

Rietveld refinement of the crystal structure of fibrolitic sillimanite using neutron powder diffraction data

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ABSTRACT

The crystal structure of natural fibrolite collected from a granulite in Brittany, France, has been refined using time-of-flight neutron powder diffraction data and the Rietveld method. Lattice parameters [$a = 7.4841(3)$ Å, $b = 7.6720(3)$ Å, and $c = 5.7707(2)$ Å] and structural parameters, including temperature factors, are in close agreement with those previously reported for sillimanite. Both refined site occupancies and ^{14}Si , Al-O interatomic distances, however, show that this fibrolite has tetrahedral site occupancies reflecting ~18% disorder (i.e., ~9% Al in the ^{14}Si site and ~9% Si in the ^{14}Al site). The neutron diffraction profile parameters reveal little or no crystallite-size broadening but a small amount of isotropic strain broadening, possibly due to a combination of the partial Al-Si disorder and the defect structure of fibrolite. Analysis of sillimanite disordering thermodynamics strongly suggests that the observed tetrahedral cation disorder is not the result of an equilibrium disordering process.

INTRODUCTION

The phase diagram of the Al_2SiO_5 polymorphs kyanite, andalusite, and sillimanite is of great importance to metamorphic petrologists, but significant variations have been observed experimentally in the phase equilibria. There has been considerable debate over the last two decades about the causes for the observed variations. Reasons proposed often include peculiarities in the material known as fibrolite, the fine-grained, acicular variety of sillimanite that occurs in a variety of metamorphic rocks. Several authors have suggested nonstoichiometry and ^{14}Al - ^{14}Si disorder in sillimanite as reasons for the observed variations in experimentally determined phase equilibria (Anderson and Kleppa, 1969; Zen, 1969; Holdaway, 1971), but Cameron and Ashworth (1972) showed that fibrolite is essentially stoichiometric Al_2SiO_5 . Using electron diffraction data and infrared spectra, they also argued that fibrolitic sillimanite has a completely ordered distribution of ^{14}Al and ^{14}Si . They suggested that the variations in phase equilibria are due to an increase in surface free energy caused by fine grain size. Sahl and Seifert (1973) disagreed with these conclusions concerning ^{14}Al - ^{14}Si order and argued on the basis of structure factor calculations for sillimanite that interpretations concerning Al-Si order are difficult to make based solely on the relative intensities of l -odd and l -even reflections.

The phase relations of the Al_2SiO_5 polymorphs were further studied by Salje and Werneke (1982) and Salje (1986). Salje and Werneke (1982) discussed the possible influence of "lattice faults" and Al-Si disordering on the

thermodynamic properties of sillimanite; they stated that preliminary neutron scattering data indicated no significant disorder. The work of Salje (1986) is the most complete investigation of the influence of fibrolitization on the phase equilibria of the Al_2SiO_5 polymorphs. He concluded that the anomalous thermodynamic behavior of fibrolite cannot be attributed to variations in chemical composition or to Al-Si disorder but is probably related to the defect properties of fibrolite.

Because complete crystal structural data on fibrolite have not been published, an investigation was undertaken to determine the state of ^{14}Al - ^{14}Si order in fibrolite. Neutron diffraction data were used because the neutron-scattering cross sections for Al and Si are significantly different. In addition, considering the suggestion of Salje (1986) that the anomalous properties of fibrolite are related to its defect properties, separation of strain and crystallite size broadening in the fibrolite diffraction pattern was attempted using the observed peak profile parameters obtained from the neutron diffraction pattern.

EXPERIMENTAL

All data were obtained on a sample of fibrolite from Pays de Leon, Brittany, France (Harvard University Mineralogical Museum no. 109970). The exact sample location in Pays de Leon was not described in the sample documentation at Harvard. The sample as received contained minor muscovite and chlorite as impurities. The bulk material was crushed under acetone in a tungsten-carbide mortar and pestle, and several size fractions were

