

REFINEMENT OF THE CRYSTAL STRUCTURE OF CRONSTEDTITE-1T

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Abstract—The crystal structure of cronstedtite-1T was refined in space group $P31m$, using two crystals: a triangular tabular crystal from Herja, Romania and a conical crystal from Lostwithiel, Cornwall, England. The Herja sample has the composition of $(\text{Fe}^{2+}_{2.20}\text{Fe}^{3+}_{0.80})(\text{Si}_{1.20}\text{Fe}^{3+}_{0.78}\text{Al}_{0.02})\text{O}_5(\text{OH})_4$ and the Lostwithiel sample has the composition of $(\text{Fe}^{2+}_{2.32}\text{Fe}^{3+}_{0.68})(\text{Si}_{1.32}\text{Fe}^{3+}_{0.66}\text{Al}_{0.02})\text{O}_5(\text{OH})_4$. The results of refinements are as follows: $a = 5.512(1)$ Å, $c = 7.106(1)$ Å, $R = 3.07\%$, and 342 independent reflections; and $a = 5.503(1)$, $c = 7.104(1)$ Å, $R = 2.24\%$, and 335 independent reflections for the Herja and Lostwithiel samples, respectively. The structure consists of one tetrahedral and one octahedral sheet. There is one octahedral site, M1, occupied by Fe only, and one tetrahedral site, T1, occupied by Si and Fe in the ratio of 0.617(8):0.383 (Herja) and 0.699(6):0.301 (Lostwithiel). Positions of two hydrogen atoms were determined from a difference map for the Lostwithiel data. The ditrigonalization angle of the tetrahedral sheet is $\alpha = -11.5^\circ$ (Herja) and $\alpha = -11.1^\circ$ (Lostwithiel), and the structures have a Franzini-layer type of B. The crystals studied are affected by $\pm b/3$ stacking faults which produced slight streaking of $h - k \neq 3n$ reflections.

Key Words—Cronstedtite, Layer Silicate, Order-Disorder (OD), Polytypism, X-ray Diffraction.

INTRODUCTION

Cronstedtite is a trioctahedral 1:1 layer silicate of the serpentine-kaolin group with octahedral positions occupied fully by Fe and tetrahedral sites partially occupied by Fe. The ideal composition assuming occupancy of one-half of the tetrahedral sites by Fe^{3+} is commonly reported as $(\text{Fe}^{2+}_2\text{Fe}^{3+})[\text{SiFe}^{3+}\text{O}_5](\text{OH})_4$. Because of a deficiency of tetrahedral Fe relative to the ideal formula in most samples studied, the formula is often given as $(\text{Fe}^{2+}_{3-x}\text{Fe}^{3+}_x)[\text{Si}_{2-x}\text{Fe}^{3+}_x\text{O}_5](\text{OH})_4$ (where $0 < x < 1$). This formula represents an intermediate chemistry between ideal cronstedtite and greenalite $(\text{Fe}^{2+}_3)[\text{Si}_2\text{O}_5](\text{OH})_4$. Presumably a corresponding proportion of trivalent Fe^{3+} in the octahedral sites balances the replacement of tetravalent Si by trivalent Fe cations in the tetrahedral sites.

Cronstedtite is a typical representative of the order-disorder (OD) structure of layers (Dornberger-Schiff and Ďurovič, 1975a, 1975b; Ďurovič, 1981, 1992). The polytypes of this OD family can be subdivided according to shifts and/or rotations of adjacent layers, into four OD-subfamilies A, B, C, D, corresponding to the A, B, C, D groups of Bailey (1969, 1988) or to the B, C, A, D groups of Zvyagin (1967). In this paper, the Bailey notation is used. The respective operations are: $\pm a/3$ shifts for subfamily A, $\pm a/3$ shifts combined with 180° rotation for subfamily B, $\pm b/3$ or no shift for subfamily C, $\pm b/3$ or no shift combined with 180° rotation for subfamily D, where a , and b correspond to the edges of trigonal and orthohexagonal cells, respectively.

This paper is a part of a series to investigate the polytypism of cronstedtite. The first paper gave a refinement of cronstedtite-3T (Smrčok *et al.*, 1994), his-

torical informative and corresponding references, as well as the theoretical considerations regarding the diffraction patterns of cronstedtite polytypes. The 3T polytype (subfamily A) was refined in the space group $P3_1$ to $R = 5.0\%$ and lattice parameters were $a = 5.497(2)$ Å, $c = 21.355(7)$ Å.

