Strätlingite: crystal structure, chemistry, and a reexamination of its polytpye vertumnite

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Abstract: The crystal structure of strätlingite $Ca_2Al(AlSi)O_2(OH)_{10} \cdot 2.25H_2O$ ($Z=3$) from Montalto di Castro (VT), Italy, was solved and refined in space group $R\bar{3}m$ (isotropic $R=0.080$). The structure contains ordered Ca^{VII} and Al^{VI} polyhedra fully occupying "octahedral" brucite-type layers (main layers of all aluminate hydrates) hydrogen bonded to partially occupied double tetrahedral (Si/Al=1) layers formed by sharing the apical oxygens of the two component tetrahedral sheets. Cell dimensions: $a=5.745(7)$; $c=37.77(1)$Å imply the stacking of three main ("octahedral") layers and three "interlayers" (double-T layers) along the [001] direction as compared with two main layers for the mineral vertumnite which has therefore been proved to be a polytype with a c parameter equal to two thirds that of strätlingite. New chemical data on vertumnite holotype, obtained by accurate electron probe microanalysis together with those obtained for strätlingite holotype as well as for this second occurrence, show very close analogies between the two mineral species also in terms of their crystal chemistry, with a tendency of strätlingite to have a larger proportion of vacant T sites and a higher hydration degree than the polytype vertumnite.

Key-words: strätlingite, vertumnite, crystal structure, crystal chemistry, polytypes, new mineral data.

1. Introduction

Strätlingite, a calcium silico-aluminate hydrate, was first described as the natural analogue of synthetic gehlenite hydrate $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, occurring in a limestone inclusion of a basalt from Bellerberg near Mayen, Eifel, Germany (Hentschel & Kuzel, 1976). The occurrence consisted of uniaxial negative ($n_\omega=1.534$), hexagonal platy crystals of very small dimensions (0.1-0.5 mm) with (001) perfect cleavage, associated with nepheline, melilite, garnet, thomsonite, gismondine, ettringite, and hydrocalumite. Identification and characterization of the new species was actually made possible only by the contemporary synthesis and crystallographic characterization of synthetic gehlenite hydrate (Kuzel, 1976), owing

to the difficulty of obtaining quantitative chemical data directly from the natural sample. In fact, the first authors could not utilize classical chemical (wet) methods due to the paucity of the material recovered from the original sample, and they experienced great difficulties in obtaining other than qualitative data with the electron microprobe, due to the highly unstable nature of the mineral under the electron beam. Attempts to dehydrate the crystals prior to electron probe microanalysis caused their disintegration into a fine powder unsuitable for EPMA work. Identification and characterization was therefore primarily based on a comparison of crystallographic data from single crystal and powder X-ray diffractions of both natural and synthetic compounds.

The second occurrence of strätlingite (Passaglia & Turconi, 1982) was reported from a marly

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inclusion in a phonolitic lava at the Campomorto quarry, near Montalto di Castro (Viterbo, Italy). The mineral is associated with tobermorite, ettringite, calcite, and vertumnite. Similarities between strätlingite and vertumnite had already been pointed out in the first description of the latter (Passaglia & Galli, 1977) and were further discussed (on the basis of a comparison between their X-ray powder patterns) in the work reporting the crystal structure determination of vertumnite (Galli & Passaglia, 1978). The conclusion was reached that, should they have the same chemical composition, vertumnite and strätlingite may actually be considered polytypes.

The structure determination of strätlingite from Montalto di Castro and a thorough chemical characterization of both strätlingite occurrences was therefore undertaken in the present work in order to clarify its crystallochemical properties and its relations with vertumnite and related compounds.

The accurate determination of strätlingite chemical composition by EPMA prompted the adoption of the same analytical procedures for a thorough reexamination of vertumnite chemistry in view of the rather unsatisfactory match between chemistry and crystal structure originally obtained (Galli & Passaglia, 1978). The new data obtained for vertumnite allowed a detailed crystallochemical reexamination of this mineral.

