

Chiavennite revisited: a high-temperature *in situ* single-crystal X-ray diffraction study

GEORGIA CAMETTI* and THOMAS ARMBRUSTER

Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

*Corresponding author, e-mail: georgia.cametti@krist.unibe.ch

Abstract: Chiavennite ($\text{CaMnBeSi}_5\text{O}_{13}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $Z = 4$) is a rare Be-bearing zeolite mineral with an interrupted framework of four-connected $[\text{SiO}_4]$ and three-connected $[\text{BeO}_4]$ tetrahedra. A sample from the type locality in the Rhetic Alps of Italy has been re-investigated at room temperature in order to clarify the space-group ambiguity discussed in the literature and to explore the system of hydrogen bonds. In addition, the thermal stability of this zeolite was tracked by *in situ* single-crystal X-ray diffraction between 25°C and 425°C. In spite of the pseudo-orthorhombic cell dimension, the new data indicate that at room temperature chiavennite is truly monoclinic $P2_1/c$ ($\beta \approx 90^\circ$) and twinned as recently shown for the new mineral ferrochiavennite. The dehydration experiments under dry conditions at different temperatures showed that chiavennite continuously released water up to at least 425°C without topological modification. The loss of more than one H_2O molecule at 250°C decreases the Ca coordination from eight- to seven-fold. After release of the first H_2O molecule, and strong dynamic disorder of the remaining H_2O , chiavennite evolves into orthorhombic symmetry of space group $Pbcn$. The continuous monoclinic–orthorhombic transition from space group $P2_1/c$ to $Pbcn$ upon dehydration is attributed to loosening of the system of hydrogen bonds with extraframework H_2O as donor and oxygen at the cavity walls as acceptor.

Key-words: chiavennite; crystal structure; dehydration; thermal stability; zeolite; phase transition.

Introduction

Chiavennite, $\text{CaMnBeSi}_5\text{O}_{13}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $Z = 4$, is a rare Be-bearing zeolite mineral with an interrupted framework of four-connected $[\text{SiO}_4]$ and three-connected $[\text{BeO}_4]$ tetrahedra. The mineral was almost contemporaneously discovered and identified in a granitic pegmatite in the Rhetic Alps of Italy (Bondi *et al.*, 1983) and in the nepheline-syenitic pegmatites in the Oslo region, Norway (Raade *et al.*, 1983). A boron-rich chiavennite was also found in the pegmatites at Utö, Stockholm, Sweden (Langhof & Holtstam, 1994; Langhof *et al.*, 2000). Chiavennite, associated with the beryl-group mineral pezzottaite, was subsequently reported from the Sakavalana pegmatite at Ambatovita in central-western Madagascar (Pezzotta *et al.*, 2004).

Chiavennite from the Italian type locality has the empirical composition $\text{Ca}_{0.97}\text{Na}_{0.05}\text{Mn}_{0.97}(\text{Be}_{1.98}\text{Al}_{0.38}\text{Si}_{4.65})\text{O}_{12.63}(\text{OH})_{2.37} \cdot 2.16 \text{H}_2\text{O}$ (Bondi *et al.*, 1983). Originally, its crystal structure was solved and refined from single-crystal X-ray diffraction data (Domeneghetti *et al.*, 1981) in the non-centrosymmetric space group $P2_1ab$. However, further X-ray analysis suggested the centrosymmetric space group $Pnab$ (Tazzoli *et al.*, 1995). The space-group uncertainty originated from the possible occurrence of

weak reflections ($0kl$: $k + l = 2n + 1$), prohibiting n -glide on (100). These reflections should be systematically absent in $Pnab$. The authors of the reinvestigation (Tazzoli *et al.*, 1995) considered the presence of the n -glide violating reflections as artefacts due to poor crystal quality leading to smeared and overlapping reflections as a consequence of the long cell parameter $b = 31.316 \text{ \AA}$. After several tests on additional crystals of better quality (Tazzoli *et al.*, 1995) the lowering of symmetry from $Pnab$ (standard setting $Pbcn$) to $P2_1ab$ was considered unjustified.

The tetrahedral framework of chiavennite is composed of $[\text{SiO}_4]$ and $[\text{BeO}_4]$ tetrahedra, the latter have one apex occupied by a hydroxyl group, responsible for framework interruption. According to Meier & Olson (1992) the framework type (**-CHI**) can be described on the basis of three zig-zag silicate chains parallel to **a** (in $Pbcn$ setting) connected into distorted 4-rings. The 9-rings and 5-rings cavities are built by connection of the chains with trimers and pentamers. Alternatively, the periodic building unit (PerBU) can be assembled by the 5-ring secondary building unit (SBU) 5–2.

The extraframework positions are occupied by Ca, Mn, and H_2O . Ca atoms, together with the H_2O molecules occupy the 9-ring channels. Mn atoms in the 4-ring

channels occupy a regular octahedron terminated by four oxygen atoms and two OH groups.

Recently, the new beryllium-silicate zeolite ferrochiavennite $\text{Ca}_{1-2}\text{FeSi}_5\text{Be}_2\text{O}_{13}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $Z = 4$, was discovered (Grice *et al.*, 2013) in syenite pegmatites of the Larvik plutonic complex (Oslo region). Although the mineral had a marked pseudo-orthorhombic cell, similar to that found for chiavennite by Tazzoli *et al.* (1995), violations of the systematic extinction conditions for the potential $Pnab$ space group yielded the monoclinic space group $P2_1/c$ (Grice *et al.*, 2013). Nevertheless, ferrochiavennite is essentially isostructural with chiavennite; octahedral Mn is replaced by Fe and an additional partially occupied Ca site occurs in the 9-ring cavity of ferrochiavennite.

