

Carlhintzeite, $\text{Ca}_2\text{AlF}_7\cdot\text{H}_2\text{O}$, from the Gigante granitic pegmatite, Córdoba province, Argentina: description and crystal structure

A. R. KAMPF^{1,*}, F. COLOMBO² AND J. GONZÁLEZ DEL TÁNAGO³

¹ Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Blvd, Los Angeles, California 90007, USA

² CICTERRA-CONICET - Cátedra de Geología General, Facultad de Ciencias Exactas, Físicas y Naturales – Pabellón Geología, Universidad Nacional de Córdoba, Vélez Sarsfield 1611, (X5016GCA) Córdoba, Argentina

³ Departamento de Petrología y Geoquímica, Facultad de Ciencias Geológicas, Universidad Complutense, 28040 Madrid, Spain

[Received 11 June 2010; Accepted 2 August 2010]

ABSTRACT

Carlhintzeite, $\text{Ca}_2\text{AlF}_7\cdot\text{H}_2\text{O}$, has been found at the Gigante pegmatite, Punilla Department, Córdoba Province, Argentina. It occurs as colourless prismatic crystals up to 0.8 mm long, ubiquitously twinned on {001}. Electron microprobe analyses provided the empirical formula $\text{Ca}_{1.98}\text{Al}_{1.02}\text{F}_{6.24}(\text{OH})_{0.76}\text{H}_{1.62}\text{O}$. A crystal fragment used for the collection of structure data provided the triclinic, $\bar{C}1$ cell: $a = 9.4227(4)$, $b = 6.9670(5)$, $c = 9.2671(7)$ Å, $\alpha = 90.974(6)$, $\beta = 104.802(5)$, $\gamma = 90.026(6)^\circ$, $V = 558.08(7)$ Å³ and $Z = 4$. The crystal structure, solved by direct methods and refined to $R_1 = 0.0322$ for 723 $F_o > 4\sigma F$ reflections, is made up of linkages of AlF_6 octahedra, CaF_8 polyhedra and $\text{CaF}_6(\text{H}_2\text{O})_2$ polyhedra. The AlF_6 octahedra are isolated from one another, but share polyhedral elements with Ca polyhedra. Most notably, the Al1 octahedron shares *trans* faces with two CaF_8 polyhedra and the Al2 octahedron shares *trans* edges with two $\text{CaF}_6(\text{H}_2\text{O})_2$ polyhedra. The linkage of the Ca polyhedra alone can be described as a framework in which edge-sharing chains along **b** are cross-linked by edge-sharing. Edge-sharing chains of Ca polyhedra along **b** in the carlhintzeite structure are similar to those along **c** in the structures of gearsutite, $\text{CaAlF}_4(\text{OH})\cdot(\text{H}_2\text{O})$, and prosopite, $\text{CaAl}_2\text{F}_4(\text{OH})_4$.

KEYWORDS: carlhintzeite, gearsutite, prosopite, crystal structure, Córdoba, Argentina.

Introduction

CARLHINTZEITE is a rare calcium aluminium fluoride hydrate first described by Dunn *et al.* (1979) from a single museum specimen simply labelled “Hagendorf”. The authors noted the matrix and associated species (rockbridgeite, pyrite, strengite and apatite) to be similar to those from the Hagendorf pegmatites in Bavaria, Germany, but they were unable to determine from which of the pegmatites in this area the specimen may have originated. Since that time, additional

specimens containing carlhintzeite have been found at the Hagendorf Süd pegmatite, and this is likely to be the source of the original specimen (Dunn *et al.*, 1979). Carlhintzeite has also been found at the Perda Niedda mine, Sardinia, Italy (Bortolozzi *et al.*, 2007), at Kreuzberg Mount, Bavaria, Germany (Dill *et al.*, 2008) and at the Serra Blanca pegmatite, Paraiba, Brazil (Wegner *et al.*, 1998).

Dunn *et al.* (1979) were unable to find a carlhintzeite crystal suitable for crystal structure analysis because of ubiquitous twinning by rotation about [010]. During on-going research of the secondary and hydrothermal minerals from the Gigante pegmatite, Córdoba province, Argentina, which has already yielded two new species (gayite and gallsikiite: Kampf *et al.*,

* E-mail: akampf@nhm.org

DOI: 10.1180/minmag.2010.074.4.623

2010*a,b*), another occurrence of carlhintzeite was confirmed. The carlhintzeite crystals from this locality also exhibit ubiquitous twinning; however, the crystals are generally simple contact twins and of sufficient size to allow the separation of an untwinned fragment for structure study.

Occurrence

The Gigante pegmatite is 18 km WSW of the town of Tanti, Punilla Department, Córdoba Province, Argentina (31°24'31.0" S, 64°46'19.6" W). It is an intragranitic body related to the Devonian Achala batholith, and it is part of the Punilla District (Galliski, 1999). Some of the most relevant features of the pegmatite were summarized by Kampf *et al.* (2010*a*).