2. Experimental methods

2.1. X-ray data collection and processing

A crystal fragment of strätlingite from Montalto di Castro, with the thickest possible cross section (approx. dimensions: 0.1×0.1×0.04 mm) was selected after screening half a dozen crystals by long precession $CuK\alpha$ exposures in order to select a crystal with the least possible streaking parallel to c^* (*i.e.* with the least possible stacking disorder). Intensity data collection, of 1396 total reflections, was carried out in the omega-2ϑ scan mode on a Philips PW1100 four-circle automatic diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy) in the range $2°{<}2\vartheta{\leq}25°$ using $MoK\alpha$ monochromatic radiation. Of the resulting 284 independent reflections in space group $R\bar{3}m$, 138 were considered observed by the $I{>}2\sigma(I)$ criterion. As a consequence of the crystal quality, the residual index for equivalent reflections $(R_{symm}{=}\Sigma|I(hkl){-}I(aver)|/\Sigma I(hkl))$ was rather high (0.18 for all reflections; 0.083 for reflections with

$I{>}2\sigma(I)$. Lorentz and polarization corrections, but no absorption $(\mu MoK\alpha{=}11.9$ cm$^{-1})$, were applied. Unit cell parameters: $a{=}5.745(7)$, $c{=}37.77(1)$Å were determined by the least squares refinement of 15 reflections with a diffractometer subroutine. Intersity statistics confirmed a centric space group. The structure was solved by direct methods using the SHELXS-86 set of programs (Sheldrix, 1986) and refined with the CRYLSQ routine of the XTAL set of computer programmes (Hall & Steward, 1989).

A few minute crystals were utilized to obtain a Gandolfi powder diffraction pattern (camera diameter 114.6 mm) with Ni-filtered $CuK\alpha$ radiation and lead nitrate as an internal standard. The observed and calculated powder data are reported in Table 1 together with the powder pattern of strätlingite holotype reported by Hentschel & Kuzel (1976). The cell dimensions least squares refinement, obtained from 20 unambiguously indexed reflections on the basis of a weighing scheme which takes account of the Fo's from the single crystal diffraction data, gave: $a{=}5.753(6)$, $c{=}37.82(5)$Å, vol.${=}1084(2)$Å^3.

2.2. Electron probe microanalysis (EPMA) and thermal analysis (TGA)

Chemical compositions of the two strätlingite occurrences (Montalto and Mayen) and of vertumnite holotype from Montalto, were obtained by analyzing several crystals of each sample with an ARL-SEMQ automated WDS EPMA instrument operated at 15 kV accelerating voltage, 15 n A sample current (on brass) and a probe cross section of approximately 10 μm. Natural and synthetic feldspars were used as reference standards; X-ray intensities ($L\alpha$ lines for Sr and Ba, $K\alpha$ lines for all others) were transformed to oxide concentrations by an on-line "Bence-Albee" procedure (Bence & Albee, 1968) with the use of Albee & Ray's (1970) empirical correction factors. Iron and magnesium were also included in the analytical routine but were found to be absent in all samples.

All precautions needed for the analysis of electron beam sensitive materials were adopted (Rinaldi, 1981, 1984 and 1985) and exposure was limited by adopting the minimum counting times compatible with counting statistics of the major elements. The crystals were embedded and polished so as to offer the beam a flat surface cut diagonally across the layers at approximately 45° in order to obtain maximum surface area, me-

Table 1. X-ray powder diffraction data of strätlingite two occurrences (data for Mayen sample are from Hentschel & Kuzel, 1976).

d_{obs}(Å)	I_{obs}	Montalto di Castro d_{cal}(Å)	h k l	*	Mayen d (Å)	I/I_1	h k l
12.69	vs	12.607	0 0 3	*	12.5	100	0 0 3
6.28	m(b)	6.304	0 0 6	*	6.2	70	0 0 6
4.902	w	4.940	1 0 1	*	4.90 b	30	1 0 1
					4.38	30	1 0 4
4.200	vs(b)	4.202	0 0 9	*			
					4.16	100	0 0 9
4.155	mw	4.161	0 1 5	*			
					3.41	10	1 0 8
2.874	s	2.877	1 1 0	*	2.87	70	1 1 0
2.810	mw	2.805	1 1 3	*	2.81	10	1 0 11
2.609	wm	2.617	1 1 6	*	2.61	40	1 1 6
2.488	m	2.486	0 2 1	*	2.49 b	40	2 0 1
2.426	vw	2.409	0 2 4	*	2.40	20	2 0 4
2.366	m	2.366	2 0 5	*	2.36	30	2 0 5
2.135	vw	2.136	1 0 16	*	2.12	40	1 1 12
2.076	vvw	2.081	0 2 10	*	2.07	10	2 0 10
		2.032	0 1 17				
2.007	w	2.017	2 0 11		2.02	30	2 0 11
1.892	vw	1.892	0 2 13	*	1.89	20	2 0 13
1.848	s(b)	1.847	2 1 4	*			
					1.82	20	2 1 5
1.806	w	1.801	0 0 21	*	1.79	10	0 0 21
1.766	vw	1.768	0 1 20	*			
1.662	wm	1.661	3 0 0	*			
1.512	vvw	1.506	2 0 20	*			
1.445	vvw	1.448	1 0 25	*			
		1.438	2 2 0				
1.436	w						
		1.437	1 2 17				

