at three-hour intervals, showed less than 3 % intensity variation during the data collection. The intensities were corrected for absorption following

Table 1. X-ray crystal and refinement data.

<i>a</i> (Å)	8.729(5)
<i>b</i> (Å)	31.326(11)
<i>c</i> (Å)	4.903(2)
Unit cell volume (Å ³)	1340.7
Space group	<i>Pnab</i>
Crystal dimensions (mm)	0.04 x 0.16 x 0.31
Radiation	MoK α
Scan mode	ω
Scan width (°)	2.50
θ range (°)	2-30
Measured reflections	4467
Independent reflections	1976
Observed reflections [*]	999
R (obs) ^{**}	0.041
R (all)	0.090

^{*} only the reflections with $I \geq 5\sigma(I)$ were considered as observed.

^{**} R is the final discrepancy index expressed as $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

the semi-empirical method of North *et al.* (1968) and the values of equivalent pairs *hkl* and $\bar{h}\bar{k}l$ were averaged. The unit-cell parameters were determined using a locally improved version of the Philips LAT routine (Cannillo *et al.*, 1983).

Structure determination and refinement

In the preliminary study (Domeneghetti *et al.*, 1981) the examination of the X-ray diffraction pattern of chiavennite allowed to recognize, with reasonable confidence, the systematic extinction of reflections *h0l* with $h = 2n+1$ and *hk0* with $k = 2n+1$. Also *0kl* reflections with $k + l = 2n+1$ appeared to be very weak, but some of them exhibited intensities higher than their standard deviations. This effect, however, could be ascribed to broadening of the peaks, due to the poor quality of the crystals, or to overlap of diffractions effects, due to the long cell parameter $b = 31.316$ Å. For this uncertainty, after structure determination by direct methods (program MULTAN78, Main *et al.*, 1978) in *Pnab* space group, refinements were performed both in the *Pnab* and

Table 2. Atomic positional parameters and equivalent isotropic thermal vibration parameter ($\times 10^4$)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Mn	0	0	0	152(3)
Ca	2500	879(1)	0	183(4)
Si1	2500	13(1)	5000	124(5)
Si2	5838(2)	2322(1)	1047(4)	185(4)
Si3	1425(2)	-1351(1)	2436(4)	194(4)
Be	-3(9)	572(2)	-4298(12)	90(16)
O1	1392(4)	-279(1)	3134(8)	155(11)
O2	1517(4)	324(1)	-2957(8)	153(11)
O3	414(6)	2391(2)	1347(11)	409(17)
O4	2500	-2478(2)	0	285(18)
O5	2500	-1187(2)	0	773(38)
O6	2500	-1387(3)	5000	1049(52)
O7	800(5)	-1824(1)	1773(10)	342(15)
O8	5(5)	-1044(1)	2905(8)	207(11)
OH	125(5)	581(1)	2430(8)	207(11)
W	1581(6)	1474(1)	2602(11)	371(15)

Numbers in parentheses are e.s.d.'s referred to the last digit.

Table 3. Anisotropic thermal vibration parameters ($\times 10^4$).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	234(6)	122(4)	99(4)	-18(5)	0	5(5)
Ca	275(9)	138(6)	138(7)	0	4(9)	0
Si1	170(9)	100(7)	101(8)	0	-14(12)	0
Si2	222(8)	113(6)	218(7)	22(7)	23(8)	9(6)
Si3	213(8)	120(6)	250(8)	-5(7)	-28(8)	13(7)
Be	166(32)	75(22)	29(28)	-10(28)	56(28)	-30(18)
O1	169(20)	124(15)	171(21)	-11(16)	-19(17)	-39(15)
O2	196(20)	123(16)	139(21)	11(17)	-7(18)	-15(15)
O3	357(30)	431(29)	437(31)	11(22)	-136(26)	-149(25)
O4	294(34)	190(26)	371(35)	0	88(36)	0
O5	768(67)	314(38)	1236(86)	0	821(68)	0
O6	1139(93)	510(54)	1497(111)	0	-1032(90)	0
O7	350(27)	141(17)	534(32)	-26(19)	91(26)	-109(20)
O8	250(20)	132(16)	239(21)	-33(18)	43(22)	-58(15)
OH	266(22)	162(17)	192(20)	17(19)	-29(24)	-1(15)
W	431(29)	322(23)	359(27)	98(23)	-32(28)	-139(24)

Numbers in parentheses are e.s.d.'s referred to the last digit.