The rather large F content of the Achala granite (and the related pegmatites) is reflected, among other features, in the ubiquitous presence of triplite and fluorapatite in the pegmatites. Late, F-bearing hydrothermal solutions are presumed to be responsible for the deposition of several unusual minerals in cracks and voids left by altered phosphates and sulphides and, although they are rather widespread, they always occur in extremely small quantities. Some species seem to be restricted to a single pegmatite. In the Gigante pegmatite, some of the F-bearing minerals (in addition to the primary phosphates mentioned above) are morinite, galliskiite, fluellite, lacroixite, and carlhintzeite, whereas fluorite, pachnolite, fluellite and benyacarite are found in the pegmatites of the nearby Cerro Blanco district.



FIG. 1. Carlhintzeite crystals up to 0.4 mm long on bermanite.

At the Gigante pegmatite, carlhintzeite occurs as single crystals (Fig. 1) up to 0.8 mm long, and as crystal aggregates up to 5 mm long, growing on drusy bermanite covering dark brown triplite. Microcrystalline crusts of lavender phosphosiderite and pale- to bright-pink strengite are found in the same paragenesis. Carlhintzeite crystals are colourless with vitreous lustre. Crystals are elongated along [010]; the best developed form is {001}, with smaller {100}, {110} and $\{\bar{1}10\}$ (Fig. 2*a*). Many crystals are twinned about [010] with {001} as the contact plane; this is evident as grooves in the forms belonging to the [001] zone (Fig. 2*b*). The streak is white.

Chemical composition

Six analyses were conducted on carlhintzeite (Table 1) at the Centro de Microscopía Electrónica Luis Br (Universidad Complutense de Madrid) using a JEOL JXA 8900M electron microprobe operating in WDS mode. The

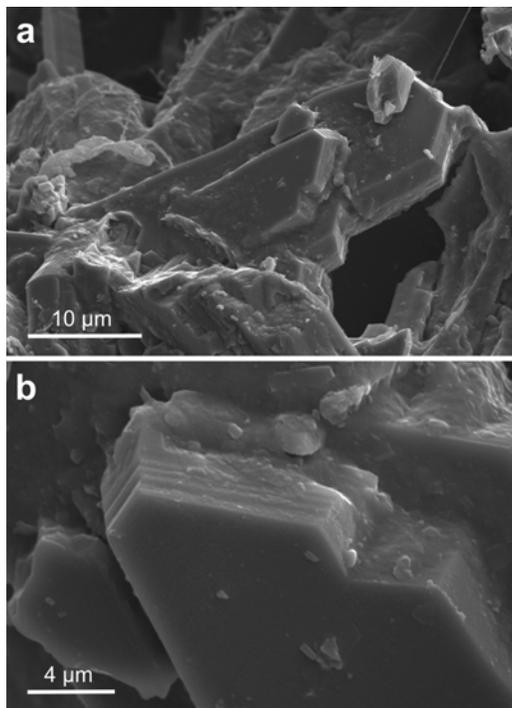


FIG. 2. SEM images of carlhintzeite crystals. (a) Crystals in parallel growth showing the dominant {001} form, with smaller {100}, {110} and $\{\bar{1}10\}$. (b) Grooves in the {110} and $\{\bar{1}10\}$ forms, due to multiple twinning.

CARLHINTZEITE, ARGENTINA

TABLE 1. EMPA results (wt.%) of carlhintzeite from the Gigante pegmatite.

Analysis #	1	2	3	4	5	6	Average	Ideal*
Al ₂ O ₃	20.52	20.69	20.47	21.12	20.31	20.13	20.54	19.75
CaO	43.08	43.46	44.69	44.20	43.51	44.34	43.88	43.45
F	47.01	47.40	46.87	45.77	48.46	45.42	46.82	51.52
–O=F	19.79	19.96	19.74	19.27	20.41	19.13	19.71	21.69
Total (less –O=F)	90.82	91.59	92.29	91.82	91.88	90.77	91.53	93.02
H ₂ O [‡]	9.18	8.41	7.71	8.18	8.12	9.23	8.47	6.98
a.p.f.u. based on 3 (Al+Ca)								
Al	1.03	1.03	1.01	1.03	1.02	1.00	1.02	1.00
Ca	1.97	1.97	1.99	1.97	1.98	2.00	1.98	2.00
F	6.34	6.34	6.18	6.01	6.52	6.05	6.24	7.00
H	2.61	2.37	2.14	2.27	2.30	2.59	2.38	2.00