Ďurovič (1995, 1997) studied a rare 1M polytype from Eisleben, Saxony. Unfortunately, this study involved only identification and the sample was not of a sufficient quality for data collection. Ďurovič also presented models for the diffraction patterns for the 1M and 3T polytypes (of the same subfamily A) coexisting in one crystal. A refinement of another polytype, 2H₂ (subfamily D), in hexagonal symmetry unique from the triclinic cell of Geiger *et al.* (1983) is in progress (Hybler, 1997; Hybler *et al.*, unpubl. data).

Structures of some related trioctahedral 1:1 layer silicates have also recently been refined: lizardite-1T (Mellini, 1982; Mellini and Zanazzi, 1987; Mellini and Viti, 1994; Zhukhlistov and Zvyagin 1998), lizardite-2H₁ (Mellini and Zanazzi, 1987), Al-bearing lizardite-2H₂ (Brigatti *et al.*, 1997), amesite-2H₂ in C-centered triclinic cell (Hall and Bailey, 1979; Anderson and Bailey, 1981), and amesite-2H₁ (Zheng and Bailey, 1997). A non-standard triclinic polytype of amesite was refined by Wiewióra *et al.* (1991). A high-temperature study of the structures of lizardite-1T and 2H₁ were presented by Guggenheim and Zhan (1998). The greenalite structure was described by Guggenheim and Eggleton (1998).

The diffraction patterns of cronstedtite (and of related structures such as lizardite and amesite) can be subdivided into two groups: reflections of the type

Table 1. Electron microprobe analysis (elemental wt. %) of cronstedtite-1T.

Element	Herja		Lostwithiel	
	average wt. %	e.s.d. ¹	average wt. %	e.s.d. ¹
Fe	52.23	0.34	51.32	0.62
Si	8.32	0.62	9.34	0.45
Al	0.13	0.01	0.13	0.01
O ²	35.58		36.17	
H ²	0.99		1.02	
Total	97.25		97.98	

¹ Estimated standard deviation.

² Calculated values.

Conditions: JEOL Superprobe 733, operating voltage 15 kV, sample current ~30 nA, standards: quartz (Si), hematite (Fe), corundum (Al), ZAF correction, average of 15 analyses.

$h - k = 3n$ or the subfamily reflections and $h - k \neq 3n$ or the polytype reflections. The former is always sharp, unaffected by stacking faults, and the intensity distribution is the same for all polytypes of the respective subfamily. The distribution and intensity of the latter is typical for the given polytype. These reflections are often weakened relative to those in a fully ordered crystal, because of diffuseness owing to stacking faults, or even missing if the structure is thoroughly disordered.

The aim of this study is to provide refined structure data of the 1T polytype, which represents a subfamily C serpentine.

SAMPLE SELECTION

More than a hundred crystal fragments were separated from samples of various localities and the hhl and $h0l$ precession photographs examined. The intensity distributions along the $11l$ and $10l$ reciprocal lattice rows were chosen as criteria to determine the subfamily and polytype, respectively. (Ďurovič, 1992, p. 678; Ďurovič, 1997; Hybler, 1997). The quality of crystals (extent of stacking errors) was determined also.

These preliminary studies revealed the relative abundance of the 1T polytype with respect to the less common 3T and relatively rare $2H_2$ polytypes. No other polytypes were found. The 1T polytype was identified in samples from Herja and Chiuzaia, Romania; Litošice and Chvaletice, Czech Republic (Hybler, 1998); Rožňava, Slovakia; Lostwithiel, Cornwall, England; and Gernrode, Germany. However, most specimens were partially or completely disordered.

Each crystal is black in color, with a vitreous luster and an excellent (001) cleavage. The habit of crystals reflects their trigonal symmetry; typical forms are trigonal plates, trigonal truncated pyramids, and acicular crystals with triangular cross-section. Also crystals of an unusual conical form are common.

Finally, two relatively well-ordered crystals were selected for diffractometer study. One crystal was a triangular plate from Herja separated from the sample provided by the late Prof. J. Bauer. Specimens from the sample were first studied by Mikloš (1975). The second crystal, in the form of a near perfect cone, was cut from the tip of a larger conical crystal from Lostwithiel (Collection of the Faculty of Science, Charles University, Prague No. 3539). These samples are hereafter referred to as HER and LOS, respectively.