* Reflections selected by the least squares cell refinement programme on the basis of a weighing scheme which takes into account the Fo's.

Cell parameters obtained in the refinement: $a = 5.753(6)$Å; $c = 37.82(5)$Å; vol. $= 1084(2)$Å^3.

chanical strength during sample preparation, and the least possible "anisotropy" to the electron beam. All these precautions overcame the problems encountered by Hentschel & Kuzel (1976) in their EPMA attempts and provided satisfactory analytical results. Several crystals with slightly different orientations were analyzed thereby obtaining a minimum of ten point-analyses to be averaged for each sample. The standard deviations of these measurements are less than 1 % absolute for the major elements.

Hydrous contents were determined by thermogravimetric analysis (TGA) with a Du-Pont instrument. Weight loss curves were calibrated by Ca oxalate runs. Due to the lack of material, the water content of the holotype strätlingite from Mayen was only calculated as the simple difference from 100 % of the sum of oxides determined by EPMA. The value thus obtained (31.8 wt %) is in good agreement with that experimentally determined for the Montalto occurrence (32.5 wt %), therefore further testifying to the correctness of the analytical procedure adopted in order to avoid the nearly complete dehydration and consequent structural disintegration otherwise suffered by these minerals within the interaction volume of the electron probe.

Analytical results for the three samples examined are reported in Table 2.

Table 2. Chemical compositions (from EPMA + TGA) of the three samples analyzed (oxide wt%).

	1	2	3
SiO_2	15.97	17.55	18.01
Al_2O_3	24.15	23.22	25.26
CaO	25.60	25.13	25.88
SrO	0.74	1.09	0.81
BaO	0.81	0.90	0.18
Na_2O	0.04	0.13	0.07
K_2O	0.01	0.18	0.02
H_2O^+	28.00	31.80*	23.74
H_2O^-	4.5		5.96
Tot.	99.82	100.0	99.93

* Calculated as difference to 100 %.
1 Strätlingite from Montalto di Castro.
2 Strätlingite holotype from Mayen.
3 Vertumnite holotype from Montalto di Castro.

3. Crystal structure analysis

The crystal structure of strätlingite was solved by direct methods which allowed location of the cations and of two of the oxygen atoms (O1 and Ow2). Subsequent alternations of Fourier syntheses and least squares cycles of refinement revealed two more oxygens (Oh1 and Oh2), one of which (Oh2) refined to an occupancy of 50 % in space group $R\bar{3}m$.
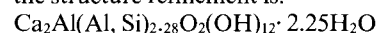
The shortest Oh2-Oh2 distance is 1.12(2)Å, hence the 50 % occupancy reflects the alternative existence of two symmetrically equivalent hydroxyl positions which, in turn, give rise to two orientations, occurring with 50 % probability for the octahedral layer. The resulting stacking disorder may be responsible for the diffuse streaks parallel to c* normally observed in the diffraction patterns of strätlingite (Hentschel & Kuzel, 1976).

One further residual peak in the difference Fourier synthesis located at the centre of the 6-rings within the double tetrahedral layers, was assigned to a water oxygen (Ow1) and refined to 25 % occupancy. A few more least squares cycles alternately refining population and position parameters converged to a final isotropic R = 0.080. T1 and T2 populations refined to values less than 1 revealing the existence of a 45 % vacancy within the double tetrahedral layer. A slight tendency of oxygen O1 (the apical shared oxygen of the tetrahedra) to refine its population to less than 1 was also observed, although being much less pronounced (approx. 92 % occupancy), it was fixed to unity in the last cycles of refinement.