A chiavennite sample from the Italian type locality was investigated by means of thermogravimetric analysis up to 1000°C (Bondi *et al.*, 1983). This study demonstrated that the mineral gradually lost water up to 640–650°C (corresponding to *ca.* 6.75 % of mostly H_2O), followed by a rapid dehydration event beginning at *ca.* 650°C and continuing up to 1000°C; this event is assigned to the release of OH groups.

The striking similarity of the two crystal structures, chiavennite and ferrochiavennite, suggests the same space group, which is not confirmed by the most recent structure refinements (Tazzoli *et al.*, 1995; Grice *et al.*, 2013). Thus, our study aims to re-investigate the crystal structure of chiavennite from the Italian type locality at room temperature, in order to clarify the space-group ambiguity and to locate the hydrogen positions, which remained unexplored in the previous structure characterizations (Domeneghetti *et al.*, 1981; Tazzoli *et al.*, 1995). In addition, given the lack of high-temperature structural data, we monitored for the first time the thermal behavior of this zeolite at low humidity by *in situ* single-crystal X-ray diffraction.

Experimental methods

The selected chiavennite single crystal (chiavennite_A) from the type locality Chiavenna, Italy, had a flat elongated morphology, with dimensions of approximately $100 \times 30 \times 10 \mu\text{m}^3$. In order to derive the complete network of hydrogen bonds at room temperature, diffraction data were collected with an Agilent Technologies SuperNova area-detector diffractometer (Chemistry Department, University of Bern) using mirror optics monochromated $\text{MoK}\alpha$ radiation. The micro-focus X-ray source of this instrument is particularly suitable to obtain high intensity data. The CrysAlisPro software (CrysAlisPro, Agilent Technologies, Version 1.171.37.35.) was used for the data collection, data reduction and empirical absorption correction. For test reasons, the same crystal was also measured with a Bruker APEX II diffractometer (see below).

Another crystal (chiavennite_B) with dimensions of approximately $100 \times 50 \times 30 \mu\text{m}^3$ was mounted on the tip of a glass fiber, supported by a long metal pin (*ca.* 3.5 cm) suitable for high-temperature experiments. This significantly larger crystal B, although representing an intergrowth of several domains, was chosen for measurements at different temperatures because of its superior scattering behavior compared to crystal A. Diffraction data were collected on a Bruker APEX II diffractometer (Institute of Geological Sciences, University of Bern) with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), equipped with a CCD area-detector. In order to obtain stronger intensity data, an exposure time of 40 s and frame width of 0.5° was set (Table 1). The Smart APEX software allows intensity integration of only one domain while contributions by the other domains are ignored. The *in situ* dehydration process was investigated by using a self-constructed temperature controlled hot-nitrogen blower, up to 425 °C in steps of 25 °C. Before starting the data collection, the crystal was kept at least 40 min at the next measuring temperature. The data were integrated and an empirical absorption correction was applied using the Apex 2v. 2011.4-1 software package.

The unit cell, preliminarily determined on the basis of 5177 reflections, was indexed as orthorhombic similarly to chiavennite from the same locality reported by Tazzoli *et al.* (1995). However, an attempt to solve the structure in the orthorhombic space group $Pbcn$ (standard setting) yielded a total of 193 space group forbidden reflections with significant intensity. According to systematic extinctions, the most reliable space group $P2_1/c$ (in standard setting) was selected, which corresponds to the subgroup $P2_1/b11$ of $Pbcn$. $P2_1/c$ ($\beta \approx 90^\circ$) is the same symmetry as determined by Grice *et al.* (2013) for the ferrochiavennite structure.

Structural refinements were carried out with SHELX-2013 (Sheldrick, 2008), using neutral atom scattering-factors. Starting coordinates and atomic labels were those reported by Tazzoli *et al.* (1995), but due to symmetry lowering to $P2_1/c$, atomic sites related by pseudo-symmetry were labeled with double digits.

Pseudo-merohedral twinning (matrix $[-100, 010, 001]$, refined twin fraction 0.430(2)/0.570(2)) was suggested by the persistence of systematic absence violations and by the higher symmetry of the unit cell ($\beta \approx 90^\circ$) compared to point-group symmetry. With the exception of Be sites, all other positions were refined anisotropically by imposing constraints on the displacement parameters of the oxygen sites O1, O11 and O2, O22. These constraints were chosen to reduce high correlations due to pseudo-orthorhombic symmetry. The population at the tetrahedral Be sites was refined using Be and Al scattering factors assuming full occupancy. This was done to test whether Al (0.38 Al pfu according to Bondi *et al.*, 1983) substitutes also at the Be sites or only at the Si sites.

Analysis of the difference-Fourier maps allowed identifying the hydrogen positions belonging to H_2O molecules and to the OH groups. For H_2O molecules, H positions

Table 1. Crystal data and refinement parameters for chiavennite.