EXPERIMENTAL

Precession photographs of the HER crystal revealed only faint streaks along the reciprocal lattice rows that are characteristic of the polytype. The photographs of the LOS crystal were nearly perfect, with no diffuseness along lattice rows.

Electron-microprobe analyses (EMA) were performed on (001) cleavage planes of several tabular fragments taken from the samples. A preliminary check by energy-dispersive spectrometry revealed the presence of Fe, Si, O, and traces of Al. No other elements were detected. An average of fifteen point analyses of each sample is summarized in Table 1.

Each crystal selected for data collection was mounted on the diffractometer, and a respective set of intensities was recorded. Crystal data, experimental details, and results of the refinements are summarized in Table 2. The intensities were corrected for Lorentz and polarization factors. Inasmuch as the measured crystals were well defined by natural faces and the (001) cleavage plane, the absorption correction was calculated analytically according to crystal shape (program AGNOST C, Templeton and Templeton, 1978). For the LOS crystal, the conical surface was approximated by 12 pyramidal planes. The JANA98 (Petříček and Dušek, 1998) program package was used for the structure determination and refinement. Scattering factors were taken from the *International Tables* (1974), and starting atomic coordinates from the theoretical model (Bailey, 1969). The results are in agreement with earlier observations of Steadmann (1964), Steadmann and Nuttall (1963, 1964), and Bailey (1988).

Separate scale factors were set for the subfamily ($h - k = 3n$) and for the characteristic polytype reflections ($h - k \neq 3n$) in the final phase of refinement. Their ratios converged to 1:0.79 and 1:0.96 for HER and LOS data, respectively. In this way, the possible deficiency of intensity of polytype reflections owing to partial stacking disorder was compensated.

Attempts to locate hydrogen atoms failed for the HER data. The difference Fourier map for the LOS data provided two peaks of heights 0.91 and 1.01 e/Å³ close to expected positions H1 and H2 in the proximity of the OH1 and OH2 oxygen atoms, respectively. The next strongest peak, 0.61 e/Å³ high was found between T1 and O4. Remaining peaks were weaker

Table 2. Crystal data, experimental conditions, and refinement of cronstedtite-17.

	Herja	Lostwithiel
Crystal system	trigonal	trigonal
Space group	P31 <i>m</i>	P31 <i>m</i>
M_r (molecular weight)	393.37	390.04
Lattice parameters	$a = 5.512(1) \text{ \AA}$ $c = 7.106(1) \text{ \AA}$ $V = 187.00(4) \text{ \AA}^3$	$a = 5.503(1) \text{ \AA}$ $c = 7.104(1) \text{ \AA}$ $V = 186.31(4) \text{ \AA}^3$
Z	1	1
D_m	not measured	not measured
D_c	3.492 Mg m ⁻³	3.475 Mg m ⁻³
Radiation	MoK α graphite monochr. (0.71073 \AA)	MoK α graphite monochr. (0.71073 \AA)
No. of reflections for lattice parameters	30	40
θ -range for lattice parameters	8.63–21.89°	8.7–23.0°
Crystal color and shape	black, triangular table with rounded corners	black, conical
Crystal size	0.312 × 0.306 × 0.056 mm ³	0.17 × 0.17 × 0.185 mm ³
Diffractometer	Hilger & Watts	Hilger & Watts
Collection method	$\omega/2\theta$ scan, learnt profile (Clegg, 1981)	$\omega/2\theta$ scan, learnt profile (Clegg, 1981)
Absorption correction	analytical (Templeton and Templeton, 1978)	analytical (Templeton and Templeton, 1978)
Reflections measured, observed, independent	1663, 1652, 342	1634, 1602, 335
θ_{\max}	35°	35°
Extent of reflections measured	$h: -8$ to 8, $k: -8$ to 8, $l: 0$ to 11	$h: -8$ to 8, $k: -8$ to 8, $l: 0$ to 11
No. of standard reflections and interval	3/30	3/30
Variation of standard reflections	<3%	<3%
Criterion for observed	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}^1	3.13%	2.92%
R, wR, S^1	3.07%, 4.03%, 5.75	2.24%, 2.37%, 3.12
No. of parameters refined	29	32
Weight	$w = 1/[\sigma^2(F_o) + (0.03 F_o)^2]$	$w = 1/[\sigma^2(F_o) + (0.03 F_o)^2]$
Treatment of hydrogen atoms	not determined	refined xyz
Δ/σ_{\max}^1	0.0001	0.0005
$\Delta\rho_{\min}^1$	-1.56 e\AA ⁻³	-0.61 e\AA ⁻³
$\Delta\rho_{\max}^1$	0.60 e\AA ⁻³	0.60 e\AA ⁻³