Due to the small number of observed reflections no attempt was made at refining the thermal parameters anisotropically.

Atomic scattering curves for neutral atoms (International Tables for X-Ray Crystallography, 1974) were used throughout. Average curves for T1 and T2 were calculated as (Al50%+Si50%).

The reduced chemical formula derived from the structure refinement is:
$Ca_2Al(Al, Si)_{2-28}O_2(OH)_{12} \cdot 2.25H_2O$
which is in good agreement with the chemical composition obtained by EPMA and TG analyses, as testified by the total number of electrons: 230 from the structure analysis, vs. 218 from EPMA and TGA (*i.e.* less than 5 % difference); the slight charge unbalance of this formula can be compensated for by an Si/Al ratio slightly different from one and by the possible vacancy of some anionic sites.

Position, thermal and population parameters from the last cycle of refinement are reported in Table 3; interatomic distances and most significant angles, in Table 4. Table 5, the list of Fo's and Fc's is available from the "Istituto di Mineralogia" of Modena University upon request (document No. 7361).

Table 3. Final position, population, and isotropic thermal parameters from strätlingite crystal structure refinement.

Atom	Type	x/a	y/b	z/c	U_{iso}	occ.
Al	3a	.0	.0	.0	.014(3)	1.
Ca	6c	.333	.667	.0142(2)	.016(2)	1.
T1	6c	.0	.0	.1237(6)	.032(5)	.54(2)
T2	6c	.667	.333	.1227(5)	.033(5)	.57(2)
O1	6c	.667	.333	.1662(10)	.086(11)	1.
Oh1	18h	.830(2)	.170(2)	.1067(6)	.112(9)	1.
Oh2	36i	.749(3)	.054(3)	.0268(3)	.012(4)	.5
Ow1	3b	.333	.667	.1667	.098(76)	.25
Ow2	6c	.333	.667	.0812(6)	.035(7)	1.

Table 4. Interatomic distances (Å) and most significant angles (°) in the crystal structure of strätlingite (e.s.d. in brackets).

a) Octahedral layer (for only one of the two equiv. Oh2 sites)

Al — Oh2	1.91(2)	(×6)	Ca — Ow2	2.53(2)	
Ca — Oh2	2.36(1)	(×3)	Oh2 — Oh2	1.13(2)*	
Ca — Oh2′	2.44(2)	(×3)			
Oh2 — Al — Oh2	180.0 (5)	(×3)	Oh2 — Ca — Oh2	116.0 (7)	(×3)
	94.4 (7)	(×6)		148.8 (5)	(×3)
	85.6 (7)	(×6)		87.0 (5)	(×3)
Oh2 — Ca — Ow2	129.4 (4)	(×3)		84.1 (5)	(×3)
	78.3 (4)	(×3)		65.3 (5)	(×3)

b) Tetrahedral layer

T1 — O1	1.64(4)		T2 — O1	1.64(4)	
T1 — Oh1	1.81(2)	(×3)	T2 — Oh1	1.73(2)	(×3)
O1 — Ow1	3.32(1)				
O1 — T1 — Oh1	110.7 (9)	(×3)	O1 — T2 — Oh1	110.5 (9)	(×3)
Oh1 — T1 — Oh1	108.2 (10)	(×3)	Oh1 — T2 — Oh1	108.4 (10)	(×3)
T1 — O1 — T2	180		T1 — Oh1 — T2	138.8 (15)	(×3)

c) Possible hydrogen bonds between layers

Oh1 — Oh2	3.07(2)		Oh1 — Ow2	3.03(2)
Ow1 — Ow2	3.23(2)			

* minimum distance between alternative anion sites.

4. Crystal chemistry of strätlingite and vertumnite

The analyses reported in Table 3 show that vertumnite and strätlingite share the same chemical compositions except for minor differences, mainly regarding the Si and water contents, which may be easily accounted for by the slight structural differences observed. In fact the structure of strätlingite showed a lower occupancy of the T sites and a higher one for the interlayer water sites, when compared with vertumnite. These differences are also reflected in the respective physical properties, and in particular the perfect (001) cleavage found in strätlingite but not in vertumnite.

