

NEW DATA FOR CHIAVENNITE AND FERROCHIAVENNITE

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ABSTRACT

Chiavennite (Mn endmember) and ferrochiavennite (Fe endmember) are beryllium silicate zeolites with chemical compositions close to $\text{Ca}_{1-2}(\text{Mn,Fe})\text{Si}_5\text{Be}_2\text{O}_{13}(\text{OH})_2\cdot 2\text{H}_2\text{O}$. Five chiavennite crystals from four different localities, Chiavenna, Italy; Telemark, Norway; Utö, Sweden; and Ambatovita, Madagascar, were chosen for crystal-structure analysis. Initially all had been reported to be orthorhombic, but all are monoclinic, with a β angle near 90° , as is ferrochiavennite from Blåfjell, Norway. Twinning on $\{100\}$ is common. Chiavennite and ferrochiavennite are isostructural. The zeolite structure consists of intersecting channels of nine-, six-, five-, and four-fold rings. All five structures have one *Ca* site in common while chiavennite from Utö and ferrochiavennite from Blåfjell have a second, partially filled, *Ca* site. Hydrogen atoms were located in all five structures. Hydrogen bonding is similar but not identical in all five structures. The H atoms associated with BeO_4 tetrahedra act as terminations to a polymerization sequence causing chiavennite and ferrochiavennite to be interrupted zeolite structures.

Keywords: ferrochiavennite, chiavennite, interrupted zeolite framework, beryllium silicate, crystal structure, syenitic pegmatite, granite pegmatite, Italy, Norway, Sweden, Madagascar.

INTRODUCTION

Chiavennite was described as a new mineral by Bondi *et al.* (1983) from Chiavenna, Italy and almost concurrently by Raade *et al.* (1983) from the Oslo Region, Norway. Subsequently a locality in Utö, Sweden was reported by Langhof *et al.* (2000) and in Ambatovita, Madagascar by Pezzotta *et al.* (2005). Recently the new mineral species ferrochiavennite was described from two localities in the Oslo Region, Norway (Grice *et al.* 2013). During the investigation of ferrochiavennite it was found that it is monoclinic and not orthorhombic as described for the previous localities. To ascertain whether or not the two species, chiavennite and ferrochiavennite, actually had different crystal systems, samples from all of the localities listed above were obtained, the chemical composition

determined, and full crystal structure analyses performed. Cametti & Armbruster (2015) have just published a paper on the thermal behavior of chiavennite from the type locality, Chiavenna, Italy and describe it as monoclinic at room temperature showing a continuous monoclinic–orthorhombic transition from space group $P2_1/c$ to $Pbcn$.

CHIAVENNITE AND FERROCHIAVENNITE SAMPLES

During the investigation of the new mineral, ferrochiavennite (Grice *et al.* 2013), the crystal structure work determined the mineral to be monoclinic, while chiavennite is described as orthorhombic (Bondi *et al.* 1983, Raade *et al.* 1983, Tazzoli *et al.* 1995). Initiated by the structural examination of ferrochiavennite and the recent results of Cametti &

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Armbruster (2015), we re-examined chiavennite from the type localities in Italy and Norway as well as the two localities in Sweden and Madagascar.

Sample “Chiavenna” (chiavennite)

Chiavenna, Lombardy, Italy, is the type locality (Bondi *et al.* 1983, Tazzoli *et al.* 1995). Chiavennite occurs as euhedral orange grains or crystals up to 0.4 mm in size, and as crusts coating beryl. It is usually associated with bavenite and several other pegmatite minerals. It occurs in an alpine pegmatite cutting Chiavenna ultramafic rocks in the Rhetic Alps in Northern Italy. At the locality magmatic beryl has been altered to bavenite and chiavennite by hydrothermal fluids rich in Ca and Mn.

Sample “Telemark I” (chiavennite)

This sample is from Langangen, Blåfjell, Telemark, Norway (Raade *et al.* 1983). The mineral forms aggregates of reddish orange spherules up to several millimetres in size in vugs in a syenitic pegmatite in the Larvik plutonic complex (LPC) in the southern Oslo region. Chiavennite was exposed during road construction of route E-18 between the Vestfold and Telemark counties.

Approximately 25 different species have been identified in this pegmatite, including the beryllium minerals hambergite, gadolinite-(Ce), leucophanite, epididymite, and eudidymite.

Chiavennite is the latest mineral to crystallize, often on analcime and natrolite. It probably formed as a result of the alteration of the primary leucophanite or meliphanite. There is no direct proof of this alteration, but these two minerals are the most abundant primary Be minerals in the LPC.

Sample “Utö” (chiavennite)

At Utö, Södermanland, Sweden (Langhof & Holtstam, 1994, Langhof *et al.* 2000), chiavennite occurs in cracks and fracture infillings as rare aggregates of bright golden yellow, transparent, platy crystals or as crystals of thin tabular habit in groups or radiating clusters up to 5 mm in size. Other associated beryllium minerals are milarite, genthelvite-helvite, and rarely thin blades of bavenite and beryl of primary origin. The mode of occurrence of the locality indicates formation at low temperature (Langhof *et al.* 2000). This is the only locality of chiavennite where boron is determined to be substituting for beryllium. The Utö pegmatite is the type locality for four mineral species: spodumene, petalite, tantalite-(Mn), and holmquistite. Cookeite and eucryptite are found as hydrothermal alteration products. This is a

Proterozoic pegmatite with a typical lithium and phosphate assemblage.

Sample “Ambatovita” (chiavennite)

The Sakavalana pegmatite, Ambatovita, Ambatofinandrahana district, Madagascar (Pezzotta *et al.* 2004, 2005) is a famous pegmatite where the new gemstone pezzottaite was discovered (Laurs *et al.* 2003, Hawthorne *et al.* 2004). A large specimen (over 7 kg) containing masses of brownish-red pezzottaite was found in 2003 and was broken into smaller pieces (Pezzotta *et al.* 2004). It contained groups of pezzottaite crystals, liddicoatite, amazonite, quartz, and large masses of brownish-red chiavennite forming small aggregates of radiating crystals or globular aggregates 1–2 mm across, with single six-sided crystals, mostly covered by a thin crust of pale blue chalcedony. Chiavennite formed as a late-stage mineral, probably from low-temperature hydrothermal B-rich solutions with strong activity of Be, Mn, Cs, and Ca, together with hambergite, bavenite, milarite, and a late generation of pezzottaite.

Sample “Telemark II” (ferrochiavennite type locality)

This sample is from Langangen, Blåfjell, Telemark, Norway (Grice *et al.* 2013). Crystal aggregates of ferrochiavennite occur as beige or pale yellow spherules up to 2 mm in diameter in vugs in a syenitic pegmatite in the Larvik plutonic complex in the southern Oslo region. The ferrochiavennite locality was exposed during road construction of route E-18 between Vestfold and Telemark counties, and is situated less than 200 meters from the type locality for chiavennite. Ferrochiavennite is the latest mineral to crystallize and is associated with albite, magnetite, fayalite, zircon, nepheline, analcime, pyrite, and hambergite and probably formed as the result of the alteration of the primary minerals leucophanite and meliphanite.