¹ Definitions of parameters:

$$R_{\text{int}}[\%] = 100 \frac{\sum_{n=1}^N |F_n - \bar{F}_n|}{\sum_{n=1}^N |F_n|} \quad R[\%] = 100 \frac{\sum_{h,k,l} ||F_o - |F_c||}{\sum_{h,k,l} |F_o|} \quad wR[\%] = 100 \left[\frac{\sum_{h,k,l} w(|F_o| - |F_c|)^2}{\sum_{h,k,l} w|F_o|^2} \right]^{1/2} \quad S = \left[\frac{\sum_{h,k,l} w(|F_o| - |F_c|)^2}{p - m} \right]^{1/2}$$

where N is the total number of reflections, F_n structure factor of the n -th reflection, \bar{F}_n average structure factor of symmetry equivalent reflections, F_o and F_c observed and calculated structure factors respectively, p number of reflections used for refinements, and m number of refined structure parameters.

Δ/σ_{\max} (maximum change/estimated standard deviation) during the last refinement cycle.

$\Delta\rho_{\min}$ minimum residual electron density on the final difference map.

$\Delta\rho_{\max}$ maximum residual electron density on the final difference map.

than 0.46 e/\AA³. The standard deviation, σ , of the peak was equal to 0.10 e/\AA³ (Ladd and Palmer, 1977, p. 292). There were 21 peaks above 3σ . The unrefined coordinates for H were as follows: H1: 0, 0, 0.232 and H2: 0.339, 0, 0.773. These hydrogen atom positions were added to the refinement and the positional parameters converged to H1: 0, 0, 0.25(1) and H2: 0.343(6), 0, 0.757(8). Temperature parameters were not refined. The R value dropped from 2.49 to 2.24%. The σ value for the LOS data was 0.09 and there were 50 peaks

above 3σ (the highest one 0.59 e/\AA³), but none could be attributed to the hydrogen atom.

RESULTS AND DISCUSSION

Refined atomic positions and atomic displacement parameters are listed in Table 3a and 3b for HER and LOS data, respectively, and interatomic distances and angles are in Table 4. Various parameters characterizing octahedral and tetrahedral sheets and the deformation of polyhedra are summarized in Table 5. Ob-

Table 3a. Atomic coordinates and displacement parameters (U_{ij}), with estimated standard deviations in parentheses, of cronstedtite-1T from Herja, Romania.

Atom	Position	x	y	z	$U_{00} \times 10^2$	$U_{11} \times 10^2$	$U_{22} \times 10^2$	$U_{33} \times 10^2$	$U_{12} \times 10^2$	$U_{13} \times 10^2$	$U_{23} \times 10^2$
M1 (Fe)	3c	0.66520(7)	0	0.5 ¹	0.86(1)	0.71(1)	0.72(1)	1.13(1)	0.363(8)	-0.002(10)	0
T1 (Si:Fe) ²	2b	1/3	2/3	0.1014(1)	1.09(2)	1.20(2)	1.20(2)	0.88(2)	0.60(1)	0	0
O1	3c	0.4416(6)	0	0.0235(3)	3.22(9)	4.2(1)	3.4(1)	1.71(9)	1.71(7)	0.10(8)	0
O4	2b	1/3	2/3	0.3457(5)	1.22(8)	1.2(1)	1.2(1)	1.3(1)	0.58(5)	0	0
OH1	1a	0	0	0.3508(5)	1.18(9)	1.2(1)	1.2(1)	1.1(1)	0.62(6)	0	0
OH2	3c	0.3321(3)	0	0.6412(3)	1.22(8)	1.23(9)	1.4(1)	0.8(1)	0.68(5)	-0.03(6)	0

¹ Fixing of origin.² Occupancy ratio (Si:Fe) = 0.617(8):0.383.Table 3b. Atomic coordinates and displacement parameters (U_{ij}), with estimated standard deviations in parentheses, of cronstedtite-1T from Lostwithiel, Cornwall, England.