The chemical compositions were recalculated in terms of formulae units, on the basis of 2 Ca (+Sr+Ba+Na+K) atoms, in conformity with the following assumptions. Full occupancy of the "octahedral" brucite-type layer was well established by the present structure analysis and by the

Table 5. List of Fc's from the last cycle of refinement of stätlingite (Table deposited; see text).

previous work on vertumnite (Galli & Passaglia, 1978). Furthermore, the Ca content is easily determined with good accuracy by EPMA even in hydrous minerals which are affected by electron beam induced cation migration (Rinaldi, 1984).

The hydrous contents determined as weight loss by TGA are assigned, firstly, to the fully occupied water sites bonded to Ca as inferred by the structure analyses of both minerals; secondly, to the partially occupied water site within the double 6-rings in accordance with the respective occupancies determined by the structure refinements. The remainder is assumed to constitute most of the anion portion of the structure, in terms of hydroxyls. The anions remaining from stoichiometry are therefore the oxygen atoms within the double tetrahedral layers. In strätlingite these provide the slightly less than full occupancy of the O1 site (1.85 out of 2 atoms); whereas in vertumnite this site results as fully occupied and a few more oxygen atoms must pertain to other tetrahedral vertices. The correctness of such crystallochemical formulae was checked by both charge balance and "backwards" calculations of the hydrous contents.

Strätlingite has three such formula units in its crystallochemical formula, whereas vertumnite

Table 6. Crystallochemical formulae, ideal formulae and calculated densities of the three samples examined.
Strätlingite from Montalto di Castro:

$(Ca_{1.94}Sr_{0.03}Ba_{0.02}Na_{0.01})_{\Sigma\,=\,2}Al(Al_{1.02}Si_{1.13})O_{1.85}(OH)_{10.85} \cdot 2.25H_2O$ or, ideally:

$Ca_2Al(AlSi)O_2(OH)_{10} \cdot 2.25H_2O \qquad D_{cal} = 1.96$

Strätlingite from Mayen (holotype):

$(Ca_{1.90}Sr_{0.04}Ba_{0.03}Na_{0.02}K_{0.01})_{\Sigma\,=\,2}Al(Al_{0.93}Si_{1.24})O_{2.13}(OH)_{10.44} \cdot 2.25H_2O$ or, ideally:

$Ca_2Al(AlSi)O_2(OH)_{10} \cdot 2.25H_2O \qquad D_{cal} = 1.98$

Vertumnite from Montalto di Castro (holotype):

$(Ca_{1.95}Sr_{0.03}Ba_{0.01}Na_{0.01})_{\Sigma\,=\,2}Al(Al_{1.09}Si_{1.27})O_{3.16}(OH)_{9.03} \cdot 2.45H_2O$ or, ideally:

$Ca_2Al(AlSi_{1.25})O_3(OH)_9 \cdot 2.45H_2O \qquad D_{cal} = 1.94$

has two. Table 6 reports the crystallochemical formulae units thus obtained together with the calculated densities and the respective idealized formulae units for the three samples (two strätlingites and one vertumnite) examined in the present work.

From these formulae one may draw a few general observations. Strätlingite and vertumnite clearly share the same "octahedral" layer characteristic of all calcium aluminate hydrates, with two out of three positions occupied by Ca (+Sr+Ba+Na+K), which is actually seven-coordinated. As regards the other structural module, consisting of a double tetrahedral layer linked to the former by hydrogen bonds, strätlingite has a marked tendency to have a lower occupancy of the T sites than vertumnite (2.15 vs. 2.36 Si+Al a.f.u., for the two minerals from Montalto), which is reflected, with the same trend, in the occupancies of the oxygen atoms (*i.e.* 1.85 vs. 3.16 a.f.u.), and with an inverse trend for the hydroxyls, whereby strätlingite, with a higher proportion of vacancies in the double-T layer, can host more hydroxyls than vertumnite.

Discrepancies between these formulae and those obtained from the refinements of the structural models are therefore mostly due to the impossibility of determining the occupancy of the hydrogen positions by X-ray structure analysis.

The new chemical data obtained for vertumnite differ considerably from those given by Passaglia & Galli (1977) especially as regards the SiO₂ and CaO contents which were over- and underestimated by 17 % and 14 % respectively, when compared with our EPMA data. Such composition had in fact already been found to be at odds with the structure analysis results (Galli & Passaglia, 1978).