* Ideal composition corresponding to Ca₂AlF₇·H₂O

‡ H₂O calculated by difference

TABLE 2. Data-collection and structure-refinement details for carlhintzeite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation / power	Mo-K α ($\lambda = 0.71075 \text{ \AA}$) / 50 kV, 40 mA
Temperature	298(2) K
Structural formula	Ca ₂ AlF ₇ ·H ₂ O
Space group	C1
Unit-cell dimensions	$a = 9.4227(4) \text{ \AA}$ $b = 6.9670(5) \text{ \AA}$ $c = 9.2671(7) \text{ \AA}$ $\alpha = 90.974(6)^\circ$ $\beta = 104.802(5)^\circ$ $\gamma = 90.026(6)^\circ$
Z	4
Volume	558.08(7) \AA^3
Density (for above formula)	2.916 g/cm ³
Absorption coefficient	2.179 mm ⁻¹
F(000)	504
Crystal size	40 $\mu\text{m} \times 30 \mu\text{m} \times 20 \mu\text{m}$
θ range	3.69 to 23.24°
Index ranges	$-10 \leq h \leq 10, -7 \leq k \leq 7, -10 \leq l \leq 10$
Reflections collected / unique	6126 / 841 [$R_{\text{int}} = 0.0546$]
Reflections with $F_o > 4\sigma F$	723
Completeness to $\theta = 27.48^\circ$	99.4%
Max. and min. transmission	0.9577 and 0.9179
Refinement method	Full-matrix least-squares on F^2
Parameters refined	109
GoF	1.056
Final R indices [$F_o > 4\sigma F$]	$R_1 = 0.0322, wR_2 = 0.0782$
R indices (all data)	$R_1 = 0.0388, wR_2 = 0.0814$
Largest diff. peak / hole	+0.565/-0.354 e/ \AA^3

$$R_{\text{int}} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum F_o^2}, \text{ GoF} = S = \frac{\{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}}{\sum F_o}, R_1 = \frac{\sum ||F_o| - |F_c||}{\sum F_o},$$

$$wR_2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}}{\sum F_o},$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } a \text{ is } 0.0522, b \text{ is } 0.5616 \text{ and } P \text{ is } [2F_c^2 + \text{Max}(F_o^2, 0)] / 3.$$

analytical conditions were 15 kV, 20 nA and a beam diameter of 5 μm . Counting times were 10 s on peak and 5 s on the background at each side of the peak. The standards were calcite (for Ca), fluorite (for F) and sillimanite (for Al). The H_2O content has been calculated by difference, as the very small amount of available material precluded a direct determination. Other elements sought but not detected (at a 2σ level, in ppm) and their standards were Mg (200, kaersutite), Fe (550, almandine), Mn (420, almandine), Zn (1100, gahnite), Na (210, albite) and P (440, fluorapatite).

The crystals appear to be free of chemical zonation. The average chemical formula, recalculated on the basis of 3 a.p.f.u. (Ca+Al) is $\text{Ca}_{1.98}\text{Al}_{1.02}\text{F}_{6.24}(\text{OH})_{0.76}\text{H}_{1.62}\text{O}$. The only significant difference between the composition of carlhintzeite from the type locality compared to that of the mineral from the Gigante pegmatite is that the latter has a somewhat smaller F content (52.1 vs. 46.8 wt.%). Nevertheless, as noted below, the structure determination provided no evidence to support the assignment of OH to any specific anion sites and the H_2O sites in the structure yield only one H_2O per formula unit.

X-ray crystallography and structure refinement

Dunn *et al.* (1979) determined carlhintzeite crystals on the type specimen to be twinned ubiquitously by rotation about [010]. Using Weissenberg and precession X-ray diffraction techniques, they correctly concluded that the mineral is triclinic and provided the *C*-centered pseudomonoclinic cell: $a = 9.48(5)$, $b = 6.98(3)$, $c = 9.30(5)$ Å, $\alpha = 91.14(10)$, $\beta = 104.85(10)$ and $\gamma = 90.0(10)^\circ$. As described above, carlhintzeite from the Gigante pegmatite is also twinned, but a careful search yielded an untwinned fragment that was subsequently used for structure data collection. To be consistent with the original description, we also used the non-standard *C*-centred cell in our determination of the carlhintzeite structure. The reduced cell is $P\bar{1}$, $a = 5.8581(3)$, $b = 5.8606(3)$, $c = 9.2671(7)$ Å, $\alpha = 78.739(6)$, $\beta = 77.551(5)$ and $\gamma = 72.957(5)^\circ$.

Single-crystal X-ray data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized Mo- $K\alpha$ radiation. The Rigaku *CrystalClear* software package was used for processing the structure data, including the application of an empirical absorption correction. The structure was

TABLE 3. Atomic coordinates and displacement parameters (\AA^2) for carlhintzeite.