Atom	Position	x	y	z	$U_{00} \times 10^2$	$U_{11} \times 10^2$	$U_{22} \times 10^2$	$U_{33} \times 10^2$	$U_{12} \times 10^2$	$U_{13} \times 10^2$	$U_{23} \times 10^2$
M1 (Fe)	3c	0.66522(6)	0	0.5 ¹	0.92(1)	0.72(1)	0.70(1)	1.13(1)	0.351(6)	0.01(1)	0
T1 (Si:Fe) ²	2b	1/3	2/3	0.1038(1)	1.10(1)	1.08(2)	1.08(2)	1.14(2)	0.54(1)	0	0
O1	3c	0.4433(4)	0	0.0290(3)	3.33(7)	4.04(9)	3.5(1)	2.27(9)	1.76(5)	0.12(7)	0
O4	2b	1/3	2/3	0.3510(5)	1.29(7)	1.17(9)	1.17(9)	1.5(1)	0.58(4)	0	0
OH1	1a	0	0	0.3556(5)	1.23(8)	1.3(1)	1.3(1)	1.1(1)	0.65(5)	0	0
OH2	3c	0.3320(3)	0	0.6436(4)	1.30(7)	1.34(8)	1.32(9)	1.2(1)	0.65(5)	-0.002(60)	0
H1	1a	0	0	0.25(1)	3.8 ³						
H2	3c	0.343(6)	0	0.757(8)	3.8 ³						

¹ Fixing of origin.² Occupancy ratio (Si:Fe) = 0.699(7):0.301.³ U_{iso} fixed value.

Atoms are labeled according to Bailey (1969).

$$U_{eq} = 1/3(U_{11}a^*a^2 + U_{22}b^*b^2 + U_{33}c^*c^2 + U_{12}a^*b^*ab \cos \gamma + U_{13}a^*c^*ac \cos \beta + U_{23}b^*c^*bc \cos \alpha).$$

served and calculated structure factors can be obtained from the first author (J.H.) on request. The atomic coordinates and the labels of individual atoms are in accordance with the ideal standard model of this polytype, characterized by zero shift and no rotation between adjacent layers (Bailey, 1969).

The structure is shown in projection along the $[00\bar{1}]$ in Figure 1. The 1T polytype has one octahedral site, M1, one tetrahedral site, T1, and four oxygen atom sites in the asymmetric unit. The occupancy ratio Si:Fe in the T1 position was refined to the values 0.617(8):0.383 and 0.699(6):0.301 for HER and LOS data, respectively. Thus the chemical formulae derived from results of the refinements are (neglecting the small Al content): $(Fe^{2+}_{2.23}Fe^{3+}_{0.77})[Si_{1.23}Fe^{3+}_{0.77}O_5(OH)_4]$ (HER) and $(Fe^{2+}_{2.40}Fe^{3+}_{0.60})[Si_{1.40}Fe^{3+}_{0.60}O_5(OH)_4]$ (LOS). These results are in reasonably good agreement with the microprobe data. For comparison, the EMA produced the formulae of: $(Fe^{2+}_{2.20}Fe^{3+}_{0.80})(Si_{1.20}Fe^{3+}_{0.78}Al_{0.02})O_5(OH)_4$ (HER) and $(Fe^{2+}_{2.32}Fe^{3+}_{0.68})(Si_{1.32}Fe^{3+}_{0.66}Al_{0.02})O_5(OH)_4$ (LOS). Because the microprobe analysis does not distinguish between divalent and trivalent iron, the content of Fe^{3+} in the tetrahedral and octahedral sites and of Fe^{2+} in the octahedral sites was calculated according to the formula in the Introduction.