The calculated densities reported in Table 6 are in good agreement with the values reported for strätlingite holotype (Hentschel & Kuzel, 1976) and for synthetic gehlenite hydrate and related compounds (Kuzel, 1976). The slight discrepancy between the measured value (2.15 g.cm⁻¹) reported by Passaglia & Galli (1977) and our calculated value for vertumnite holotype cannot be easily accounted for and a new determination would be highly desirable.

5. Discussion

The crystal structures of strätlingite and vertumnite are made up of the same structural modules consisting of: a) an "octahedral" or "brucite-type" layer which is also common to all calcium aluminate hydrates and has been referred to as the principal layer (Kuzel, 1976), with ideal composition $[Ca_2Al(OH)_6 \cdot 2H_2O]^+$ and, b) a double tetrahedral layer with ideal composition $[(T, \Box)_4(OH,O)_8 \cdot O.25H_2O]^-$. The "octahedral" layer has an overall positive charge, the double tetrahedral layer negative.

The structure analysis indicates full occupancy, with an ordered scheme, of the two cation sites pertaining to the "octahedral" layer where each Al octahedron is laterally linked to six edge-sharing Ca^{VII} polyhedra; therefore two out of three positions in the layer are occupied by the seven coordinated Ca-type cation. The seventh vertex, alternately pointing up or down (Fig. 1), is the site of a water molecule (Ow2) projecting towards the centre of the 6-membered rings of the double tetrahedral layers and participating to the hydrogen bonding scheme linking the modules (see Table 4 and Fig. 1). One further water molecule site (Ow1, with partial occupancy in both minerals) is located at the centre of the 6-rings of the double T-layers. The "octahedral" layer could actually be de-
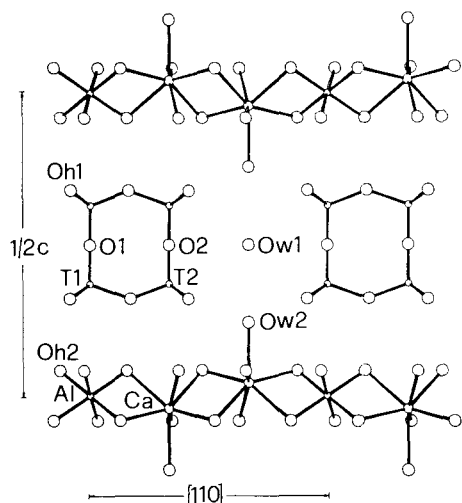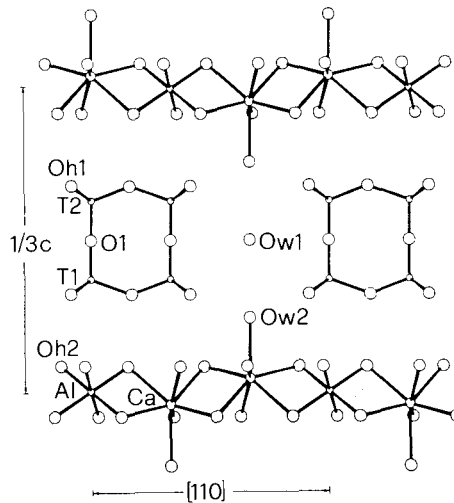
Fig. 1a.

Fig. 1b.

Fig. 1c.

Fig. 1. Projection onto (110) of the crystal structures of strätlingite-type polytypes. a: vertumnite (note the mirror plane passing through O1 and O2); b and c: the two possible orientations of the "octahedral" layer of strätlingite occurring with 50% probability in accordance with the 50% occupancy of the hydroxyl site Oh2, which has been labelled Oh3 for clarity in c; (note the centre of inversion at the O1 position).

A sandwiched double-T layer corresponds to 1/2c in vertumnite and 1/3c in strätlingite.
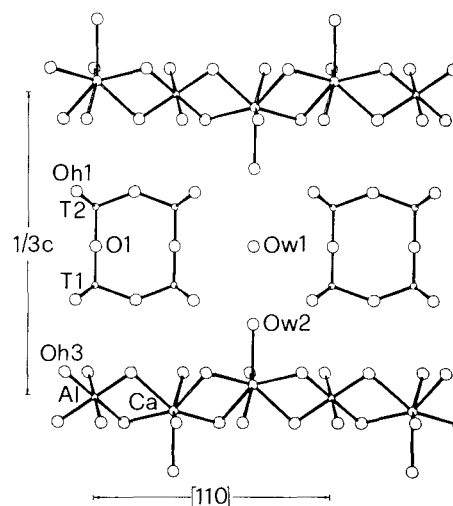
scribed as a hydrocalumite-type layer having the same topology and composition as found in this mineral structure (Sacerdoti & Passaglia, 1988). The "octahedral" layer has overall symmetry 3, but the positional disorder of hydroxyl Oh2, gives the layer a 3m symmetry and the crystal a $\bar{3}$m symmetry as the layer at $c=0$ is repeated at $c=1/3$ by centre of inversion.