$P2_1ab$ space groups. The results seemed to indicate the non-centric $P2_1ab$ space group as the most reliable. Although the final structural model was very close to a centrosymmetric arrangement, the anomalous high values of thermal parameters of some atoms in the centrosymmetric refinement suggested that the n glide plane had to be removed. In fact the refinement in the $P2_1ab$ space group converged to a discrepancy factor slightly lower than in $Pnab$. Although it is known that not too much weight can be given to this argument, Raade *et al.* (1983) have suggested that the hemimorphic appearance of the crystals of chiavennite could represent a confirmation of the non-centric space group.

The non-centric hypothesis, however, is not justified by the results of the present work. A check of the diffraction effects obtained from a crystal of better quality showed that the systematic extinction of reflections $0kl$ with $k + l = 2n + 1$ can be considered as reliable as the other already observed extinctions. This check was made using both $\text{MoK}\alpha$ and $\text{CuK}\alpha$ radiations, the last one to avoid the effect of possible overlapping of reflections due to the long cell parameter b . For the following structure determination and refine-

ment, the intensities collected with $\text{MoK}\alpha$ radiation proved better since they permitted to reduce the strong variation of the absorption at different ϕ angle values, due to the flat shape of the crystals.

Starting from the atomic coordinates obtained by direct methods, the refinement was done in the space group $Pnab$ without chemical constraints, using a locally modified version of the least-squares program ORFLS (Busing *et al.*, 1962). Isotropic temperature factors were used in the first cycles of refinement and anisotropic temperature factors for all atoms in the last ones. The ionization states used in the refinement were 2^+ for Si, Mn, Be and Ca and 1.5^- for O. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1974) and from Tokonami (1965). Reflections with $I \geq 5\sigma(I)$ were considered as observed and were used in the refinement with equal weight. The extinction correction of Coppens & Hamilton (1970) was applied. All parameters were varied simultaneously during refinement; no correlation greater than 0.65 was observed. The refinement converged to a discrepancy factor $R = 0.041$ for the 999 reflections with $I \geq 5\sigma(I)$ and

Table 4. Bond distances (Å) and angles (°).

Si1-O1	1.615(4) x 2	Si3-O5	1.603(3)
Si1-O2	1.640(4) x 2	Si3-O6	1.573(2)
Mean	1.627	Si3-O7	1.611(4)
TQE	1.0012	Si3-O8	1.586(4)
		Mean	1.593
		TQE	1.0021
O1-Si1-O1	111.1(1)	O5-Si3-O6	105.6(1)
O1-Si1-O2	111.6(1) x 2	O5-Si3-O7	110.0(3)
O1-Si1-O2	107.7(1) x 2	O5-Si3-O8	111.8(2)
O2-Si1-O2	107.1(1)	O6-Si3-O7	107.3(4)
		O6-Si3-O8	113.2(3)
		O7-Si3-O8	108.8(2)
Si2-O3	1.606(5)	Be-O1	1.625(8)
Si2-O3	1.619(5)	Be-O2	1.672(8)
Si2-O4	1.615(2)	Be-O8	1.628(7)
Si2-O7	1.599(4)	Be-OH	1.608(7)
Mean	1.610	Mean	1.633
TQE	1.0016	TQE	1.0068
O3-Si2-O3	110.3(2)	O1-Be-O2	101.0(2)
O3-Si2-O4	106.8(2)	O1-Be-O8	111.4(3)
O3-Si2-O7	111.4(2)	O1-Be-OH	114.4(4)
O3-Si2-O4	109.6(1)	O2-Be-O8	104.9(4)
O3-Si2-O7	106.1(3)	O2-Be-OH	110.2(4)
O4-Si2-O7	112.6(3)	O8-Be-OH	113.7(3)
Mn-O1	2.144(4) x 2	Ca-O2	2.420(4) x 2
Mn-O2	2.211(4) x 2	Ca-O8	2.661(4) x 2
Mn-OH	2.179(4) x 2	Ca-OH	2.566(4) x 2
Mean	2.178	Ca-W	2.397(5) x 2
		Mean	2.511