Tetrahedral sheet

The size of the T1 tetrahedron is close to values reported for previously refined polytypes of cronstedtite (Geiger *et al.*, 1983; Smrčok *et al.*, 1994; Hybler, 1997). The tetrahedron is relatively regular, although the apical bond length is longer than the basal bond lengths. The central atom is displaced from the center toward the plane of basal oxygen atoms thus the tetrahedral flattening angle, τ_{T1} , is 108.82° (HER) and 108.18° (LOS) and is less than its ideal value. The ditrigonalization angle, α , of the tetrahedral sheet (Radoslovich, 1961) is highly negative at -11.5° (HER) and -11.1° (LOS). The negative sign of α indicates that the basal oxygen atoms are moved away from the octahedral cations of the same layer, thus the layer is a Franzini type B (Franzini, 1969). The observed values are in the range of $11.1^\circ < |\alpha| < 12.1^\circ$ as determined for cronstedtite-2H₂ and 3T.

Lizardite-1T belongs to the same Franzini layer type, however, with a small ditrigonalization angle (-1.4° to -3.5°, Zhukhlistov and Zvyagin, 1998; Mellini and Zanazzi, 1987; Mellini and Viti, 1994; Mellini, 1982). This less-common Franzini type has been explained qualitatively by "more efficient hydrogen bonding" (Mellini, 1982; Mellini and Viti, 1994), and it holds for all polytypes of the subfamily C.

Table 4. Selected bond lengths and angles of cronstedtite-1T (in Å, degrees, with estimated standard deviations in parentheses).

	Herja	Lostwithiel
Octahedron:		
M1-O4 × 2	2.136(2)	2.114(2)
M1-OH1	2.128(2)	2.108(2)
M1-OH2 × 3	2.094(2)	2.099(2)
O4-O4	3.1824(0)	3.1772(0)
O4-OH1 × 2	3.1826(1)	3.1773(0)
O4-OH2 × 4	2.793(3)	2.775(3)
OH1-OH2 × 2	2.758(3)	2.743(3)
OH2-OH2 × 2	3.188(2)	3.183(1)
OH2-OH2	3.170(2)	3.164(2)
O4-M1-O4	96.29(7)	97.41(7)
O4-M1-OH1 × 2	96.54(8)	97.60(7)
O4-M1-OH2 × 2	82.65(7)	82.40(8)
O4-M1-OH2 × 2	82.62(8)	82.38(8)
O4-M1-OH2 × 2	177.7(1)	178.89(9)
OH1-M1-OH2 × 2	81.58(8)	81.36(7)
OH1-M1-OH2	178.8(1)	180.00(1)
OH2-M1-OH2 × 2	99.21(7)	98.64(7)
OH2-M1-OH2	98.40(8)	97.81(8)
Tetrahedron:		
T1-O1 × 3	1.715(1)	1.704(1)
T1-O4	1.736(3)	1.756(3)
O1-O1 × 3	2.812(2)	2.804(2)
O1-O4 × 3	2.806(3)	2.802(3)
O1-T1-O1 × 3	110.1(1)	110.7(1)
O1-T1-O4 × 3	108.82(9)	108.18(8)
Other important distances and angles:		
OH1-H1	not determined	0.76(9)
OH2-H2	not determined	0.81(6)
O1-H2	not determined	2.01(6)
O1-H2-OH2 (hydrogen bond angle)	not determined	168(4)
Tilt of OH2-H2 bond from vertical	not determined	4(2)
OH2-O1 (interlayer contact)	2.783(3)	2.805(4)
O1-O1-O1 (tetrahedral ring angle)	97.1(4)	97.8(1)

The lizardite polytypes of subfamily D are significantly ditrigonalized: $\alpha = +6.4^\circ$ for $2H_1$ (Mellini and Zanazzi, 1987), and $\alpha = +9.7^\circ$ for the Al-bearing $2H_2$ polytype (Brigatti *et al.*, 1997). The degree of the ditrigonalization in amesite is even higher ($13.6^\circ < \alpha < 15.6^\circ$) than that in cronstedtite (Hall and Bailey, 1979; Anderson and Bailey, 1981; Zheng and Bailey, 1997; Wiewióra *et al.*, 1991). All polytypes of amesite referred to here belong to the subfamily D and the ditrigonalization angles are positive.

The structure of greenalite, approximately $(\text{Fe}^{2+}_3)[\text{Si}_2\text{O}_5](\text{OH})_4$, is close to cronstedtite based on the chemical composition, but greenalite has a modulated tetrahedral sheet because the tetrahedral sheet is too small to fit with the octahedral sheet (Guggenheim and Eggleton, 1998). Thus the substitution of Fe for Si in the tetrahedral sites of cronstedtite stabilizes the more idealized structure.