CHEMICAL DATA

Chemical analyses were done at the Canadian Museum of Nature by wavelength-dispersive electron-microprobe (EMP) at 15 kV, 20 nA, 10 µm beam diameter, with a counting of 20 s on the peak and 10 s on background. Fluorine was below detection limits. H₂O was calculated by stoichiometry from the results of the crystal structure analysis (Hawthorne & Grice 1990); all H atoms were found. BeO was calculated by stoichiometry from the results of the crystal structure analysis. Intensity data were corrected for inter-element overlaps, and for matrix effects using a

TABLE 1. CHIAVENNITE AND FERROCHIAVENNITE ANALYTICAL DATA

Constituent	CHIAVENNA ^[1]	TELEMAR I ^[2]	UTÖ ^[3]	AMBATOVITA ^[4]	TELEMAR II ^[5]	EMP standard	Emission line
SiO ₂ (wt.%)	50.84	49.30	51.16	51.07	46.00	diopside	SiK α
Al ₂ O ₃	3.44	5.01	3.55	4.45	4.64	sanidine	AlK α
FeO	1.70	0.52	1.67	1.37	5.29	hematite	FeK α
MnO	10.64	12.30	10.78	11.00	4.04	tephroite	MnK α
MgO	0.04	0.05	0.06	0.15	0.13	diopside	MgK α
CaO	10.27	10.33	10.08	10.06	17.62	diopside	CaK α
Na ₂ O	0.33	0.27	0.68	0.55	0.73	albite	NaK α
K ₂ O	0.01	0.00	0.01	0.03	0.02	sanidine	KK α
BeO	(8.24)	(8.04)	(8.32)	(8.07)	(10.37)		
H ₂ O	(9.59)	(9.57)	(9.68)	(9.73)	(9.81)		
Total	95.10	95.39	95.99	96.48	98.65		
Si ⁴⁺ (<i>apfu</i>)	4.76	4.63	4.75	4.72	4.22		
Al ³⁺	0.38	0.56	0.39	0.48	0.50		
Fe ²⁺	0.13	0.04	0.13	0.22	0.41		
Mn ²⁺	0.84	0.79	0.85	0.86	0.31		
Mg ²⁺	0.01	0.01	0.01	0.02	0.02		
Ca ²⁺	1.03	1.04	1.00	1.00	1.73		
Be ²⁺	1.86	1.81	1.86	1.80	2.28		
Na ⁺	0.06	0.05	0.12	0.10	0.13		
K ⁺	0.00	0.00	0.00	0.10	0.00		
H ⁺	6	6	6	6	6		
O	17	17	17	17	17		
Total cation	9.08	9.12	9.11	9.10	9.60		

The empirical formulae (based on 17 anions *pfu* and 7 tetrahedral framework sites) are as follows.

[1]: (Ca_{1.03}Na_{0.06}) Σ 1.09(Mn_{0.84}Fe_{0.13}Mg_{0.01}) Σ 0.98(Si_{4.76}Al_{0.38}Be_{1.86}) Σ 7O₁₃(OH)₂·2H₂O

[2]: (Ca_{1.04}Na_{0.05}) Σ 1.09(Mn_{0.79}Fe_{0.04}Mg_{0.01}) Σ 0.84(Si_{4.63}Al_{0.56}Be_{1.81}) Σ 7O₁₃(OH)₂·2H₂O

[3]: (Ca_{1.00}Na_{0.12}) Σ 1.12(Mn_{0.85}Fe_{0.13}Mg_{0.01}) Σ 0.99(Si_{4.75}Al_{0.39}Be_{1.86}) Σ 7O₁₃(OH)₂·2H₂O

[4]: (Ca_{1.00}Na_{0.10}) Σ 1.10(Mn_{0.86}Fe_{0.22}Mg_{0.02}) Σ 1.10(Si_{4.72}Al_{0.48}Be_{1.80}) Σ 7O₁₃(OH)₂·2H₂O

[5]: (Ca_{1.73}Na_{0.13}) Σ 1.86(Fe_{0.41}Mn_{0.31}Mg_{0.02}) Σ 0.74(Si_{4.22}Al_{0.50}Be_{2.28}) Σ 7O₁₃(OH)₂·2H₂O

Cameca version of the 'PAP PhiRhoZ' program (Pouchou & Pichoir 1984).

Analytical data and calculated formulae based on 17 anions and seven tetrahedral sites are given in Table 1.

CRYSTAL STRUCTURE ANALYSES

The crystals of chiavennite and ferrochiavennite chosen for crystal structure determinations are deliberately very small in an effort to eliminate multiple crystals. Intensity data were collected with a Bruker D8 three-circle diffractometer equipped with a rotating anode generator, multi-layer optics, and an APEX-II CCD detector, and operated at 50 kV, 40 mA, with MoK α radiation. This setup yields a very intense X-ray beam. A full sphere of intensity data was collected up to $2\theta = 60^\circ$ using 10 s frames with frame widths of 0.2° . Data pertinent to the intensity-data collection are given in Table 2. The unit-cell parameters for the single crystals were refined using approximately 9500

indexed reflections. The estimated standard deviations are the random-error ESDs with no systematic-error component. The mineral has a marked pseudo-orthorhombic cell which was that used in the original structure determination of chiavennite described from Italy (Tazzoli *et al.* 1995). As there was a small, but significant, change from an orthonormal cell, the ferrochiavennite data were collected using a monoclinic cell. For chiavennite from the other four localities both orthorhombic and monoclinic symmetry was investigated and all were found to be monoclinic. For four of the samples (Table 2), Chiavenna, Telemark I, Ambatovita, and Telemark II, the unit cell is metrically monoclinic, but for Utö the cell is not unequivocally monoclinic as the β angle is 90° within one standard deviation.

The three-dimensional data were corrected for Lorentz, polarization, and background effects, and multiple measured reflections were averaged using the Bruker program SAINT. An empirical absorption-correction was applied (SADABS, Sheldrick 1998).