	Chiavennite_A	Chiavennite_A	Chiavennite_B RT	Chiavennite_B 300
<i>Crystal data</i>				
<i>a</i> (Å)	8.7466(3)	8.7524(5)	8.7481(3)	4.9145(3)
<i>b</i> (Å)	4.8972(3)	4.8998(3)	4.9147(2)	31.5168(17)
<i>c</i> (Å)	31.3160(16)	31.3292(16)	31.3420(14)	8.6645(4)
α (°)	90	90	90	90
β (°)	90.128(4)	90.071(4)	90.067(3)	90
γ (°)	90	90	90	90
Cell volume (Å ³)	1341.39(12)	1343.55(13)	1347.53(9)	1342.04(13)
<i>Z</i>	4	4	4	4
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>Pbcn</i>
Chemical formula	CaMn(BeOH) ₂ Si ₅ O ₁₃ · 2H ₂ O	CaMn(BeOH) ₂ Si ₅ O ₁₃ · 2H ₂ O	CaMn(BeOH) ₂ Si ₅ O ₁₃ · 2H ₂ O	CaMn(BeOH) ₂ Si ₅ O ₁₃ · 0.8H ₂ O
<i>Intensity measurement</i>				
Diffractometer	Supernova	APEX II SMART	APEX II SMART	APEX II SMART
X-ray radiation	MoK α λ = 0.71073 Å	MoK α λ = 0.71073 Å	MoK α λ = 0.71073 Å	MoK α λ = 0.71073 Å
X-ray power	50 kV, 1 mA	50 kV, 30 mA	50 kV, 30 mA	50 kV, 30 mA
Monochromator	Mirrors	Graphite	Graphite	Graphite
Temperature	25 °C	25 °C	25 °C	300 °C
Time per frame	60 s		40 s	40 s
Max. 2 θ	56.56		56.56	60.99
Index ranges	−11 ≤ <i>h</i> ≤ 11 −6 ≤ <i>k</i> ≤ 6 −41 ≤ <i>l</i> ≤ 41		−11 ≤ <i>h</i> ≤ 11 −4 ≤ <i>k</i> ≤ 6 −39 ≤ <i>l</i> ≤ 41	−7 ≤ <i>h</i> ≤ 4 −44 ≤ <i>k</i> ≤ 42 −12 ≤ <i>l</i> ≤ 12
No. of measured reflections	41471		9537	12829
No. of unique reflections	3350		3343	2048
No. of observed reflections <i>I</i> > 2 σ (<i>I</i>)	2750		2854	1612
<i>Structure refinement</i>				
No. of parameters used in the refinement	240 + 8 restraints		236 + 6	120
<i>R</i> (int)	0.0939		0.0521	0.0493
<i>R</i> (σ)	0.0548		0.0584	0.0400
GooF	1.112		1.126	1.083
<i>R</i> 1, <i>I</i> > 2 σ (<i>I</i>)	0.0478		0.0743	0.0431
<i>R</i> 1, all data	0.0641		0.0857	0.0577
w <i>R</i> 2 (on <i>F</i> ²)	0.1003		0.1812	0.1262
$\Delta\rho_{min}$ (−eÅ ^{−3}) close to	−0.65 Si3		−1.31 O88	−0.55 Si2
$\Delta\rho_{max}$ (eÅ ^{−3}) close to	0.66 O5		0.94 O6	0.75 Owa

were refined with fixed isotropic displacement parameters applying the restraints on bond distances H–O = 0.97(2) Å and H–H = 1.63(5) Å. The structure refinement finally converged to *R* = 4.78 %, a significantly lower agreement factor than that obtained for test refinements in the orthorhombic space group (*R* = 11.22 %).

In contrast, structural data obtained above 250 up to 425 °C were successfully refined in the orthorhombic space group *Pbcn* (Tazzoli *et al.*, 1995). In this temperature range we observed a decrease in systematic-absence violations. Thus, their low number and very weak intensity were not rated sufficient for lowering the symmetry to *P2₁/c*. An additional crystal was selected and analyzed after it was kept at 700 °C for 1 hour, in order to investigate if any phase transition was occurring after the loss of the last H₂O molecule.

In the following paragraphs we will refer to chiavennite_A when we will discuss the results obtained

at room temperature, and to chiavennite_B in the section concerning the higher-temperature experiments.

Results and discussion

Atomic coordinates of chiavennite at room temperature and the corresponding hydrogen-bond system are reported in Tables 2 and 3. Atomic displacement parameters (ADPs), T–O–T angles, bond distances and bond-valence calculation are shown in Tables S1, S2 and S3, freely available as Supplementary Material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>. Structural parameters and ADPs of chiavennite at 300 °C are displayed in Table 4 and Table S4 and the corresponding bond distances and T–O–T angles in Table S5. Table S6 shows the variation of cell parameters and unit-cell volume as a function of temperature.

Table 2. Atomic coordinates, displacement parameters and occupancy of chiavennite_A under ambient conditions (space group $P2_1/c$).

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)	Occ.
Mn1	$\frac{1}{2}$	$\frac{1}{2}$	0	0.0135(3)	0.5
Mn2	0	$\frac{1}{2}$	0	0.0139(3)	0.5
Ca1	0.7512(2)	0.5015(3)	−0.08894(3)	0.0178(2)	1
Si1	0.7501(3)	0.0012(4)	−0.00170(4)	0.0106(2)	1
Si2	0.4155(2)	0.5924(3)	−0.23256(7)	0.0132(4)	1
Si22	0.0840(3)	0.3718(3)	−0.23235(7)	0.0144(4)	1
Si3	0.1402(3)	0.2243(3)	−0.13461(7)	0.0134(4)	1
Si33	0.3543(3)	0.7169(3)	−0.13557(7)	0.0131(4)	1
Be4	0.5025(10)	0.0721(14)	0.0574(2)	0.0128(11)	0.966(8)
Al4	0.5025(10)	0.0721(14)	0.0574(2)	0.0128(11)	0.034(8)
Be44	0.0034(11)	0.9219(14)	0.0571(2)	0.0128(11)	0.971(8)
Al44	0.0034(11)	0.9219(14)	0.0571(2)	0.0128(11)	0.029(8)
O1	0.8615(6)	−0.1867(9)	0.02741(15)	0.0149(5)	1
O11	0.6405(6)	0.1902(9)	0.02744(14)	0.0149(5)	1
O2	0.8463(6)	0.2102(8)	−0.03256(14)	0.0122(4)	1
O22	0.6511(6)	−0.2003(8)	−0.03293(14)	0.0122(4)	1
O3	0.0465(6)	0.1040(9)	−0.26092(19)	0.0290(14)	1
O33	0.4604(7)	0.8414(9)	−0.26423(18)	0.0272(13)	1
O4	0.2500(10)	0.4827(11)	−0.24795(10)	0.0254(8)	1
O5	0.2806(5)	0.4253(8)	−0.12065(13)	0.0262(11)	1
O6	0.2120(5)	0.9201(9)	−0.13427(17)	0.0347(12)	1
O7	0.4161(8)	0.6969(10)	−0.18318(18)	0.0300(14)	1
O77	0.0826(8)	0.3001(11)	−0.18250(18)	0.0307(14)	1
O8	0.0021(8)	0.7712(8)	0.10325(16)	0.0155(11)	1
O88	0.4939(8)	0.7998(9)	−0.10513(16)	0.0182(11)	1
OH3	0.4906(8)	0.7375(8)	0.05799(16)	0.0166(12)	1
OH4	0.0166(8)	0.2540(8)	0.05754(18)	0.0198(13)	1
Ow1	0.8328(9)	0.7401(9)	−0.1511(2)	0.0344(17)	1
Ow2	0.6531(8)	0.2258(9)	−0.14612(19)	0.0248(13)	1
H3	0.572(7)	0.688(17)	0.077(2)	0.05*	1
H4	−0.049(9)	0.345(18)	0.077(2)	0.05*	1
H1A	0.851(9)	0.678(13)	−0.1801(11)	0.05*	1
H1B	0.877(9)	0.921(8)	−0.151(2)	0.05*	1
H2A	0.567(6)	0.249(14)	−0.165(2)	0.05*	1
H2B	0.633(8)	0.081(11)	−0.1262(19)	0.05*	1
Ca2	0.729(5)	0.534(8)	−0.2014(12)	0.03**	0.033(3)