Octahedral sheet

The M1 octahedron of the LOS crystal is smaller than that of the HER crystal (LOS: 2.105 Å, HER:

2.114 Å). Both values are close to those reported for the $3T$ and $2H_2$ polytypes (Smrčok *et al.*, 1994; Hybler, 1997) and also for cronstedtite- $2H_2$ with a considerable content of Mg and Mn (Geiger *et al.*, 1983). The differences in average cation-to-anion distances are <0.01 Å. The octahedron is flattened (the octahedral flattening angle ψ_{M1} 60.38° HER, 60.56° LOS) and is similar to other cronstedtite polytypes and to lizardite and amesite. In these minerals, ψ_M varies in a narrow range of $\sim 58.9^\circ < \psi_M < 61^\circ$. The plane of the central cation is slightly (0.08 Å HER, 0.04 Å LOS) closer to the plane of OH2 groups than to the plane of the apical oxygen atoms (O4). Consequently, M1-OH2 bonds are shorter than the other bonds in the octahedron. Moreover, the oxygen atom belonging to the central hydroxyl (OH1) group is closer (0.036 Å HER, 0.046 Å LOS) to the plane of M1 atoms than the apical oxygen atoms (O4). The plane defined by OH1 and O4 atoms is thus corrugated. These deviations from the ideal positions produce an octahedral sheet that is polar (with respect to the stacking direction) in contrast, for example, to micas where this sheet is non-polar.

Table 5. Cronstedtite-1T, characteristics of octahedra and tetrahedra and selected distortion parameters.

	Herja	Lostwithiel
Octahedral sheet		
d_{M1-A}	2.114 Å	2.105 Å
ψ_{M1}	60.38°	60.57°
δ_{M1}	0.32°	0.70°
e_{M1}	2.982 Å	2.971 Å
$e_{M1}(\text{shared})$	2.781 Å	2.765 Å
$e_{M1}(\text{unshared})$	3.182 Å	3.177 Å
OAV_{M1}	65.82 ²²	69.24 ²²
BLD_{M1}	0.930%	0.309%
ELD_{M1}	6.692%	6.944%
$e_{M1}(\text{unshared})/e_{M1}(\text{shared})$	1.144	1.149
Octahedral thickness	2.100 Å	2.079 Å
Tetrahedral sheet		
d_{T1-O}	1.720 Å	1.717 Å
Δz	0 Å	0 Å
e_{T1}	2.809 Å	2.803 Å
$e_{T1}(\text{apical})$	2.806 Å	2.802 Å
$e_{T1}(\text{basal})$	2.812 Å	2.804 Å
α	-11.4°	-11.1°
TAV_{T1}	0.42 ²²	1.91 ²²
BLD_{T1}	0.450%	1.136%
ELD_{T1}	0.107%	0.036%
τ_{T1}	108.82°	108.18°
Tetrahedral thickness	2.289 Å	2.287 Å
Other important values		
Δ_{TM}	0.772 Å	0.782 Å
Interlayer separation	2.717 Å	2.738 Å

d_{M-A} = mean octahedral cation-anion bond length,
 ψ_M = flattening angle (for an ideal, unflattened octahedron,
 $\psi_M = 54.73^\circ$),
 δ_M = counter-rotation angle, e_M = mean octahedral-edge
length,
 d_{T-O} = mean tetrahedral cation-oxygen bond length,
 Δz = tetrahedral tilt, e_T = mean tetrahedral-edge length (To-
raya, 1981; Weiss *et al.*, 1985, 1992);
 α = ditrigonalization angle (Radoslovich, 1961);
OAV = octahedral angle variance, TAV = Tetrahedral
angle variance (Robinson *et al.*, 1971);
BLD = Bond-length distortion, ELD = Edge-length dis-
tortion (Renner and Lehmann, 1986);
 $e_{M1}(\text{shared})/e_{M1}(\text{unshared})$ = Ratio of mean lengths of
shared and unshared edges;
 τ_T = Tetrahedral flattening angle (for an ideal tetrahedron
 $\tau_T = 109.47^\circ$) (Robinson *et al.*, 1971);
 Δ_{TM} = Dimensional misfit of tetrahedral and octahedral
sheet (Toraya, 1981).