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.58447(8)	0.99988(11)	0.35406(8)	0.0124(3)	0.0111(5)	0.0142(5)	0.0121(5)	0.0003(3)	0.0035(4)	0.0001(3)
Ca2	0.15860(8)	0.00061(11)	0.20308(8)	0.0132(3)	0.0111(5)	0.0156(5)	0.0125(5)	0.0009(3)	0.0024(4)	0.0004(3)
Al1	0.5000	0.0000	0.0000	0.0118(4)	0.0120(9)	0.0153(9)	0.0082(9)	0.0001(7)	0.0028(7)	-0.0004(7)
Al2	0.0000	0.0000	0.5000	0.0104(4)	0.0082(9)	0.0137(9)	0.0096(9)	0.0009(7)	0.0028(7)	0.0009(6)
F1	0.3830(3)	0.0293(4)	0.1242(2)	0.0234(6)	0.0166(12)	0.0413(15)	0.0136(13)	0.0000(11)	0.0063(10)	-0.0004(11)
F2	0.6195(2)	0.1794(3)	0.1143(3)	0.0192(6)	0.0187(12)	0.0180(12)	0.0187(13)	-0.0020(10)	0.0010(10)	-0.0001(10)
F3	0.6020(2)	0.8208(3)	0.1247(2)	0.0178(6)	0.0226(13)	0.0137(12)	0.0145(13)	0.0008(9)	0.0002(10)	0.0013(9)
F4	0.8251(2)	0.0012(4)	0.3695(2)	0.0219(6)	0.0099(12)	0.0401(15)	0.0147(13)	0.0015(10)	0.0015(10)	0.0016(10)
F5	0.5654(2)	0.6760(3)	0.3878(2)	0.0169(5)	0.0235(13)	0.0136(11)	0.0173(13)	0.0015(9)	0.0119(10)	-0.0009(10)
F6	0.5626(2)	0.3232(3)	0.3821(2)	0.0175(6)	0.0235(13)	0.0158(12)	0.0162(13)	-0.0003(10)	0.0106(10)	-0.0005(10)
F7	0.3564(2)	0.9934(3)	0.3963(2)	0.0186(6)	0.0111(12)	0.0323(14)	0.0122(12)	0.0018(10)	0.0024(10)	0.0001(10)
OW	0.8927(3)	0.9824(4)	0.0868(3)	0.0224(7)	0.0161(16)	0.0332(18)	0.0176(17)	0.0019(14)	0.0036(13)	-0.0001(14)
H1	0.852(5)	0.091(4)	0.104(6)	0.050						
H2	0.845(5)	0.882(5)	0.108(6)	0.050						

TABLE 4. Selected bond distances (Å) and angles (°) for carlhintzeite.

Ca1–F4	2.235(2)	Ca2–F7	2.232(2)	Al1–F1 (×2)	1.795(2)	Al2–F4 (×2)	1.778(2)
Ca1–F7	2.236(2)	Ca2–F2	2.367(2)	Al1–F2 (×2)	1.816(2)	Al2–F5 (×2)	1.826(2)
Ca1–F6	2.278(2)	Ca2–F3	2.376(2)	Al1–F3 (×2)	1.817(2)	Al2–F6 (×2)	1.828(2)
Ca1–F7	2.281(2)	Ca2–F1	2.417(2)	<Al1–F>	1.809	<Al2–F>	1.811
Ca1–F5	2.297(2)	Ca2–F5	2.427(2)	F1–Al1–F2 (×2)	86.96(10)	F5–Al2–F6 (×2)	84.52(9)
Ca1–F1	2.476(2)	Ca2–F6	2.436(2)	F2–Al1–F3 (×2)	87.36(9)	F4–Al2–F6 (×2)	89.39(10)
Ca1–F3	2.488(2)	Ca2–OW	2.464(3)	F1–Al1–F3 (×2)	88.61(10)	F4–Al2–F5 (×2)	89.47(10)
Ca1–F2	2.660(2)	Ca2–OW	2.610(3)	F1–Al1–F3 (×2)	91.39(10)	F4–Al2–F5 (×2)	90.53(10)
<Ca1–F>	2.369	<Ca2–F>	2.376	F2–Al1–F3 (×2)	92.64(9)	F4–Al2–F6 (×2)	90.61(10)
		<Ca2–O>	2.537	F1–Al1–F2 (×2)	93.04(10)	F5–Al2–F6 (×2)	95.48(9)

Hydrogen bonds (D = donor, A = acceptor)

D–H	d(D–H)	d(H···A)	<DHA	d(D···A)	A	<HDH
OW–H1	0.88(3)	2.30(4)	135(4)	2.983(4)	F2	
		2.62(5)	96(4)	2.851(4)	F4	
		2.67(4)	104(4)	3.013(4)	F2	111(4)
OW–H2	0.88(3)	2.38(4)	135(4)	3.066(4)	F3	
		2.49(3)	137(4)	3.185(4)	F1	
		2.60(5)	97(4)	2.851(4)	F4	

solved by direct methods using *SIR92* (Altomare *et al.*, 1994) and the location of all non-hydrogen atoms was straightforward. *SHELXL-97* software (Sheldrick, 2008) was used, with neutral atom scattering factors, for the refinement of the structure. A table of structure factor data has been deposited with the Principal Editor of the journal and is available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

With all non-hydrogen atoms refined anisotropically in the centrosymmetric space group $C\bar{1}$, R_1 converged to 3.28% for 732 reflections with $F_o > 4\sigma F$. Bond-valence calculations indicate that one site in the structure (designated OW) is occupied by the O atom of an H_2O molecule. A difference Fourier analysis revealed likely locations for the H atoms related to this site. The positions of the H atoms were constrained to an H–O distance of 0.90(3) Å and an H–H distance of 1.45(3) Å and their isotropic displacement parameters were held constant at 0.05 Å² in the final refinement, which converged to 3.22%.