TABLE 2. CRYSTAL STRUCTURAL DATA FOR CHIAVENNITE AND FERROCHIAVENNITE SAMPLES

Locality	CHIAVENNA	TELEMARK I	UTÖ	AMBATOVITA	TELEMARK II
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.7487(5)	8.7603(7)	8.7302(4)	8.7597(3)	8.7499(5)
b (Å)	4.9088(3)	4.8727(4)	4.9192(2)	4.8933(1)	4.9160(3)
c (Å)	31.338(2)	31.286(2)	31.283(2)	31.2450(9)	31.431(2)
β (°)	90.236(1)	90.250(1)	89.993(8)	90.4566(4)	90.1574(9)
V (Å ³)	1345.8(2)	1335.5(3)	1343.5(2)	1339.2(1)	1352.0(3)
μ (mm ⁻¹)	1.91	1.92	1.93	1.92	2.63
Crystal size (μ m)	25 × 15 × 5	60 × 30 × 2	120 × 40 × 30	100 × 25 × 25	40 × 30 × 10
Measured reflections	15707	15529	15660	15651	15716
Unique reflections	3951	3065	3935	3932	3956
Observed reflections [> 4 $\sigma(f)$]	3658	2828	3911	3813	3651
R (int) (%)	0.04	0.04	0.02	0.01	0.02
$ E^2 - 1 $	0.948	0.939	0.945	1.008	0.968
Final max. and min. $e^-/\text{Å}^3$	+1.12 / -1.10	+1.36 / -1.03	+0.88 / -0.90	+0.52 / -0.49	+0.81 / -0.99
Goodness of fit on F^2	1.18	1.08	1.05	1.16	1.25
R index for all data	0.063	0.056	0.043	0.023	0.052
R index for observed data	0.058	0.050	0.042	0.022	0.051
Twin component	Pseudo merohedral	Pseudo merohedral	Merohedral	No twin	Pseudo merohedral
Twin component fraction	0.276(3)	0.306(2)	0.436(2)		0.371(2)

All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors of neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). The twinned crystal required the newer programs of Sheldrick (2008), TWINCELL and TWINABS. The twin law, reflection on {100}, is not a merohedral twin except for the orthonormal Utö data set. In TWINABS a single 'detwinned' file was produced as in all cases the crystals have a β angle close to 90° which does not sufficiently resolve the two data sets. Refinement was based on assuming a merohedral or pseudo-merohedral twin, except for the Ambatovita sample, which is not twinned. This untwinned sample gave the best structure refinement so one could conclude that twinning is affecting the refinement, perhaps due to the proximity of the β angle to 90°. Extinction conditions yielded the $P2_1/c$ as the most probable space group. This space group, transformed to the setting of Tazzoli *et al.* (1995) is $P112_1/b$ (SG 14), a subgroup of their structure space group $P2_1/n2/a2_1/b$ or $Pnab$ (SG 60). The refined twin domain proportions are given in Table 2. The atomic site labels of Tazzoli *et al.* (1995) were maintained and the sites generated by the change in symmetry are designated by a double digit, *i.e.*, $Si2$ is the original and $Si22$ is the new monoclinic symmetry-generated site. In this way readers may easily compare the two structures. Atom site $Si1$ is a special position in the orthorhombic crystal structure of Tazzoli *et al.* (1995),

whereas in the monoclinic cell it becomes a single, general site.

The H atoms were refined with a fixed isotropic displacement factor and with the O-H distance constrained to 0.980 Å ± 0.020. The addition of an isotropic extinction correction did improve the refinements. The R index for each sample, except Ambatovita, is disappointing. Since the Ambatovita crystal is the only one not twinned, we must conclude that the twin correction applied is not of great quality. This is likely due to a considerable overlap of the two individuals in the twin because of the near-orthonormal cell. In addition we noted that reflections were somewhat diffuse, indicating a poor degree of crystallinity.

The final positional and isotropic displacement parameters of atoms are given in Table 3 and selected bond lengths in Table 4 for the Chiavenna, Utö, and Telemark II samples. For all five samples tables listing the observed and calculated structure-factors along with the .CIF file may be obtained from the MAC website (document Chiavennite and ferrochiavennite CM54_1500068).

DESCRIPTION OF THE STRUCTURE

Tetrahedral framework

Chiavennite and isostructural ferrochiavennite (Telemark II) have an interrupted zeolite structure (-CHI) (Baerlocher *et al.* 2007). The structure consists

TABLE 3A. CHIAVENNITE, CHIAVENNA, ITALY: ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2)

Atom	x/a	y/b	z/c	sof	U_{eq}
Mn1	1/2	1/2	0	1	0.0112(1)
Mn2	0	1/2	0	1	0.0112(1)
Ca	0.75065(7)	0.4999(1)	-0.08849(1)	1	0.01465(8)
Si1	0.74974(8)	0.0015(1)	-0.00147(1)	1	0.0083(1)
Si2	0.41566(7)	0.5896(1)	-0.23239(2)	1	0.0105(1)
Si22	0.08358(7)	0.3748(1)	-0.23212(2)	1	0.0104(1)
Si3	0.14024(7)	0.2297(1)	-0.13471(2)	1	0.0106(1)
Si33	0.35491(7)	0.7200(1)	-0.13548(2)	1	0.01046(1)
Be4	0.5020(3)	0.0709(5)	0.05743(8)	0.961(2)	0.0144(6)
Si4	0.5020(3)	0.0709(5)	0.05743(8)	0.039	0.0144(6)
Be44	0.0024(3)	0.9238(5)	0.05710(8)	0.965(2)	0.0123(6)
Si44	0.0024(3)	0.9238(5)	0.05710(8)	0.035	0.0123(6)
O1	0.6512(2)	-0.2030(3)	-0.03296(4)	1	0.0097(3)
O2	0.8466(2)	0.2067(3)	-0.03221(4)	1	0.0096(3)
O3	0.8611(2)	-0.1884(3)	0.02776(5)	1	0.0119(3)
O4	0.6410(2)	0.1889(3)	0.028070(4)	1	0.0112(3)
O5	0.2486(3)	0.4861(3)	-0.24786(5)	1	0.0230(4)
O6	0.4617(2)	0.8403(4)	-0.26371(6)	1	0.0247(4)
O7	0.4190(2)	0.6888(4)	-0.18331(6)	1	0.0285(5)
O8	0.0462(2)	0.1064(4)	-0.25987(7)	1	0.0304(5)
O9	0.0815(2)	0.3087(5)	-0.18194(5)	1	0.0311(5)
O10	0.0021(2)	0.7763(3)	0.10340(5)	1	0.0149(4)
O11	0.2149(2)	0.9276(5)	-0.13569(8)	1	0.0384(6)
O12	0.2774(2)	0.4336(4)	-0.11992(6)	1	0.0258(5)
O13	0.4962(2)	0.7984(3)	-0.10530(5)	1	0.0139(4)
OH14	0.4912(1)	0.7392(3)	0.05793(3)	1	0.0146(4)
OH15	0.0160(1)	0.2550(2)	0.05790(3)	1	0.0144(4)
OW16	0.8343(1)	0.7418(3)	-0.15052(3)	1	0.0313(4)
OW17	0.6537(9)	0.2253(2)	-0.14604(5)	1	0.0244(5)
H14	0.573(8)	0.71(2)	0.0789(3)	1	0.05
H15	-0.04(1)	0.35(1)	0.080(2)	1	0.05
H16A	0.916(8)	0.85(1)	-0.138(3)	1	0.05
H16B	0.86(1)	0.73(2)	-0.180(1)	1	0.05
H17A	0.567(8)	0.25(2)	-0.165(3)	1	0.05
H17B	0.63(1)	0.08(1)	-0.126(2)	1	0.05

of cross-connecting channels of nine-, six-, five-, and four-fold rings. The nine-fold ring channel contains the Ca atoms and H_2O groups; the six- and five-fold channels are empty, and the four-fold channels contain the Mn and Fe atoms. The two *Mn*, *Fe* sites have octahedral coordination with very little variation in bond lengths.