The atomic coordinates x of M1 and OH2 are very close to $\frac{2}{3}$ and $\frac{1}{3}$, respectively, which are characteristic for an ideal OD model where the octahedral sheet has the layer group symmetry $H(3)1m$. The symbol H refers to an alternative choice of the hexagonal cell with centering points at $\frac{1}{3}$, $\frac{2}{3}$, 0 and $\frac{2}{3}$, $\frac{1}{3}$, 0 (*International Tables*, 1983, p. 5). The consequence is that the octahedral sheet and the tetrahedral sheet, which are connected by hydrogen bonds, remain geometrically equivalent even where there is a shift by $\pm b/3$ between these sheets. An analogous effect was observed in cronstedtite-3T (Smrček *et al.*, 1994). This symmetry

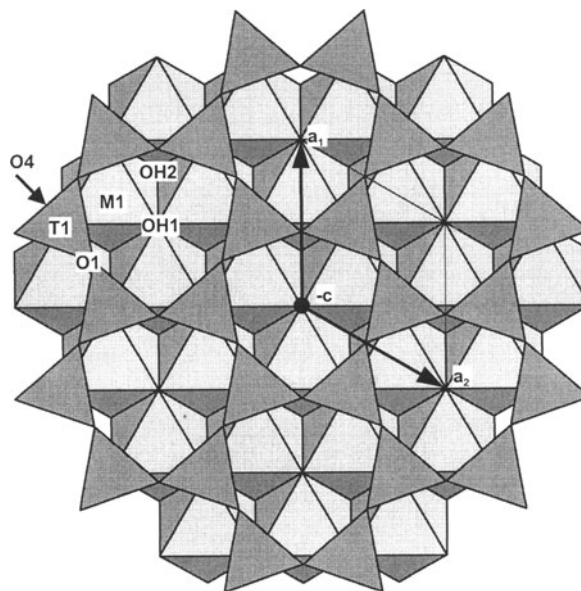


Figure 1. The structure of cronstedtite-1T, projected down the $[00\bar{1}]$ direction. The picture was prepared using the program ATOMS (Dowty, 1991).

also explains the strong tendency of cronstedtite crystals to be disordered. In fact, no fully ordered stacking arrangement in cronstedtite is reported to date. Similarly, the same characteristics hold also for structurally related lizardite-1T. The streaking of the polytype reflections ($h - k \neq 3n$) has been reported in all structural studies (Mellini, 1982; Mellini and Zanazzi, 1987; Mellini and Viti, 1994) except that by Zhukhlisov and Zvyagin (1998) where limited streaking might not be observed from the less sensitive technique of oblique-texture electron diffraction.

Hydrogen bonds

One of the two hydrogen atoms, H1, is located in the center of the tetrahedral ring, whereas the other (H2) is engaged in the $OH2 \cdots H2-O1$ hydrogen bond linking adjacent 1:1 layers. The $OH2-O1$ interlayer donor to acceptor distance for the HER sample is 2.783(3) Å and 2.805(4) Å for the LOS sample. The LOS data produced positions of both hydrogen atoms. The refinement reveals that the H2 atom is shifted slightly towards the acceptor. Thus the interatomic bond $OH2-H2$ is tilted by $4(2)^\circ$ from vertical. The $OH2 \cdots H2-O1$ hydrogen-bond angle is $168(4)^\circ$. The interlayer separation (HER: 2.717 Å, LOS: 2.738 Å) is slightly smaller than that of lizardite (2.86 Å), but comparable with that of amesite (2.71–2.74 Å).

CONCLUDING REMARK

A detailed study of the 1T polytype revealed certain deviations from the ideal model because of stacking faults which reduce the intensities of the characteristic

polytype reflections ($h - k \neq 3n$) relative to those of the subfamily reflections ($h - k = 3n$). Because the ratio of the corresponding scale factors converged to two different values, the LOS crystal with a ratio of near 1:1 was more ordered than the HER crystal.

Thus, more complex structure models involving domains with layers shifted by $+b/3$ or $-b/3$ in various proportions might also be used to describe this material. For instance, a good agreement ($R = 3.07\%$) was achieved also for a structure model containing only domains of layers shifted by $+b/3$ and $-b/3$ in equal proportions, but no domains with a zero shift (Hybler, 1997). Descriptions of these structure models with differing domains will be developed in another paper. However, these stacking faults do not affect the refined values reported here.

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