The details of the data collection and structure refinement are provided in Table 2. The final atomic coordinates and displacement parameters are listed in Table 3. Selected interatomic distances are given in Table 4 and a bond-valence analysis in Table 5.

Description of the structure

The carlhintzeite structure (Figs 3, 4) is made up of linkages of AlF_6 octahedra (Al1 and Al2), CaF_8 polyhedra (Ca1) and $CaF_6(H_2O)_2$ polyhedra (Ca2). The AlF_6 octahedra are isolated from one

another, but share polyhedral elements with Ca polyhedra. Most notably, the Al1 octahedron shares *trans* faces with two CaF_8 polyhedra and the Al2 octahedron shares *trans* edges with two $CaF_6(H_2O)_2$ polyhedra. The linkage of the Ca polyhedra alone can be described as a framework in which edge-sharing chains along **b** are cross-linked by edge-sharing. All Ca and Al polyhedra are centred at approximately the same height along **b**. Figure 4 shows one such slice through the structure parallel to {010}.

The Ca polyhedra

As noted by Marchetti and Perchiazzi (2000) for gearsuite, the eightfold coordination geometry of Ca^{2+} in carlhintzeite cannot be easily described in terms of an idealized polyhedron. In carlhintzeite, the geometries of the Ca coordination polyhedra (Fig. 5) and, in particular, the lengths of their F–F edges can be readily correlated with their linkages to AlF_6 octahedra and to other Ca polyhedra. In general, the shortest polyhedral edges in both of the Ca polyhedra (Ca1 and Ca2), ranging from 2.458 to 2.523 Å, correspond to edges and faces shared with AlF_6 octahedra, while somewhat longer F–F edges, ranging from 2.613 to 2.891 Å, correspond to edges shared with other Ca polyhedra. The longest F–F edges and the edges that include O atoms are not shared with any other polyhedra.

The CaF_8 polyhedron (Ca1) shares a face (F1–F2–F3) with an AlF_6 octahedron (Al1), one edge (F7–F7) with another Ca1 polyhedron, and three edges (F1–F7, F2–F6 and F3–F5) with

TABLE 5. Bond-valence analysis for carlhintzeite. Values are expressed in valence units.

	Ca1	Ca2	Al1	Al2	H1	H2	Sum
F1	0.180	0.211	0.509 × 2↓			0.045	0.945
F2	0.110	0.242	0.481 × 2↓		0.065,0.030		0.928
F3	0.174	0.236	0.479 × 2↓			0.055	0.944
F4	0.346			0.533 × 2↓	0.035	0.035	0.949
F5	0.292	0.206		0.468 × 2↓			0.966
F6	0.308	0.201		0.465 × 2↓			0.974
F7	0.345,0.305	0.349					0.999
OW		0.261,0.176			0.870	0.865	2.172
Sum	2.060	1.882	2.938	2.932	1.00	1.00	

Al^{3+} –F, Ca^{2+} –F and Ca^{2+} –O bond strengths from Brown and Altermatt (1985); hydrogen-bond strengths based on H...F bond lengths, also from Brown and Altermatt (1985).

CARLHINTZEITE, ARGENTINA

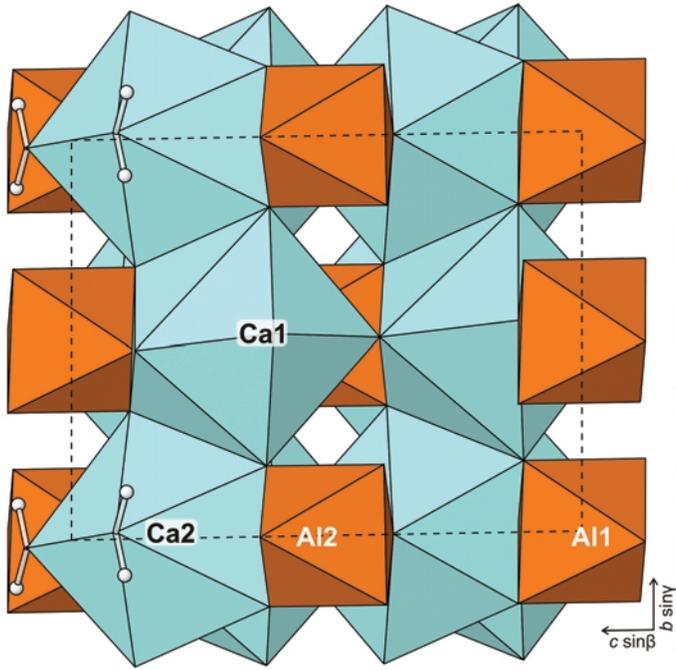


FIG. 3. Crystal structure of carlhintzeite along [100].