In all chiavennite samples and the ferrochiavennite sample there is one fully occupied *Ca1* site having eight-fold coordination with four O atoms, two OH groups, and two H_2O groups. In chiavennite from Utö and ferrochiavennite from Telemark II there are two *Ca* sites, *Ca1* as described above, and *Ca2*, which is partially occupied. The *Ca2*-site has six-fold coordination with four O atoms and two H_2O groups. In

ferrochiavennite *Ca2/Ca22* is a split site in one sample and a single site, with a considerably smaller site occupancy of 0.03, in another sample, as it is for the Utö chiavennite. For the split site some of the bond distances are unrealistically short. The splitting of the site compensates for this problem in terms of the O atoms. For example, when $\text{Ca2-O6} = 2.48 \text{ \AA}$, $\text{Ca22-O6} = 2.12 \text{ \AA}$ (Table 4a), and so for all four O atoms when one distance is too short the other is reasonable. But for both *Ca2* and *Ca22* the two H_2O groups are a bit too close. It is likely that if the *Ca2/Ca22* site was fully occupied there would be room for only one H_2O group. Cametti & Armbruster (2015) found a *Ca2* site in the chiavennite from Chiavenna but with a very low site occupancy of 0.03 atoms of Ca.

TABLE 3B. CHIAVENNITE, UTÖ, SWEDEN: ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (Å²)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	sof	<i>U</i> _{eq.}
Mn1	½	½	0	0.960(3)	0.0116(3)
Mn2	0	½	0	0.930(3)	0.0107(3)
Ca1	0.7497(2)	0.4998(2)	-0.08826(2)	1	0.0131(2)
Ca2	0.739(2)	0.475(6)	-0.1988(5)	0.084(6)	0.058(7)
Si1	0.7498(2)	0.0012(3)	-0.00131(3)	1	0.0075(2)
Si2	0.4152(2)	0.5933(2)	-0.23254(5)	0.962(8)	0.0092(4)
Si22	0.0839(2)	0.3705(3)	-0.23219(5)	0.962(8)	0.0100(4)
Si3	0.1424(2)	0.2268(2)	-0.13513(4)	0.968(8)	0.0090(4)
Si33	0.3570(2)	0.7185(3)	-0.13513(4)	0.966(8)	0.0089(4)
Be4	0.5010(8)	0.0716(2)	0.0574(2)	0.97(1)	0.017(2)
Si4	0.5010(8)	0.0716(2)	0.0574(2)	0.03	0.017(2)
Be44	0.0020(8)	0.9171(1)	0.0568(2)	0.94(14)	0.012(1)
B44	0.0020(8)	0.9171(1)	0.0568(2)	0.06	0.012(1)
O1	0.6530(4)	-0.2035(7)	-0.0329(1)	1	0.0100(6)
O2	0.8479(5)	0.2057(7)	-0.0322(1)	1	0.0107(6)
O3	0.8614(5)	-0.1873(7)	0.0280(1)	1	0.0107(6)
O4	0.6403(5)	0.1878(7)	0.0282(1)	1	0.0010(7)
O5	0.2507(7)	0.4854(1)	-0.2481(1)	1	0.0232(7)
O6	0.4611(5)	0.8452(8)	-0.2637(2)	1	0.0242(1)
O7	0.4192(6)	0.6922(1)	-0.1834(1)	1	0.0266(1)
O8	0.0470(5)	0.1029(1)	-0.2609(2)	1	0.0283(1)
O9	0.0852(6)	0.296(1)	-0.1819(1)	1	0.027(1)
O10	0.9991(5)	0.7728(7)	0.1026(1)	1	0.0135(7)
O11	0.2135(4)	0.9239(1)	-0.1343(2)	1	0.0321(9)
O12	0.2799(4)	0.4284(8)	-0.1207(1)	1	0.0226(8)
O13	0.4989(5)	0.7960(8)	-0.1056(1)	1	0.0153(7)
OH14	0.4880(5)	0.7435(6)	0.0589(1)	1	0.0085(6)
OH15	0.0179(6)	0.2456(8)	0.0581(1)	1	0.0194(9)
OW16	0.8329(8)	0.739(1)	-0.1505(2)	1	0.038(1)
OW17	0.6557(5)	0.2307(8)	-0.1463(1)	1	0.0196(8)
H14	0.569(7)	0.67(2)	0.077(2)	1	0.05
H15	-0.043(8)	0.33(2)	0.081(2)	1	0.05
H16a	0.904(8)	0.88(1)	-0.140(3)	1	0.05
H16b	0.88(1)	0.68(1)	-0.177(2)	1	0.05
H17a	0.61(1)	0.30(2)	-0.173(2)	1	0.05
H17b	0.709(9)	0.09(1)	-0.130(2)	1	0.05

In the tetrahedral framework there are seven tetrahedral sites: five are dominantly Si while the remaining two are dominantly occupied by Be. This gives 24 positive charges. The chiavennite crystals from Chiavenna, Telemark I, and Ambatovita refine to these 'ideal' proportions, while Utö and Telemark II refine to 24.37 and 23.45 positive charges, respectively. Utö has a high positive charge total since B³⁺ substitutes for Be²⁺ at the Be44 site, while Telemark II is low due to the addition of positive charge at the second, partially filled Ca site. The B substitution is further evidenced by the significantly shorter average bond length for this site (Table 4a); 1.616 Å versus 1.641 Å average for BeO₄. Note that the average Si–O

bond length is shorter than the average Be–O bond length: 1.620 versus 1.641 Å. In all crystals studied there was about one-half of an atom of Al per formula unit (Table 1). Substitution of Al at a Si or Be site would increase the bond lengths somewhat. Although we cannot be certain of the role of Al³⁺ in the crystal structure, it is most likely at the tetrahedral sites. Cametti & Armbruster (2015) refined Al populations at the two Be sites, but there is very little substitution of Al for Be. A more likely site for Al substitution at a tetrahedral site would be the Si1 site, which has a decidedly larger average bond length for chiavennite, and the Si1 and Si2 sites in ferrochiavennite have larger average bond lengths (Table 4a). For chiavenn-

TABLE 3C. FERROCHIAVENNITE, TELEMAR II, NORWAY: ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2)