*fixed to 0.05 Å²**fixed to 0.03 Å²

Table 3. Hydrogen bond system of chiavennite_A at room temperature. Bond distances (Å), O-H...O, O-H-O and H-O-H angles (°) are reported.

Hydrogen bond	D–H	H...A	D...A	<(DHA)	<(HOH)
Room temperature					
OW1-H1A...O3	0.97(5)	2.09(5)	3.027(9)	162.5(15)	102.9(11)
OW1-H1B...O8	0.97(5)	2.37(6)	3.170(8)	139.7(11)	
OW2-H2A...O33	0.96(6)	2.27(7)	3.029(9)	134.6(11)	110.0(13)
OW2-H2B...O88	0.96(6)	1.95(7)	2.820(8)	148.7(13)	
OH3-H3...O5	0.96(7)	1.96(7)	2.911(8)	173.2(13)	
OH4-H4...O8	0.95(8)	2.29(9)	2.912(7)	122.8(12)	

D = donor, A = acceptor.

Structure at room temperature

In spite of the strong pseudo-orthorhombic character of the structure, under ambient conditions chiavennite was found to be monoclinic (Table 2). Apart from the occurrence of the forbidden reflections, two main factors confirmed the

space group $P2_1/c$: (i) the final *R* value obtained by refining the present data set in the monoclinic space group was significantly lower than that for a structural refinement in the orthorhombic space group; (ii) only the structure solution in $P2_1/c$ allowed to extract reliable structural parameters. In particular, the oxygen sites O5 and O6 in *Pbcn*

Table 4. Atomic coordinates, displacement parameters and occupancy of chiavennite_B at 300°C (space group *Pbcn*).

Site	x	y	z	U_{eq} (Å ²)	Occ.
Mn1	0	0	0	0.02346(19)	1
Ca1	0	0.08646(3)	$\frac{1}{4}$	0.0282(2)	1
Si1	$-\frac{1}{2}$	0.00080(4)	$\frac{1}{4}$	0.0155(2)	1
Si2	0.11095(19)	0.23180(3)	0.58247(9)	0.0198(2)	1
Si3	0.24304(19)	0.13527(3)	0.63975(10)	0.0215(2)	1
Be	−0.4253(8)	0.05803(12)	0.0023(4)	0.0146(6)	1
O1	−0.3133(5)	0.02843(7)	−0.1392(2)	0.0211(5)	1
O2	−0.7063(4)	0.03204(7)	0.3464(2)	0.0187(4)	1
O3	0.3844(6)	0.25838(10)	0.5487(3)	0.0411(7)	1
O4	0	0.24624(13)	$\frac{3}{4}$	0.0369(9)	1
O5	0	0.11813(15)	$\frac{3}{4}$	0.0560(14)	1
O6	$\frac{1}{2}$	0.1381(2)	$\frac{1}{4}$	0.0717(17)	1
O7	0.1713(7)	0.18156(8)	0.5746(3)	0.0447(8)	1
O8	0.2824(5)	0.10407(8)	0.4954(3)	0.0278(5)	1
OH	0.2430(5)	0.05945(8)	0.0149(3)	0.0267(5)	1
Ow	−0.176(4)	0.1568(6)	0.277(2)	0.070(5)*	0.240(5)
OwA	0	0.1612(6)	$\frac{1}{4}$	0.070(5)*	0.357(16)

*isotropic ADPs constrained to be equal

were affected by strong disorder as demonstrated by the high values of isotropic displacement parameters, $U_{eq} = 0.108(9)$ Å² and $U_{eq} = 0.117(9)$ Å², respectively. The attempt at refining O5 and O6 as split positions led to a tetrahedral arrangement that was not consistent with a continuous tetrahedral framework.

The structural refinement in the monoclinic space group indicated that the arrangement and the coordination environment of the extraframework cations are consistent with the orthorhombic structure by Tazzoli *et al.* (1995) (Fig. 1). The refinement of the Al populations located at the Be4 and Be44 sites confirmed the low amount of Al (0.034(8) at Be4 and 0.029(8) at Be44). In addition, similarly to ferrochiavennite (Grice *et al.*, 2013), a partially occupied (sof = 0.033(3)) Ca2 site was detected in the 9-rings channels, 3.53(4) Å distant from Ca1.