suspended in sodium metatungstate heavy liquid ($\rho = 2.99$). The fraction passing a 100-mesh sieve and settling on a 200-mesh sieve was used for all subsequent diffraction experiments, as this material contained the least amount of contaminant minerals. Heavy-liquid separation of this fraction resulted in removal of virtually all but trace amounts of the chlorite and muscovite; the separated sample contained <1% of these phases. Electron microprobe analyses of the fibrolite were obtained with a Cameca microprobe using an accelerating potential of 15 kV, a beam current of 15 nA on brass, and Bence-Albee corrections, with kyanite as a standard for Si and Al and synthetic fayalite as a standard for Fe (C. Francis, analyst). The analyses gave an average composition of $\text{SiO}_2 = 36.27\%$, $\text{Al}_2\text{O}_3 = 62.24\%$, and $\text{Fe}_2\text{O}_3 = 0.25\%$, yielding a formula of $\text{Al}_2\text{Si}_{0.99}\text{O}_5$, based on five O atoms. The Fe content corresponds to 0.0053 Fe^{3+} atoms per five O atoms; it was therefore neglected in remaining calculations. Peterson and McMullan (1986) concluded that the bulk of Fe in the sillimanite studied by them occupied the $^{64}\text{Al1}$ site; thus there is little chance the neglected Fe content could influence our determination of ^{41}Al - ^{49}Si distribution.

X-ray powder diffraction data were measured at 23 °C using an automated Siemens D-500 θ - θ diffractometer with $\text{CuK}\alpha$ radiation and a Kevex solid-state Si detector. The 100–200 mesh material was ground under acetone to a mean particle size of $\sim 3 \mu\text{m}$ in a Brinkmann Micro-Rapid Mill and backpacked into a cavity mount in an attempt to minimize preferred orientation. Data were obtained using $0.02^\circ 2\theta$ steps from 10 to $70^\circ 2\theta$ counting for 8 s per step and from 70 to $150^\circ 2\theta$ counting for 48 s per step. Neutron diffraction data were obtained on an unground portion of the same sample using the high-intensity powder diffractometer (HIPD) at the Los Alamos Neutron Scattering Center. Data were collected at 23 °C in four detector banks (± 153.4 and ± 90 °C) for approximately 24 h.

The Rietveld refinement program GSAS (Larson and Von Dreele, 1988) used for these refinements incorporates features not available in most other Rietveld programs. The code simultaneously accommodates multiple data sets (e.g., both X-ray and neutron data) and allows constrained refinement of numerous instrument- and sample-related parameters. Initial refinements included both sillimanite and muscovite, with starting structures taken from Peterson and McMullan (1986) and Rothbauer (1971), respectively. Throughout the refinements, the atomic positions for muscovite were fixed and only the cell parameters (with X-ray data only) and scale factors were varied. Profile parameters for muscovite were constrained to sillimanite values, as the amount of muscovite was too small to yield reliable refined parameters. Although this treatment of muscovite is an approximation, it should have no effect on the final results for fibrolite because of the very small amount of muscovite in the sample.

The pseudo-Voigt profile function described by

Thompson et al. (1987), modified to consider anisotropic broadening, was employed with the X-ray data, and the convolution function described by Von Dreele et al. (1982), also considering anisotropic broadening, was used with the neutron data. A six-term cosine Fourier series modeled the backgrounds. The March function correction for preferred orientation (Dollase, 1986) implemented in GSAS was varied for both the neutron and X-ray data using [001] (the fiber axis) as the special axis. During the refinements, the positions of all atoms in the sillimanite structure were varied, along with individual isotropic temperature factors and the occupancies of the ^{41}Al and ^{49}Si sites. Changes in site occupancies of the ^{41}Al and ^{49}Si sites were constrained to obey the measured composition. Refinement using the neutron data quickly converged, but inclusion of the X-ray data gave unrealistic results. The difficulty with the X-ray data apparently arose from the significant amount of preferred orientation in the X-ray sample due to the fibrous nature of the material. As other applications of the March function have shown, the correction does not work well with data strongly influenced by preferred orientation, particularly with fibrous materials (Post and Bish, 1989; Bish and Post, unpublished data for hollandite and romanechite). Therefore, in order to correct for minor imprecision in the calibration of the neutron diffractometer, the cell parameters were refined using only the X-ray data. In these refinements with X-ray data only, all appropriate parameters except the atomic positions and temperature factors were varied. Subsequent refinements using only the neutron data employed the fixed X-ray lattice parameters and included variation of the parameters relating to the time of flight for the HIPD.