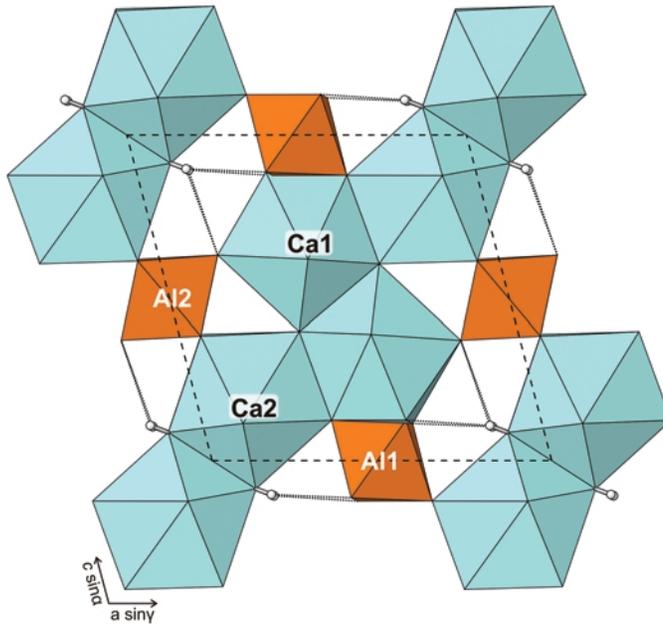


FIG. 4. Crystal structure of carlhintzeite along [010]. Note that only one layer parallel to (010) is shown. H bonds are shown as dotted lines.

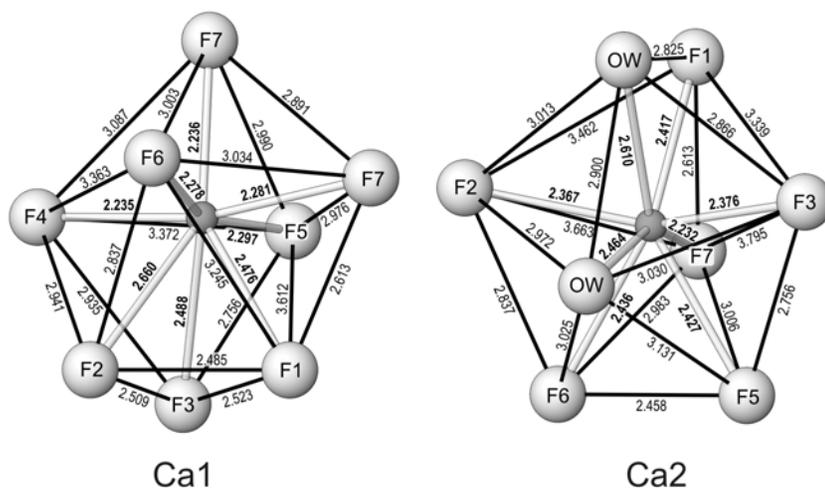


FIG. 5. Ca coordinations in carlhintzeite. Bold numbers correspond to bond distances; non-bold to lengths of polyhedral edges; both are in Å.