The present diffraction data allowed the location of the six H sites and the evaluation of the corresponding hydrogen-bond system. As reported in Table 3, H positions of both H₂O molecules and hydroxyl groups are fixed by weak hydrogen bonds with donor-acceptor distances D...A between 2.81 and 3.18 Å and H...O acceptor distances between 1.90 and 2.40 Å. In particular, each H₂O molecule is involved in one very weak and one modest hydrogen bond. For the OH groups OH4 and OH3, which are related by orthorhombic pseudo-symmetry, hydrogen bonds of different strength were evaluated. The hydrogen bond originating at OH3 is moderate whereas the corresponding one at OH4 is very weak (Table 3). The O–H stretching region in the IR spectrum of chiavennite showed broad absorptions at 3590, 3490 and, 3410 cm^{−1} (Bondi *et al.*, 1983). These bands were attributed to adsorbed water and, in particular, the 3590 cm^{−1} band to the stretching vibrations of structural OH. According to Libowitzky (1999), IR absorptions between 3400 and 3600 cm^{−1}

correspond to donor-acceptor distances between 2.8 and 3.10 Å, in agreement with the D–A distances in Table 3.

The chiavennite structure refined in this study is strongly related to that found by Grice *et al.* (2013) for ferrochiavennite, agreeing in the same space group and same twin law. The main difference is represented by the hydrogen-bond system; in ferrochiavennite H1B (H161 in Grice *et al.*, 2013) is located between and thus connecting the two H₂O molecules. The Ow2 atom (Ow17 in Grice *et al.*, 2013) is acting as acceptor in the interaction OW1–H1B...OW2. We actually considered this network of hydrogen bonds suggested by Grice *et al.* (2013) but our adopted model led to a strongly unfavorable DHA angle of 100.7(10)° compared to 123(8)° reported for ferrochiavennite. Most important, the inspection of difference Fourier maps did not reveal any indication of H involved in hydrogen bonds between Ow1 and Ow2. Therefore, a configuration slightly different from the one by Grice *et al.* (2013) is suggested in Table 3. A list of bond valences (Brese & O'Keeffe, 1991) and additional contribution by hydrogen bonds (Ferraris & Ivaldi, 1988) is presented in Table S4.

The cell parameters of the sample (chiavennite_A) used in this study for the structure solution at room temperature were in agreement with those reported in the literature for a chiavennite sample from the same locality (Domeneghetti *et al.*, 1981, and Tazzoli *et al.*, 1995), but the unit cell of the chiavennite_B crystal at ambient conditions resulted in a considerably larger volume (1347.53(9) Å³). Such differences are probably due to the presence of slightly interfering domains comprising “crystal B” and are independent of the instrumental set-up (Table 1). On the other hand, the space-group ambiguity was solved by using an area detector allowing determination of weak reflections and discrimination of resolved spots that were previously treated as artifacts due to peak broadening.