RESULTS AND DISCUSSION

Lattice parameters obtained from the refinement using only the X-ray data are virtually identical to other published values for fibrolite and sillimanite (Table 1). The structure refinements using the neutron data with the fixed X-ray lattice parameters converged smoothly to a final weighted R factor for all four data sets of 3.29% (reduced $\chi^2 = 5.4$; unweighted $R = 2.29\%$) (Fig. 1). Results of the structure refinement using only the four banks of neutron data (Table 2) are similar to those reported by Burnham (1963) and Peterson and McMullan (1986), with one notable exception. Significant ^{41}Al - ^{49}Si disorder is present in our fibrolite. The refinements, constrained to Al_2SiO_5 stoichiometry, yielded a final ^{41}Al site occupancy of 0.91(3) Al plus 0.09 Si. Likewise, the Si site occupancy was 0.91(3) Si plus 0.09 Al. It is noteworthy that the isotropic temperature factors are close to those given by Burnham (1963) and Peterson and McMullan (1986) for sillimanite.

Bond lengths (Table 3) calculated from the atomic positions in Table 2 are consistent with these site occupancies. The ^{41}Al -O distances are close to those obtained by Burnham (1963) and Peterson and McMullan (1986), and the $\langle \text{Al-O} \rangle$ ($\langle \rangle$ denote average) distance is virtually iden-

TABLE 1. Unit-cell parameters for fibrolite and sillimanite

Reference	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Sample, Fe content
This study	7.4841(3)	7.6720(3)	5.7707(2)	331.34(1)	fibrolite, 0.25% Fe ₂ O ₃
Burnham (1963)	7.4856(6)	7.6738(3)	5.7698(8)	331.43	sillimanite, n.r.
Cameron and Ashworth (1972)	7.4844(4)	7.6722(4)	5.7701(3)	331.33(4)	fibrolite, 0.30% Fe ₂ O ₃
Cameron and Ashworth (1972)	7.4963(4)	7.6851(4)	5.7764(3)	332.78(4)	sillimanite, 2.6% Fe ₂ O ₃
Winter and Ghose (1979)	7.4883(7)	7.6808(7)	5.7774(5)	332.29(5)	sillimanite, n.r.
Salje (1986)	7.4813(17)	7.6739(18)	5.7673(17)	331.11	fibrolite, 0.16% Fe
Salje (1986)	7.4809(23)	7.6664(27)	5.7662(23)	330.70	sillimanite, 0.35% Fe
Salje (1986)	7.4858(22)	7.6647(25)	5.7696(19)	331.04	sillimanite, 0.08% Fe

Note: n.r. = not reported.

tical to theirs. The ¹⁴¹Al₂-O(B) and ¹⁴¹Al₂-O(C) distances are within experimental error of those determined by Peterson and McMullan, but the Al₃-O(D) distances for fibrolite are significantly shorter than for sillimanite. The ⟨Al₂-O⟩ distance for fibrolite is 1.753 Å compared with 1.759 Å (Peterson and McMullan) or 1.770 Å (Burnham) for sillimanite. Likewise, the Si-O distances are all significantly longer than found for sillimanite by Burnham or Peterson and McMullan; the ⟨Si-O⟩ distance for fibrolite is 1.634 Å compared with 1.623 Å (Peterson and McMullan) or 1.615 Å (Burnham) for sillimanite.

It is common practice to determine the ¹⁴¹Al/Si ratio of silicates using observed trends between ⟨T-O⟩ distance and occupancy. Numerous authors have examined the relationship between these two variables for framework silicates (e.g., Smith and Bailey, 1963) and for layer silicates (e.g., Hazen and Burnham, 1973). Unfortunately, the relationships derived for framework or layer silicates are not directly applicable to sillimanite. End-member sillimanite has an ⟨Si-O⟩ distance between 1.615 Å (Burnham, 1963) and 1.627 Å (Winter and Ghose, 1979), whereas the pure Si tetrahedron in framework and layer silicates is typically about 1.605 Å. In the absence of a usable linear relationship for the aluminosilicates, we attempted several methods to relate ⟨T-O⟩ distance to Al/Si ratio. If one uses the equation proposed by Ribbe and Gibbs (1969) for feldspars but modifies the intercept to equal observed ⟨Si-O⟩ values for sillimanite (⟨T⟩_{obs}), the equation Al/(Al + Si) = 6.58(⟨T-O⟩ - ⟨T⟩_{obs}) is obtained. Using in this equation the ⟨Si-O⟩ values determined by Burnham (1963) or by Peterson and McMullan (1986), we obtain amounts of ¹⁴¹Al substitution in the Si site of 12.5% or 7.2%, respectively. If we calculate determina-