Atom	x/a	y/b	z/c	sof	$U_{eq.}$
Fe1	$\frac{1}{2}$	$\frac{1}{2}$	0	0.463(3)	0.0116(4)
Fe2	0	$\frac{1}{2}$	0	0.451(3)	0.0110(4)
Ca1	0.7494(2)	0.4996(2)	-0.08735(2)	1	0.0151(2)
Ca2	0.789(7)	0.40(2)	0.802(2)	0.05	0.06(1)
Ca22	0.732(3)	0.490(7)	0.7996(7)	0.111(7)	0.06(1)
Si1	0.7502(2)	0.0004(3)	-0.00143(3)	0.949(8)	0.0081(3)
Be1	0.7502(2)	0.0004(3)	-0.00143(2)	0.051	0.0081(3)
Si2	0.4147(2)	0.5925(3)	-0.23246(5)	0.92(1)	0.0107(5)
Be2	0.4147(2)	0.5925(3)	-0.23246(5)	0.08	0.0107(5)
Si22	0.0833(2)	0.3662(3)	-0.23209(6)	0.94(1)	0.0122(5)
Be22	0.0833(2)	0.3662(3)	-0.23209(6)	0.06	0.0122(5)
Si3	0.1403(2)	0.2353(3)	-0.13452(5)	0.96(1)	0.0099(4)
Be3	0.1403(2)	0.2353(3)	-0.13452(5)	0.04	0.0099(4)
Si33	0.3554(2)	0.7230(3)	-0.13537(5)	0.95(1)	0.0104(5)
Be33	0.3554(2)	0.7230(3)	-0.13537(5)	0.05	0.0104(5)
Be4	0.501(1)	0.070(1)	0.0573(2)	1	0.013(1)
Be44	0.0008(8)	0.921(1)	0.0570(2)	1	0.010(1)
O1	0.6521(5)	-0.2035(8)	-0.0328(1)	1	0.0115(7)
O2	0.8460(5)	0.2062(8)	-0.0322(1)	1	0.0140(8)
O3	0.8607(5)	-0.1869(8)	0.0276(1)	1	0.0119(7)
O4	0.6400(5)	0.1887(8)	0.0281(1)	1	0.0146(8)
O5	0.2493(8)	0.478(1)	-0.2480(1)	1	0.0284(8)
O6	0.4554(6)	0.851(1)	-0.2627(2)	1	0.030(1)
O7	0.4162(4)	0.681(1)	-0.1825(1)	1	0.035(1)
O8	0.0500(6)	0.083(1)	-0.2574(2)	1	0.037(1)
O9	0.0794(6)	0.320(1)	-0.1814(2)	1	0.031(1)
O10	0.0030(5)	0.7780(8)	0.1037(2)	1	0.0152(8)
O11	0.2174(5)	0.942(1)	-0.1369(2)	1	0.048(2)
O12	0.2723(6)	0.444(1)	-0.1189(1)	1	0.031(1)
O13	0.4949(6)	0.8030(9)	-0.1054(1)	1	0.0188(8)
OH14	0.4915(5)	0.7411(7)	0.0582(2)	1	0.0132(8)
OH15	0.0189(6)	0.2546(8)	0.0582(1)	1	0.0176(9)
OW16	0.8405(9)	0.745(1)	-0.1498(2)	1	0.038(1)
OW17	0.6569(6)	0.223(1)	-0.1455(1)	1	0.026(1)
H14	0.577(7)	0.66(2)	0.074(3)	1	0.05
H15	-0.060(8)	0.33(2)	0.076(2)	1	0.05
H16a	0.766(8)	0.84(1)	-0.131(2)	1	0.05
H16b	0.86(1)	0.69(2)	-0.179(1)	1	0.05
H17a	0.564(6)	0.257(2)	-0.162(2)	1	0.05
H17b	0.597(9)	0.06(1)	-0.138(2)	1	0.05

ite from Ambatovita and ferrochiavennite from Telemark II the Mn/Fe site occupancy is low (Table 1) if only Mn, Fe, and Mg are included at the site. It is quite possible the site occupancy deficiency could indicate the necessity for the inclusion of some Al. There are two good supporting evidences for this possibility in both crystals. The refined scattering power is lower than ideal for Fe or Mn, indicating the possibility of a lighter element (Al) substitution. The other indicator is the high BVS for each Mn/Fe site. Ideally the BVS should be 2, but in Ambatovita

chiavennite the two sites have BVSs of 2.32 and 2.15, and for the Telemark II ferrochiavennite the BVSs are 2.06 and 2.06.

Beryllium tends to segregate in a beryllosilicate structure such that it avoids adjacent sites. This phenomenon is explained by Grice (2010) in terms of bond-valence considerations. The BeO_4 tetrahedra are in ribbons parallel to the a -axis (Fig. 1) where individual BeO_4 tetrahedra are interspersed with SiO_4 tetrahedra. The interruption in the tetrahedral framework can be clearly seen in Figure 2. Each of the two

TABLE 4A. CHIAVENNITE AND FERROCHIAVENNITE SELECTED BOND LENGTHS (Å)