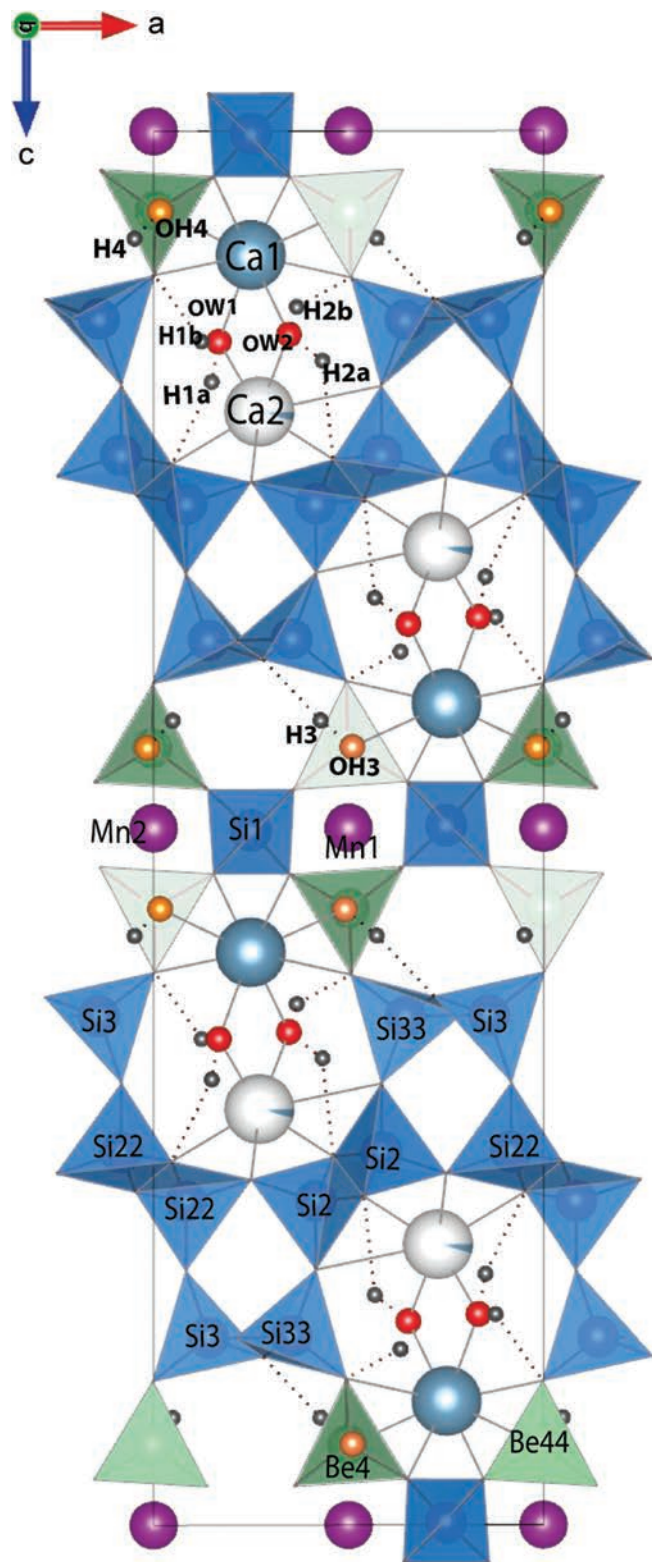


Fig. 1. Chiavennite_A crystal structure at room temperature. Atomic labels of different sites are reported. Oxygen sites of water are reported as red spheres whereas those of hydroxyl groups in orange. Gray spheres represent hydrogen atoms. Purple and light blue atoms correspond to Mn and Ca, respectively. Si tetrahedra are depicted in blue and Be tetrahedra in green. The Ca2 occupancy is represented by partially colored sites. Hydrogen bond interactions are shown as dotted lines.

Dehydration behavior

The *in situ* dehydration experiments showed that chiavennite continuously released water up to at least 425 °C without any significant topological modification. The general trend of cell parameters (Fig. 2) upon heating can be summarized as a contraction of the *a*-parameter and an expansion along the *c* axis. The *b*-parameter varies in a narrow range between 4.915 and 4.911 Å. The monoclinic β angle decreases from 90.067(3)° to 90.015(1)° at 225 °C, indicating the approaching change to the orthorhombic symmetry at 250 °C. These variations marginally reduce the volume from 1347.53(9) Å³ to 1340.7(4) Å³ at 425 °C (Fig. 3).

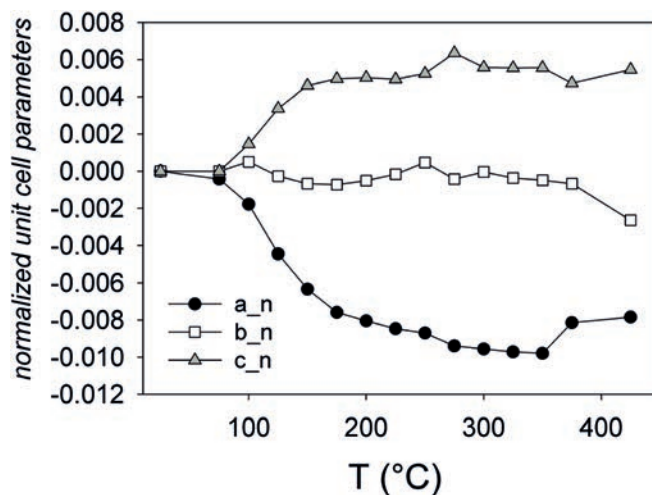


Fig. 2. Temperature dependence of normalized unit-cell parameters $((a-a_{RT})/a_{RT}; (b-b_{RT})/b_{RT}; (c-c_{RT})/c_{RT})$ of chiavennite_B between 25 °C and 425 °C. The size of the symbols is larger than the associated e.s.d. values. Orthorhombic unit-cell parameters (from 250 °C to 425 °C) are transformed to *Pnca* setting for better comparison with *P2₁/c* monoclinic setting.

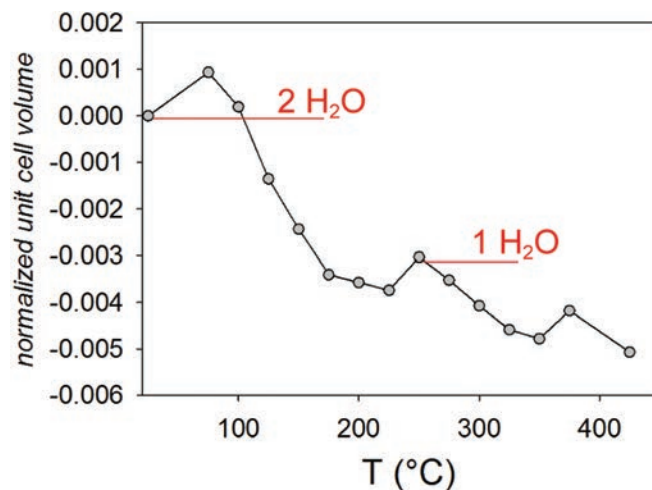


Fig. 3. Temperature dependence of normalized unit-cell volume $((V-V_{RT})/V_{RT})$ of chiavennite_B between 25 °C and 425 °C. The size of the symbols is larger than the associated e.s.d. values.

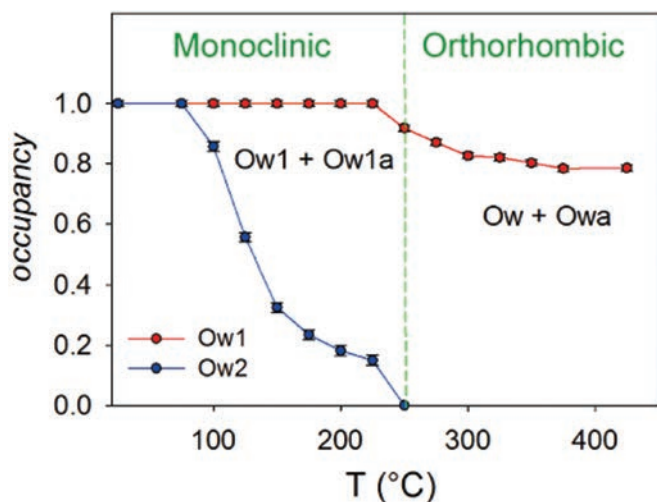


Fig. 4. Occupancy of H₂O sites (Ow1 and Ow2) of chiavennite_B as function of temperature.