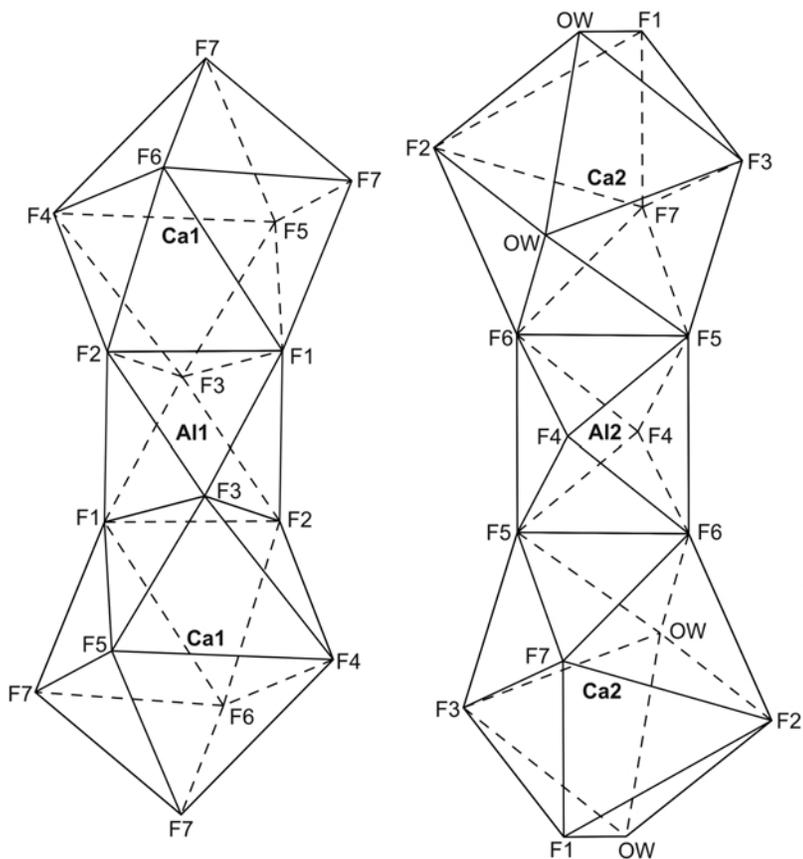


FIG. 6. Face-sharing Ca1–Al1–Ca1 trimer (left) and edge-sharing Ca2–Al2–Ca2 trimer (right) in carlhintzeite. Upper Ca1 and Ca2 polyhedra are in the same orientation as in Fig. 4.

CaF₆(H₂O)₂ polyhedra (Ca2). The CaF₆(H₂O)₂ polyhedron (Ca2) shares an edge (F5–F6) with an AlF₆ octahedron (Al2) and three edges (F1–F7, F2–F6 and F3–F5) with Ca1 polyhedra.

Ca–Al–Ca polyhedral trimers

The AlF₆ octahedron (Al1) shares *trans* F1–F2–F3 faces with two CaF₈ polyhedra (Ca1) forming an unusual face-sharing Ca1–Al1–Ca1 trimer (Fig. 6). In apparent response to cation-cation repulsion, the Ca bonds to each of the F atoms in the shared face are appreciably longer than the other Ca–F bonds in the CaF₈ polyhedra and the Al1 octahedron exhibits significant elongation in the direction of the normal to the shared faces, as shown by the smaller F–Al1–F angles (from 86.96 to 88.61°; Table 4) corresponding to the F atoms in the shared faces.

The AlF₆ octahedron (Al2) shares *trans* F5–F6 edges with two CaF₆(H₂O)₂ polyhedra (Ca2) forming an edge-sharing Ca2–Al2–Ca2 trimer (Fig. 6). Again, in apparent response to cation-cation repulsion, the Ca bonds to the F atoms in the shared edges are the longest Ca–F bonds in the CaF₆(H₂O)₂ polyhedron and the Al2 octahedron exhibits significant elongation in the direction of the normal to the shared edges, as is shown by the much smaller F–Al2–F angles corresponding to the F atoms in the shared faces (84.52°; Table 4).

Hydrogen bonding

The H atoms (H1 and H2) of the H₂O molecule (OW) project into open space in the framework and are surrounded by F atoms. Without considering hydrogen bonds, all F atoms except F7 are undersaturated (Table 5) and, in fact, the only F atom that is not positioned to participate in at least weak hydrogen bonding is F7. We have assigned three hydrogen bonds to each H atom (Table 4, Fig. 7); however, F1 to F6 remain somewhat undersaturated and the O atom of the H₂O molecule remains oversaturated. It appears likely, therefore, that H1 and H2 participate in additional longer hydrogen bonds to surrounding F atoms.

Comparison with the structures of gearsutite and prosopite

Three other minerals with similar chemical constituents are known: gearsutite,

CaAlF₄(OH)·(H₂O), prosopite, CaAl₂F₄(OH)₄, and yarovskite, Ca₃Al₂F₁₀(OH)₂·(H₂O). The structure of yarovskite is not known (Novikova *et al.*, 1966); however, the structures of both gearsutite (Marchetti and Perchiazzi 2000) and prosopite (Pudovkina *et al.*, 1973) exhibit similarities with that of carlhintzeite. All three structures contain Al(F,OH)₆ octahedra and Ca in similar eightfold coordinations to F and O atoms. All three structures also contain very similar edge-sharing chains of Ca polyhedra. The chains in gearsutite and prosopite are parallel to *c* and correspond to the cell parameters 6.978 and 7.32 Å, respectively. These match closely with the *b* cell parameter of 6.9670 Å for carlhintzeite, which corresponds to its chain direction.

The Ca:Al ratios in carlhintzeite, gearsutite and prosopite are 2:1, 1:1 and 1:2, respectively, and these are reflected in quite different polymerizations of Al and Ca polyhedra. The Al octahedra are isolated from one another in

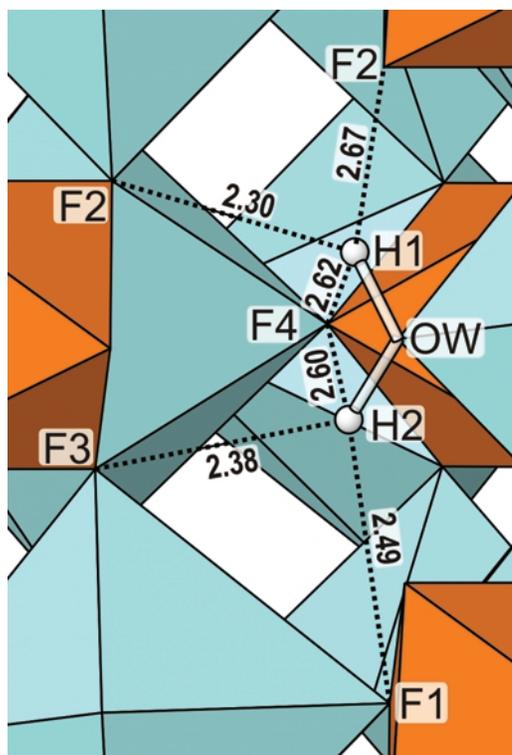


FIG. 7. Hydrogen bonding scheme in carlhintzeite with hydrogen bonds shown as dotted lines. View is along *c* with *b* approximately vertical. Distances in Å.