TQE = tetrahedral quadratic elongation as defined by Robinson et al. (1971).
Numbers in parentheses are the e.s.d.'s referred to the last digit.

$R = 0.090$ for the all measured reflections. The final difference-Fourier map was featureless. The final atomic parameters are given in Tables 2 and 3; bond distances and angles are listed in Table 4. A list of observed and calculated structure factors may be obtained on request from the authors or through the E.J.M. Editorial Office.

Description and discussion of the structure

The Si-Be framework

Chiavennite has an interrupted framework of $[\text{SiO}_4]$ and $[\text{BeO}_4]$ tetrahedra (Fig. 1). While all

oxygens in $[\text{SiO}_4]$ tetrahedra are bridging, in $[\text{BeO}_4]$ tetrahedra one of the corners is occupied by the oxygen of a hydroxyl group, which interrupts the framework. Thus chiavennite can be defined (Rossi, 1975) a "quasi-tectosilicate", with a sharing index (Coda, 1969) $c = 3.72$. The "framework density", i.e. the number of tetrahedral atoms per 1000 Å^3 , is $\text{FD} = 20.9$: this value places chiavennite in the boundary zone between zeolite-type and dense tetrahedral framework structures (Meier & Olson, 1992).

The framework of a zeolite can be generally described on the basis of a "secondary building unit" (SBU), assuming that zeolite nets would contain only one type of SBU. The SBU which describes the framework of chiavennite is built up of one five-membered ring of tetrahedra, sharing an edge with one four-membered ring as in SBU type 5-2 of Figure 2 in Meier & Olson (1992). The sequence of the atoms of this SBU is Si(1), Be, Si(3), Si(2), Si(3), Be.

The framework of many zeolites was described by combining helix, zig-zag, crankshaft and saw chains with two dimensional (2D) nets (Smith, 1979). The framework of chiavennite can be easily sketched (Merlino, 1983) as built up by alternating slabs characterized by zig-zag silicate chains, connected according to a $4 \cdot 8^2$ 2D net, and slabs characterized by $\text{Si}(\text{Be})_2$ chains (Fig. 2). Nine-membered rings Si(1), Be, Si(3), Si(2), Si(2), Si(2), Si(2), Si(3), Be are formed and their overlapping gives rise to a 1-dimensional system of channels parallel to $[001]$, with minimum free diameters of 3.3 and 4.3 Å, assuming the effective radius of O to be 1.35 Å.

The extra-framework structural sites

The four extra-framework positions are occupied respectively by Mn, Ca and two H_2O molecules. Ca atoms, in 8-fold coordination, lie together with the H_2O molecules in the channels parallel to $[001]$: they are surrounded by four O, two OH and two H_2O to form square antiprisms, whose square bases are normal to $[001]$. These polyhedra pile up along $[001]$ without directly connecting to each other. Mn atoms, in 6-fold coordination, are surrounded by four O and two OH to form a regular octahedron with a couple of faces normal to $[001]$. These polyhedra pile up along $[001]$, without connecting to each other but sharing two edges O2-OH with two adjacent Ca polyhedra. The oxygen atoms of the water