At 75 °C, Ow1 and Ow2 are fully occupied but H₂O located at Ow1 displayed positional disorder and it was split in two sub-sites Ow1 and Ow1a, *ca.* 1.80(12) Å apart. The onset of the dehydration process starts at 100 °C, when the occupancy of Ow2 slightly decreased to 0.86(1). The release of the water from the structure proceeded by a continuous decrease of the population at the Ow2 site whereas the split Ow1 site remained fully occupied (Fig. 4). This trend continued up to 225 °C, when 0.85 H₂O were expelled and the unit-cell volume slightly decreased to 1342.49(8) Å³ compared to 1347.53(9) Å³ at room temperature.

At 250 °C, when the Ow2 site is vacant, the structure is no longer monoclinic and, as reported above, it was refined in the orthorhombic space group *Pbcn*. The change to the higher symmetry is not regarded as an abrupt phase

transition, but with increasing temperature and degree of dehydration the number of space group *Pbcn* violations decreases continuously and the intensity of forbidden reflections weakened (Fig. 5). Moreover, structural refinements in space group *Pbcn* yielded favorable *R* agreement factors, and the occurrence of a few weak reflections was no longer sufficient to justify the increase in the number of refined parameters by applying monoclinic symmetry. However, most convincingly, the disordered arrangement of the sites O6 and O5 that is observed for *Pbcn* symmetry at room temperature disappears after heating to 250 °C and higher temperatures. The ADP's of these critical positions behave regularly compared to other oxygen sites in the structure.

Up to 425 °C, the maximum temperature of this study, the structure preserves orthorhombic symmetry, and the occupancy of the split Ow1 site (Ow1 + Ow1a) gradually decreases to 0.78(1). The loss of more than one H₂O molecule influences the Ca coordination, which decreases from 8- to 7-fold. Upon heating from 25 to 425 °C, the cell volume decreased by 0.5 %. In addition, the T-O-T angles changed by only 4° (Table S2, Table S5) over this temperature range, indicating that the gradual release of water had little impact on the porous framework. An exception is the Si3-O6-Si33 angle (Si3-O6-Si3 in the orthorhombic setting), which significantly increases during the earlier steps of the dehydration (from 154.7(4)° at room temperature to 167.2(4)° at 125 °C) and further increases up to 173.6(1)° between 250 and 425 °C (Fig. 6).

The X-ray measurement of a single crystal preliminarily heated to 700 °C did not reveal any X-ray reflections, indicating that, after the loss of the last H₂O molecule, chiavennite becomes X-ray amorphous. On the basis of our results and of the thermo-gravimetric curve reported by Bondi *et al.* (1983), we have reason to believe that above 425 °C the dehydration process proceeds by the gradual release of the last H₂O molecule without any additional topological

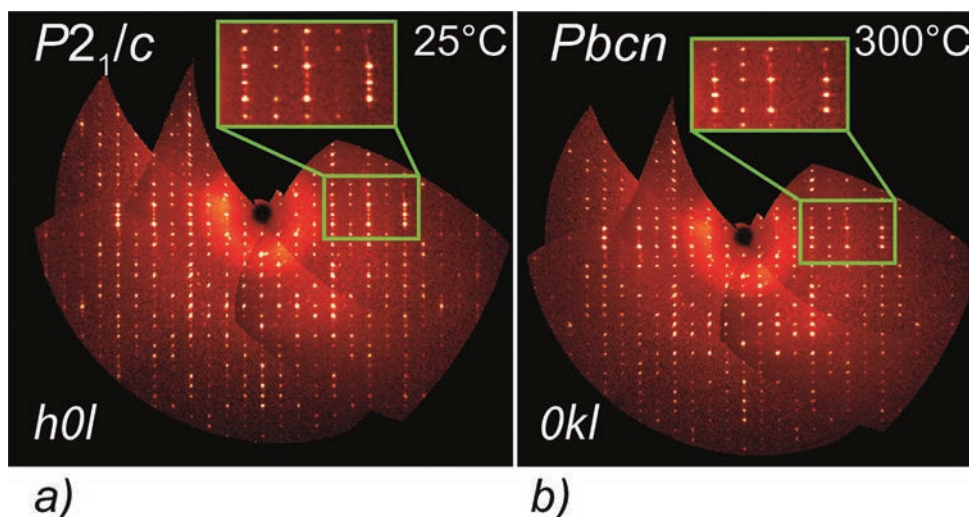


Fig. 5. Reconstructed reciprocal layers of chiavennite_B at 25 °C (a) and 300 °C (b). The 31 Å axis is vertical. Forbidden reflections for space group *Pbcn* at room temperature, highlighted in the green box (a), are not observable at 300 °C (b).

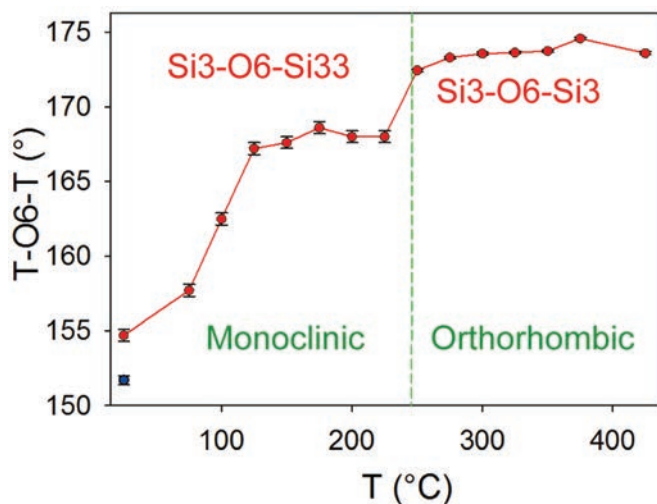


Fig. 6. Variation of the T-O6-T angle as function of temperature for chiavennite_B. The corresponding value of the T-O6-T angle for chiavennite_A is reported as a blue circle.

modification, until the breakdown of the structure between 600 and 700 °C. This behavior is in agreement with the observation that high-silica zeolites (Si/Al ratio ≥ 3.80) always display high thermal stability (Cruciani, 2006).