carlhintzeite, form edge-sharing dimers in gearksutite and edge-sharing chains in prosopite. The Ca polyhedra, on the other hand, decrease in polymerization from an edge-sharing framework in carlhintzeite, to an edge-sharing sheet in gearksutite, to an edge-sharing chain in prosopite. When the edge-sharing linkages of both Al octahedra and Ca polyhedra are considered, prosopite is seen to be a framework, while gearksutite is a sheet. Finally, it is noteworthy that face-sharing between Al octahedra and Ca polyhedra only occurs in the carlhintzeite structure.

Acknowledgements

Associate Editor Stuart J. Mills and reviewer Francesco Demartin are thanked for their constructive comments on the manuscript, and the latter especially for pointing out an error in our structure determination. Harald Dill is acknowledged for providing the reference to the report of the occurrence of carlhintzeite at Hagendorf. This study was funded, in part, by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

References

- Altomare, A., Cascarano, G., Giacobozzo, C., Guagliardi, A., Burla, M.C., Polidori, G. and Camalli, M. (1994) SIR92 – a program for automatic solution of crystal structures by direct methods. *Journal of Applied Crystallography*, **27**, 435.
- Bortolozzi, G., Ciriotti, M.E., Galli, E. and Bonacina, E. (2007) Carlhintzeite e cowlesite della Sardegna: primi ritrovamenti italiani. *Micro* (UK report), **1/2007**, 33–38.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, **B41**, 244–247.
- Dill, H.G., Gerdes, A., Melcher, F., Weber, B., Techmer, T. and Fül, M. (2008) Die Hagendorfer Pegmatitprovinz (Oberpfalz / Deutschland) aus Sedimentologisch-Geomorphologischer und Mineralogisch-Lagerstättenkundlicher Sicht. *Mitteilungen der Österreichischen Mineralogischen Gesellschaft*, **154**, 7–34.
- Dunn, P.J., Peacor, D.R. and Sturman, B.D. (1979) Carlhintzeite, a new calcium aluminum fluoride hydrate from the Hagendorf pegmatites, Bavaria, Germany. *The Canadian Mineralogist*, **17**, 103–105.
- Galliski, M.A. (1999) Distrito pegmatítico Punilla. In: Zappettini, E.O. (Ed.) Recursos Minerales de la República Argentina. Instituto de Geología y Recursos Minerales. *SEGEMAR, Anales*, **35**, 547–550.
- Kampf, A.R., Colombo, F. and González del Tánago, J. (2010a) Gayite, a new dufrénite-group mineral from the Gigante granitic pegmatite, Córdoba province, Argentina. *American Mineralogist*, **95**, 386–391.
- Kampf, A.R., Colombo, F., Simmons, W.B., Falster, A.U. and Nizamoff, J.W. (2010b) Galliskiite, $\text{Ca}_4\text{Al}_2(\text{PO}_4)_2\text{F}_8 \cdot 5\text{H}_2\text{O}$, a new mineral from the Gigante granitic pegmatite, Córdoba province, Argentina. *American Mineralogist*, **95**, 392–396.
- Marchetti, F. and Perchiazzi, N. (2000) The crystal structure of gearksutite, $\text{CaAlF}_4(\text{OH}) \cdot \text{H}_2\text{O}$. *American Mineralogist*, **85**, 231–235.
- Novikova, M.I., Sidorenko, G.A. and Kuznetsova, M.N. (1966) Yaroslavite – a new calcium aluminum fluoride. *Zapiski Vserossiyskogo Mineralogicheskogo Obshchestva*, **95**, 39–44.
- Pudovkina, Z.V., Chernitsova, N.M. and Pyatenko, Yu.A. (1973) Refinement of the crystalline structure of prosopite $\text{CaAl}_2\text{F}_4(\text{OH})_4$. *Journal of Structural Chemistry*, **14**, 345–347.
- Sheldrick, G.M. (2008) *SHELXL97 – Program for the refinement of crystal structures*. University of Göttingen, Germany.
- Wegner, R., Pöllmann, H., Witzke, T. and Schuckmann, W. (1998) Colquiriite, carlhintzeite, ralstonite and pchnolite from Serra Blanca pegmatite, Brazil. 17th General Meeting of the International Mineralogical Association, Abstract volume, **A151**, Toronto, Canada.