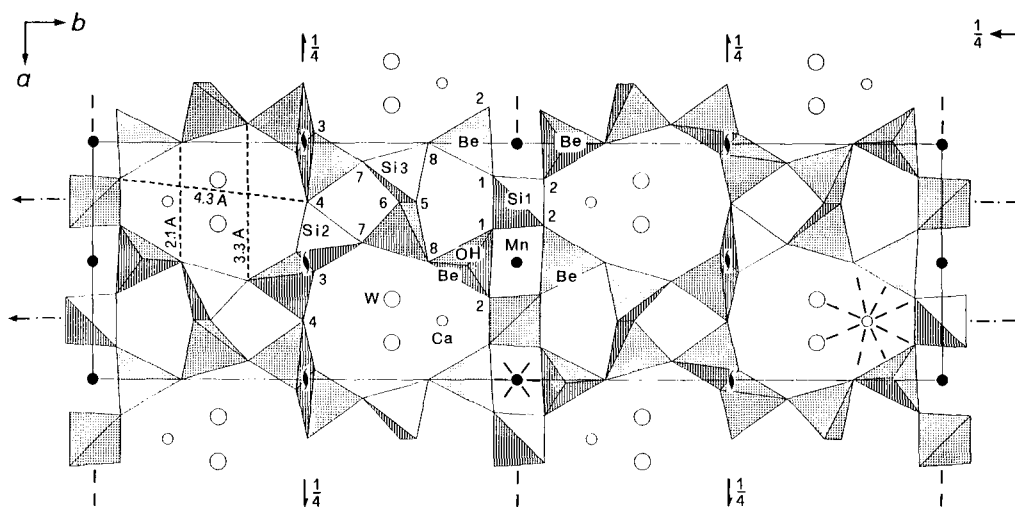


Fig. 1. [001] projection of the crystal structure of chiavennite.

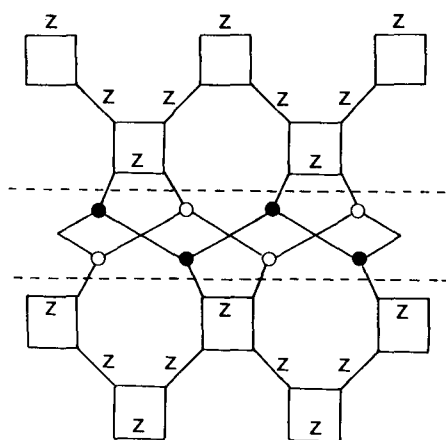


Fig. 2. Schematic drawing of the framework of chiavennite. Filled and empty circles indicate 3-connected upwards and downwards beryllium tetrahedra respectively (from Merlino, 1983).

molecules occupy well defined positions in the channels parallel to [001], taking part in the Ca coordination polyhedron. The shortest contacts of these oxygens with oxygens not belonging to the same coordination polyhedron are W-W (2.846 Å) and W-O8 (2.930 Å), which are consistent with the presence of hydrogen bonds. However, it was not possible to locate the hydrogen atoms. The hydroxyl group seems not to be involved in

hydrogen bonds since its distance from the nearest oxygen, O5, is 3.206 Å.

Conclusions

The quality of the structure refinement was not sufficient to verify the small isomorphic substitutions Al for Si, Al for Be and Na for Ca, as indicated by the results of microprobe analysis reported in Bondi *et al.* (1983). Moreover, the relatively short distance O6-Si3 (1.573 Å), together with the unusually high value of the Si3-O6-Si3 angle (171.78°) and the strong anisotropy of the thermal ellipsoid of the O6 atom, suggest a disordered distribution of this oxygen in the direction of the major axis of the ellipsoid. This axis is approximately normal to the plane defined by the line joining Si3 to Si3 and [010] direction. Such statistical disorder, however, does not justify a symmetry lower than *Pnab*. Attempts to refine the structure in all the orthorhombic and monoclinic subgroups of *Pnab* did not provide any significant indications. Therefore, with the experimental data available, the choice of the simplest model which describes the chiavennite structure, *i.e.* that with *Pnab* symmetry, seems to be the most correct.

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