Driving force for the monoclinic–orthorhombic transition

The structural transformation of chiavennite upon heating is not characterized by an exact point at which the monoclinic symmetry changes to orthorhombic. As reported above, the intensity of reflections indicating monoclinic symmetry gradually decreased between 100 and 225 °C. However, we may refer to 250 °C as the transformation temperature at which one H₂O molecule (Ow2) was expelled. The gradual change toward higher symmetry may be explained by considering the H₂O distribution inside the channels. At temperatures as low as 75 °C, H₂O located at the Ow1 site displays positional disorder. With the increase of temperature this disorder becomes strongly dynamical and we can no longer refer to split positions (although such an approach was used in our refinement to model a strongly smeared, banana-shaped electron density). More reasonably, the distribution of H₂O is random between the refined sites Ow1 and Ow1a. This becomes obvious from inspection of the calculated electron-density distributions related to the positions of the H₂O molecules (Fig. 7): up to 125 °C it is still possible to recognize the peaks corresponding to Ow2, Ow1, and Ow1a sites, respectively. However, with increasing

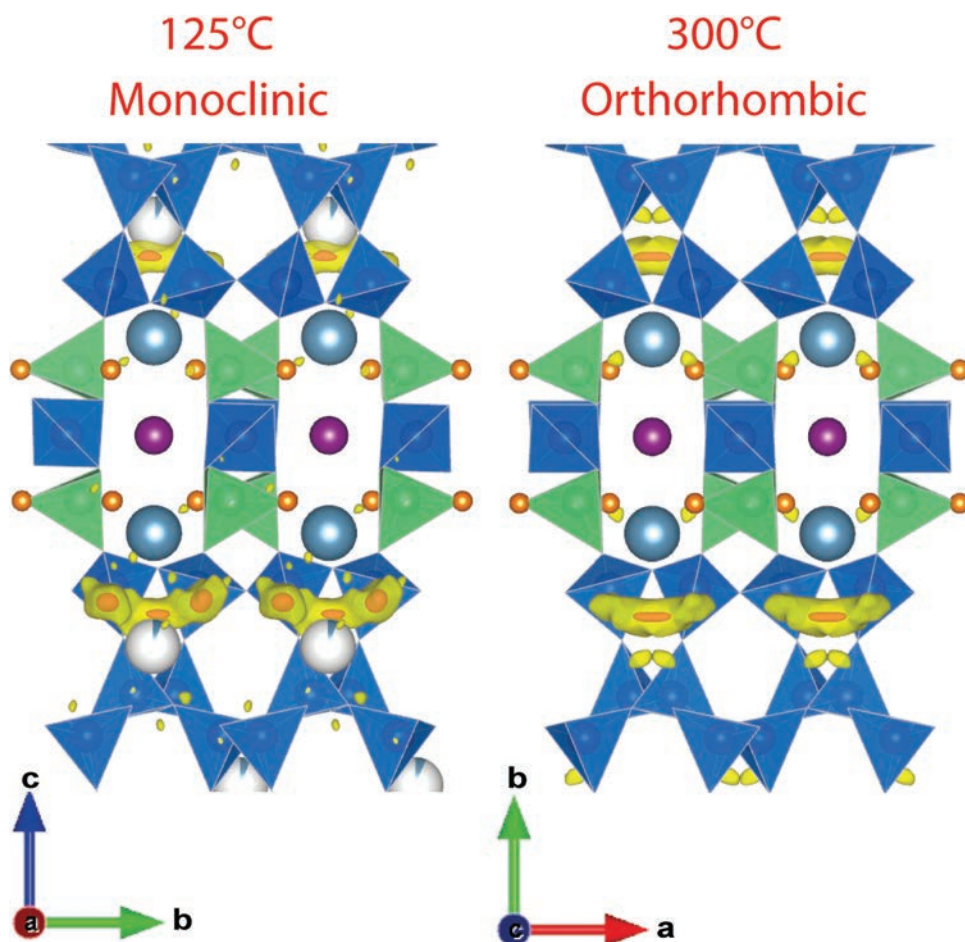


Fig. 7. Crystal structure of chiavennite_B at 125 °C and 300 °C. The calculated electron-density of H₂O sites is displayed. Yellow and orange isosurfaces correspond to electron density ≤ 0.7 and $\leq 3 \text{ e}^-/\text{\AA}^3$, respectively. Atom colors as reported in Fig. 1.

temperature, these peaks become smeared and broaden, indicating that H₂O is randomly distributed over a large volume. In this highly disordered configuration, the monoclinic distortion is no longer favorable.

An interesting comparison can be drawn between chiavennite and other Ca-bearing zeolites. It has been demonstrated (Cruciani *et al.*, 2003; Wadoski-Romeijn & Armbruster, 2013) that, upon heating, Ca-bearing zeolites usually undergo notable structural changes induced by Ca re-arrangement inside the structure. After the loss of coordinating H₂O, Ca migrates to create new bonds to preserve its coordination. From this point of view, chiavennite represents a unique case, since the structure remains almost unchanged during the whole dehydration process. Under ambient conditions Ca in chiavennite is 8-fold coordinated by six potentially underbonded oxygen framework sites belonging to Be tetrahedra (O and OH) and to two H₂O molecules. Upon heating the loss of one H₂O reduces the Ca coordination to seven-fold, which still represents a stable coordination. Thus, Ca migration toward a new accommodation is not required.

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