Cation–O	CHIAVENNA	UTÖ	TELEMARK II	Cation–O	CHIAVENNA	UTÖ	TELEMARK II
*Mn1–O4	2.149(5) × 2	2.154(4) × 2	2.148(5) × 2	*Mn2–O3	2.141(4) × 2	2.144(4) × 2	2.147(4) × 2
*Mn1–OH14	2.164(4) × 2	2.200(3) × 2	2.183(4) × 2	*Mn2–OH15	2.181(5) × 2	2.212(4) × 2	2.196(4) × 2
*Mn1–O1	2.226(4) × 2	2.230(4) × 2	2.229(4) × 2	*Mn2–O2	2.210(4) × 2	2.208(4) × 2	2.218(4) × 2
<*Mn1–O>	<2.180>	<2.195>	<2.187>	<*Mn2–O>	<2.177>	<2.188>	<2.187>
Ca–OW16	2.395(6)	2.389(5)	2.438(6)	TELEMARK II			
Ca–OW17	2.404(5)	2.393(4)	2.416(5)	Ca2–Ca22	0.66(8)	Ca22–Ca2	0.66(8)
Ca–O2	2.424(4)	2.429(4)	2.406(4)	Ca2–O8	2.18(7)	Ca22–O6	2.12(2)
Ca–O1	2.434(4)	2.416(4)	2.408(4)	Ca2–OW17	2.21(7)	Ca22–OW16	2.23(3)
Ca–OH15	2.554(5)	2.564(4)	2.530(4)	Ca2–OW16	2.30(7)	Ca22–OW17	2.27(3)
Ca–O10	2.597(5)	2.609(4)	2.611(5)	Ca2–O6	2.48(5)	Ca22–O8	2.37(3)
Ca–OH14	2.605(5)	2.566(4)	2.586(5)	Ca2–O9	2.62(6)	Ca22–O5	2.90(3)
Ca–O13	2.715(5)	2.685(5)	2.739(6)	Ca2–O5	2.72(8)	Ca22–O7	2.98(3)
<Ca–O>	<2.516>	<2.506>	<2.517>	<Ca2–O>	<2.42>	<Ca22–O>	<2.48>
Si1–O1	1.649(4)	1.645(4)	1.647(4)	UTÖ			
Si1–O2	1.633(4)	1.637(4)	1.633(4)	Ca2–OW16	2.15(2)	Ca2–O8	2.34(3)
Si1–O3	1.628(5)	1.629(4)	1.615(5)	Ca2–OW17	2.16(2)	Ca2–O5	2.93(3)
Si1–O4	1.618(4)	1.615(4)	1.628(5)	Ca2–O6	2.20(3)	Ca2–O5'	3.01(3)
<Si1–O>	<1.632>	<1.632>	<1.631>	<Ca2–O>	<2.55>	Ca2–O7	3.03(4)
Si2–O5	1.620(6)	1.607(6)	1.626(7)	Si33–O7	1.610(5)	1.609(4)	1.589(5)
Si2–O6	1.626(5)	1.626(4)	1.629(5)	Si33–O11	1.593(5)	1.610(4)	1.619(5)
Si2–O6'	1.632(5)	1.634(4)	1.650(5)	Si33–O12	1.636(5)	1.641(4)	1.635(5)
Si2–O7	1.614(5)	1.614(4)	1.629(5)	Si33–O13	1.600(5)	1.591(4)	1.588(5)
<Si2–O>	<1.623>	<1.620>	<1.634>	<Si33–O>	<1.610>	<1.613>	<1.608>
Si22–O5	1.623(6)	1.640(6)	1.633(7)	Be4–O1	1.672(9)	1.677(8)	1.675(10)
Si22–O8	1.612(5)	1.626(5)	1.628(5)	Be4–O4	1.634(8)	1.625(8)	1.636(9)
Si22–O8'	1.625(5)	1.631(4)	1.615(5)	Be4–O13	1.632(8)	1.643(7)	1.638(8)
Si22–O9	1.606(5)	1.615(4)	1.610(5)	Be4–OH14	1.631(8)	1.618(7)	1.618(8)
<Si22–O>	<1.616>	<1.628>	<1.622>	<Be4–O>	<1.642>	<1.641>	<1.642>
Si3–O9	1.612(5)	1.607(4)	1.620(5)	Be44–O2	1.666(8)	1.636(8)	1.673(9)
Si3–O10	1.589(4)	1.585(4)	1.593(5)	Be44–O3	1.633(9)	1.606(7)	1.623(8)
Si3–O11	1.621(5)	1.614(4)	1.593(5)	Be44–O10	1.622(8)	1.598(7)	1.620(8)
Si3–O12	1.628(5)	1.614(7)	1.621(5)	Be44–OH15	1.630(8)	1.623(7)	1.649(8)
<Si3–O>	<1.612>	<1.605>	<1.607>	<Be44–O>	<1.638>	<1.616>	<1.641>

* Fe-site in ferrochiavennite (TELEMARK II)

' denotes a symmetry related site

BeO₄ tetrahedra have an apical OH group that terminates polymerization into the channel.

Role of hydrogen

In chiavennite and ferrochiavennite H atoms are in two OH groups and two H₂O groups. Hydrogen bonding for the OH groups is consistent in all five structures, with OH14 H-bonded to O12, and OH15 H-bonded to O10 (Table 4c). For the H₂O groups there are two variations in H-bonding. This is evident in Tables 4b and 4c. The two water groups are both bonded to Ca and both have H-bonding to other O atoms. OW16 is H-bonded to O8 and either O10 (Chiavenna and Utö) or OW17 (Telemark I, Ambatovita, and Telemark II). OW17 is H-bonded to O13 and O6 for all five structures. The variation in H-bonding

for OW16 is due to only one of the H atoms, H16A. In chiavennite from Chiavenna and Utö, OW16 is H-bonded to O10 through H16A with a H...A distance of 2.24 Å (Fig. 3). In the other three samples, Telemark I, Ambatovita, and Telemark II (ferrochiavennite), OW16 is H-bonded to OW17 through H16A with a H...A distance of 2.21 Å (Table 4b) (Fig. 4).

Cametti & Armbruster (2015) determined that the two H₂O groups in the Italian chiavennite dissociated at different temperatures; OW17 (Ow2 in Cametti & Armbruster 2015) was lost by 250 °C while OW16 (Ow1 in Cametti & Armbruster 2015) persisted until the end of their experiment at 425 °C, at which point the site for the water group was still 80% occupied. The reason for the differential two-step water loss is due to the difference in bond strengths. Table 4c

TABLE 4B. CHIAVENNITE AND FERROCHIAVENNITE SELECTED HYDROGEN BONDS; BOND DISTANCES (Å), O-H...O, O-H-O AND H-O-H ANGLES (°)

	D-H	d(D-H)	d(H...A)	d(D...A)	<DHA	A	BVS*	BVSΣ**	<O-W-O
CHIAVENNA chiavennite	OH14-H14	0.980(2)	1.96(2)	2.926(6)	168.4(6)	O12	1.92	2.14	
	OH15-H15	0.980(2)	2.23(8)	2.933(2)	128(2)	O10	1.75	2.09	
	OW16-H16a	0.980(2)	2.24(5)	3.132(8)	151(9)	O10	1.75	2.09	100(8)
	OW16-H16b	0.980(2)	2.12(3)	3.073(8)	164(9)	O8	1.99	2.18	
	OW17-H17a	0.960(2)	2.29(8)	3.052(7)	135(8)	O6	1.94	2.09	110(9)
UTÖ chiavennite	OW17-H17b	0.960(2)	1.95(5)	2.817(7)	149(9)	O13	1.66	1.86	
	OH14-H14	0.980(2)	1.968(2)	2.933(1)	168.77(6)	O12	1.99	2.23	
	OH15-H15	0.977(2)	2.309(4)	2.947(1)	122.05(5)	O10	1.86	1.99	
	OW16-H16a	0.978(2)	2.250(3)	3.192(1)	161.15(6)	O10	1.86	1.99	105(8)
	OW16-H16b	0.979(2)	2.074(5)	3.043(1)	169.99(7)	O8	2.01	2.22	
TELEMARK II ferrochiavennite	OW17-H17a	0.980(2)	2.093(7)	3.047(9)	165.04(7)	O6	2.01	2.22	152(7)
	OW17-H17b	0.978(2)	2.459(5)	2.841(1)	102.83(5)	O13	1.75	1.89	
	OH14-H14	0.980(2)	1.982(4)	2.953(4)	170.4(9)	O12	2.03	2.27	
	OH15-H15	0.980(2)	2.330(8)	2.943(4)	119.8(6)	O10	1.88	2.05	
	OW16-H16a	0.980(2)	2.211(7)	2.844(3)	121.2(6)	OW17	0.37	1.95	141(7)
	OW16-H16b	0.980(2)	2.231(6)	3.179(5)	162.4(9)	O8	2.07	2.25	
	OW17-H17a	0.980(2)	2.348(6)	3.105(4)	133.5(5)	O6	1.92	2.08	80(7)
	OW17-H17b	0.980(2)	1.836(4)	2.803(4)	168.2(8)	O13	1.80	2.08	