The double tetrahedral layer is not fully occupied in either mineral structures with T sites vacancies of 45 % in strätlingite and 36 % in vertumnite. No Si-Al order was detected in either structures. The symmetry of a single tetrahedral layer is 3 m which becomes $\bar{3}$m in the double tetrahedral layer with Si/Al disorder. An ordering scheme, which would necessarily involve Si, Al, and vacancies, would result in a lowering of the symmetry of straetlingite from R$\bar{3}$m to R3m. An effective check of such lowering of the symmetry by Fo's statistics was hampered by the intrinsic centricity of the octahedral layer portion of the structure (which carries most of the formula weight) and could not be tested by an appropriate refinement because of the small number of observed reflections.

Double tetrahedral layers of this kind are rather rare; they have been described as "Zwirer-Doppelschicht" (Liebau, 1972) and were found to occur, although with full occupancy, in the synthetic hexagonal forms of BaAl$_2$Si$_2$O$_8$ (Takeuchi,

1958) and $CaAl_2Si_2O_8$ (Takeuchi & Donnay, 1959). Similarly to this latter compound, the structure of straetlingite also implies the existence of a very unusual T-O-T angle of 180° (Table 4.). In strätlingite however, this could be favoured by the large proportion of tetrahedral vacancies, not to mention the large thermal displacement of the apical oxygen O1 which could mask an effectively smaller T-O-T angle.

Stacking of the octahedral and double tetrahedral modules along the c direction in strätlingite yields repetition at every fourth octahedral layer in conformity with the centre of inversion at the Owl site. In vertumnite, the mirror plane passing through the apical oxygen of the double-T layers, lowers the repetition to every third octahedral layer along the c direction, hence the c parameter of vertumnite is two thirds that of strätlingite as it contains two as opposed to three sandwiched double-T modules (see Fig. 1). The staking sequence is of the type O T -T -O in strätlingite and O T mT mO in vertumnite, where "O" stands for the octahedral layer and "T" for half the double tetrahedral layer; the symbols "—" and "m" stand for related by centre and mirror symmetry, respectively. Furthermore, in strätlingite the occurrence of two alternate positions occupied, with 50 % probability, by Oh2, yields two possible configurations of the octahedral layer, thus introducing an alternative to the stacking sequence of the modules. These two positions have been labelled Oh2 and Oh3 for clarity in Fig. 1b) and 1c), respectively.

According to the definition of polytypism recommended by the IMA/IUCr Joint Committee on Nomenclature as reviewed by Angel (1986), strätlingite and vertumnite are to be classified as mixed module polytypes with constant module proportions (tpye II polytypes).

Formation of vertumnite or strätlingite polytypes seems to be controlled by hydration degree and number of vacant T sites which are higher in strätlingite. Stacking disorder between the two polytypes is certainly possible and it is likely to occur in strätlingite, as shown by the streaking parallel to c*.

All minerals pertaining to this group of polytypes could be classified as layered Ca-silicoaluminate hydrates. For priority reasons strätlingite ought to be considered the type species of this group until a natural polytype with the simplest possible stacking sequence (*i.e.* one main layer and one double-T layer) and a c parameter of approximately 12.6Å is found.

Note

Even though the minerals examined in the present work are not zeolites, they do share several mineralogical analogies with zeolitic materials, such as the highly hydrated nature, the genetic environment, and the crystallographically intriguing aspects of the silicate portion of their structures. Needless to say, all these characteristics would certainly have stirred prof. Gottardi's inquisitive mind, especially as regards the amount of mineralogical and crystallographical information to be obtained from such a small amount of available material. It is to the memory of this aspect of prof. Gottardi's scientific mind that we wish to dedicate this paper.

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