* bond valence sum of acceptor to all cations except H (constants of Brese & O'Keeffe 1991)

** bond valence sum to all cations including H calculated on the basis of site population (constants of Brese & O'Keeffe 1991)

summarizes the bond valence sums for these two sites in each structure. In the Chiavenna sample the bond valence sum for *OW16* is higher than that for *OW17*. This would indicate that the *OW17* water group would be lost first as it is. The reason for the higher BVS to *OW16* is a direct result of the BVS at *O10*, which is under-bonded, thus making it susceptible to having two H-bonds, one from *H15* and the other from *H16a* (Table 4c). For the chiavennite from Telemark I and Utö and the ferrochiavennite from Telemark II, the *O10* site is less under-bonded and has only one H-bond from *H15*. The H-bond from *H16a* is directed towards

OW17. For these three samples it is quite likely that *OW17* would be retained longer than *OW16* upon heating, but we have no experimental data to confirm this.

Coordination sequences for all subtended angles and vertex symbols to six shells for each tetrahedral site are given in Table 5. Coordination sequences are identical for tetrahedral sites that are related by the orthorhombic pseudo-symmetry; *i.e.*, *Si2/Si22*, *Si3/Si33*, and *Be4/Be44*. The topological density (TD) is the sum of tetrahedral nodes for a defined series of shells in a coordination sequence, in this case six

TABLE 4C. CHIAVENNITE AND FERROCHIAVENNITE HYDROGEN BONDS AND SELECTED BOND-VALENCE SUMS

D-H	CHIAVENNA	UTÖ	TELEMARK I	AMBATOVITA	TELEMARK II
OH14-H14	O12	O12	O12	O12	O12
OH15-H15	O10	O10	O10	O10	O10
OW16-H16a	O10	O10	OW17	OW17	OW17
OW16-H16b	O8	O8	O8	O8	O8
OW17-H17a	O6	O6	O6	O6	O6
OW17-H17b	O13	O13	O13	O13	O13
OW16	1.70	1.93	1.66	1.69	1.76
OW17	1.59	1.73	1.80	1.86	1.95
O10	1.75	1.77	1.86	1.82	1.88
O10 + H-bonds	2.09	2.11	1.99	2.00	2.05

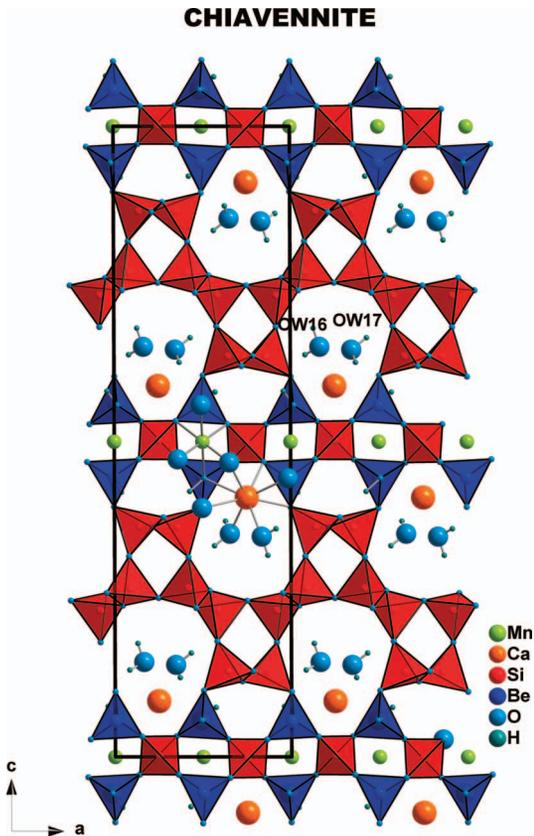


FIG. 1. Chiavennite: a [010] projection of the crystal structure showing the Si–Be-tetrahedral framework. The one Ca atom and two H₂O groups are shown centered in the nine-fold ring channels.

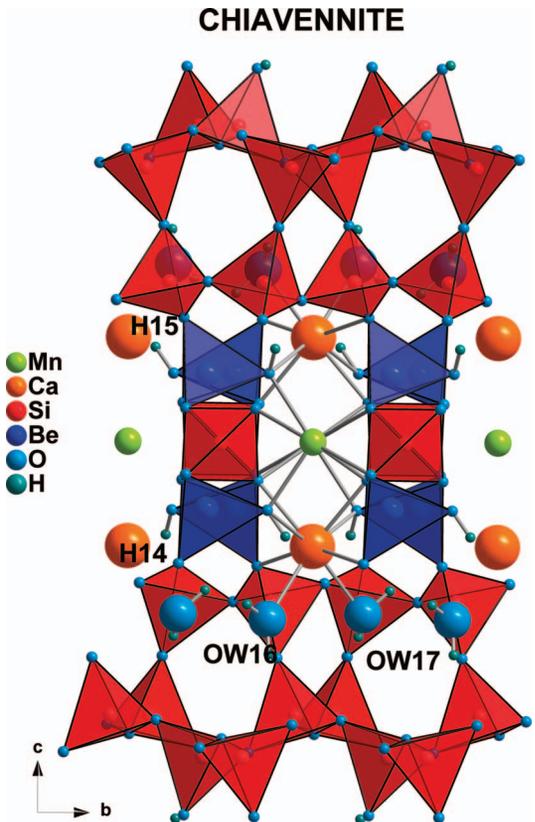


FIG. 2. Chiavennite: a [100] projection of the crystal structure showing the OH group terminations of the BeO₃OH tetrahedra that interrupts polymerization in the [010] direction.

shells. The TD is lower for *Be* sites than *Si* sites and Grice (2010) explains this effect in detail. The uniqueness of the *Si1* site is evident here; *i.e.*, the TD is between that of *Be* and *Si* sites. Again, this is more evidence for this being a site favorable for Al substitution. Similarly, the vertex symbols are identical for pseudo-symmetry related sites. Due to the direct fact that the *Be* sites in tetrahedral coordination are interrupted by H atoms, the polymerization scheme has a very short and quite different vertex symbol. The *Si1* site, surrounded by *Be* sites, has a TD and vertex symbol more similar to *Be* than the other *Si* sites. Framework density (FD) is the number of tetrahedral sites in 1000 Å³. For chiavennite and ferrochiavennite the FD = 20.0 tetrahedra/1000 Å³. In Baerlocher *et al.* (2007) the maximum observed FD for a zeolite is 20.7 and they list five, all synthetic, over 20. Alflarsenite (Grice *et al.* 2010) is a mineral example of a zeolite with a slightly higher FD of 21.7/ 1000 Å³.

Figure 5 is modified after Grice (2010). The TD for a structure is the average of all tetrahedral sites in that structure. The plot shows a very good correlation ($R^2 = 86$) between topological density and Be content in tetrahedral coordination with oxygen; the Be fraction = Be atoms / Be atoms + Si atoms). The binomial regression function is $y = 1402x^2 - 718x + 291$, where y is the topological density and x is Be content (Be / Be + Si). For chiavennite the Be content is 0.286 which is at the minimum topological density for Be silicates. Other minerals and synthetic compounds near this minimum are tugtupite, nabesite, roggianite, odintso-vite, synthetic OBW [K₄₄(H₂O)₉₆][Be₂₂Si₅₄O₁₅₀] (Baerlocher *et al.* 2007) and synthetic OSO [K₆(H₂O)₉][Be₃Si₆O₁₈] (Baerlocher *et al.* 2007). As the Be content exceeds 0.3 the topological density increases rapidly to a maximum TD = 966 for the mineral bromellite, BeO.

CHIAVENNITE

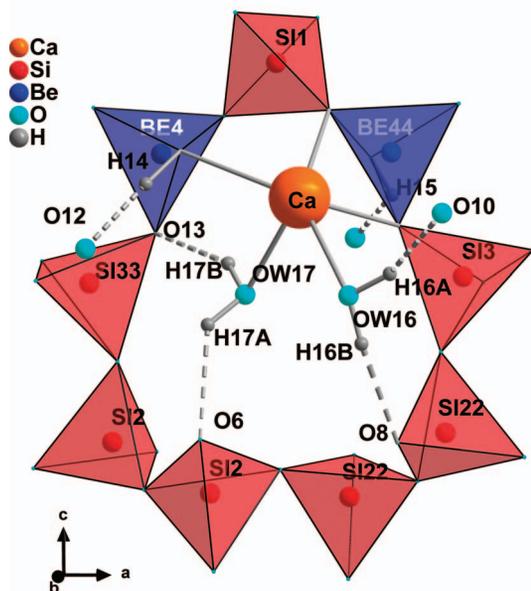


FIG. 3. Chiavennite: approximately a [010] projection showing the nine-fold ring of tetrahedra centered by one Ca atom and two H₂O groups. Note the H16A bond to O10.

CONCLUSIONS

Differences between the present five structure descriptions and that of Tazzoli *et al.* (1995) for the Chiavenna material are: (1) a change in crystal system from orthorhombic to monoclinic, (2) presence of a twin law, (3) all H sites were determined, and (4) there are two Ca sites, one only partially occupied for the Utö chiavennite and Telemark II ferrochiavennite, *versus* one Ca site in the Chiavenna, Telemark I, and

TABLE 5. CHIAVENNITE AND FERROCHIAVENNITE COORDINATION SEQUENCES AND VERTEX SYMBOLS

Tetrahedral site	Coordination Sequence	TD 6 shells	Vertex symbol
Si1	4 6 14 28 56 80	188	4•4•5•9•10•10
Si2	4 11 22 40 64 89	230	4•6 ₃ •6•6•6 ₂ •6 ₂
Si22	4 11 22 40 64 89	230	4•6 ₃ •6•6•6 ₂ •6 ₂
Si3	4 10 20 36 60 86	216	4•5•6•6 ₃ •10 ₂
Si33	4 10 20 36 60 86	216	4•5•6•6 ₃ •10 ₂
Be4	3 8 13 29 53 80	186	4•5•9
Be44	3 8 13 29 53 80	186	4•5•9

TD6 sum 1452 giving an average/shell 207

FERROCHIAVENNITE

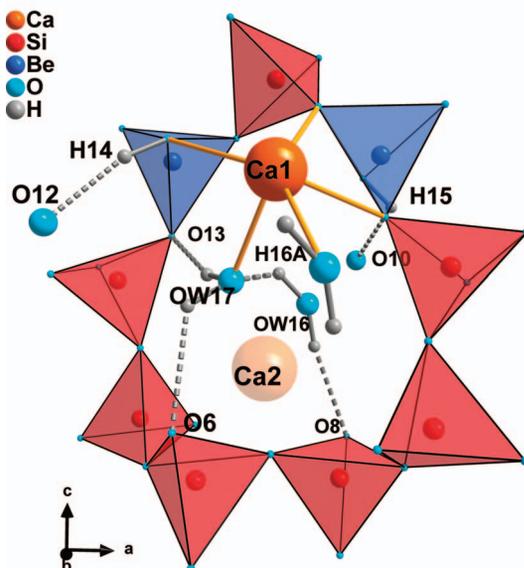


FIG. 4. Ferrochiavennite: approximately a [010] projection showing the nine-fold ring of tetrahedra centered by two Ca atoms and two H₂O groups. Note the H16A bond to OW17.

Ambatovita chiavennite samples. These findings confirm the results of Cametti & Armbruster (2015). The role of Al³⁺ in the crystal chemistry of these two minerals is primarily substitution at the Si1 site for

Variation of topological density with Be content

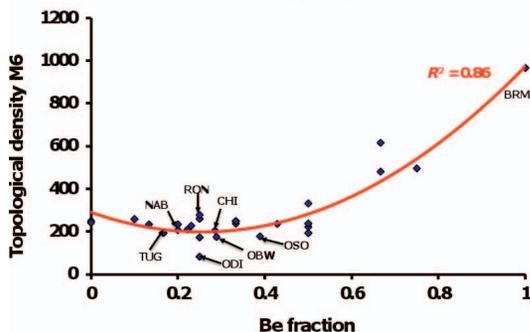


FIG. 5. Variation plot of the topological density to six shells with Be content in beryllsilicates. Labeled phases are: tugtupite (TUG), nabesite (NAB), roggianite (RON), odintsovite (ODI), synthetic OBW [K₄₄(H₂O)₉₆][Be₂₂Si₅₄O₁₅₀] (Baerlocher *et al.* 2007), synthetic OSO [K₆(H₂O)₉][Be₃Si₆O₁₈] (Baerlocher *et al.* 2007), and bromellite.

chiavennite and *Si1* and *Si2* sites in ferrochiavennite. There are two apparent H-bonding schemes for one of the water groups. The difference in the two schemes is dependent on the BVS of one oxygen atom, O10, which is underbonded in the Chiavenna and Utö crystals.

ACKNOWLEDGMENTS

The authors acknowledge with thanks two individuals at the University of Manitoba: Frank Hawthorne provided his laboratory for the crystal structure data collection and Mark Cooper provided technical expertise. The manuscript was improved by the comments of two reviewers, Cristian Biagioni and Fernando Cámara, Associate Editor Jim Evans, and Editor Lee Groat.

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Received June 12, 2015. Revised manuscript accepted November 5, 2015.