tive equations based on the results of individual structural determinations for sillimanite, significantly different equations are obtained, although the final results are not greatly different. Using the results of Burnham (1963), with 1.6148 Å (Si) and 1.7698 Å (Al) as end-member ⟨T-O⟩ distances, our ⟨T-O⟩ values for fibrolite yield substitutions of 12.1% in Al in the Si site and 10.8% Si in the Al₂ site. An analysis using the results of Peterson and McMullan (1986) yields 8.1% Al in the Si site and 4.4% Si in the Al₂ site. Comparable curves can be determined using the variety of literature data on the three Al₂SiO₃ polymorphs, but the absence of chemical data for some of the materials used in structure refinements makes further consideration of limited value. Both the site-occupancy refinements and the bond-length systematics suggest that this fibrolite is ~18% disordered, i.e., ~9% Al in the ¹⁴¹Si site and ~9% Si in the ¹⁴¹Al site.

Analysis of the profile parameters from the four independent neutron data sets suggests that there is no significant crystallite-size broadening in the pattern, as might be expected from the relatively large particle size used in the experiment. However, a small amount of strain broadening exists. Although we used a profile function capable of modeling anisotropic strain broadening, no significant anisotropy was detected. Using the experimental profile parameters, the relationships in Larson and Von Dreele (1988), and measured values for the instrument profile parameters, a strain of 0.23 ± 0.09% was obtained for the four sets of neutron data.

The small but significant amount of strain observed in this fibrolite is consistent with transmission electron microscope observations of high defect densities by Lefebvre and Paquet (1983). In addition, the observed strain

TABLE 2. Refined atom parameters for fibrolite

Site	Occupancy	x	y	z	U _{iso} × 100*
Al1	1.0	0	0	0	0.21(2)**
Al2	0.91(3) Al, 0.09 Si	0.1428(3)	0.3433(2)	¼	0.31(3)
Si	0.91(3) Si, 0.09 Al	0.1524(2)	0.3412(2)	¾	0.28(3)
OA	1.0	0.3607(2)	0.4069(1)	¾	0.17(2)
OB	1.0	0.3554(1)	0.4361(1)	¼	0.23(2)
OC	1.0	0.4783(1)	0.0035(2)	¾	0.87(2)
OD	1.0	0.1256(1)	0.2222(1)	0.5131(1)	0.33(1)

* U_{iso} = B_{iso}/8π².

** Values in parentheses are estimated standard deviations in the last place.

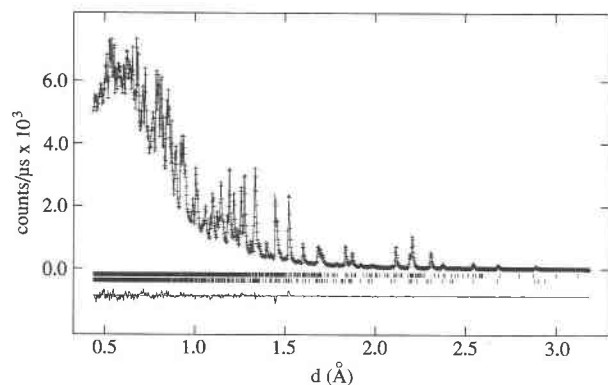


Fig. 1. Observed (pluses) and calculated (solid line) time-of-flight neutron diffraction pattern for fibrolite obtained with detector bank one ($2\theta = 153.4^\circ$). The background at the low- d end of the pattern is elevated by the incident spectrum. Tick marks indicate positions for allowed reflections of sillimanite (lower) and muscovite (upper). Lower curve is the difference between observed and calculated profiles.

is compatible with the results obtained by Salje (1986), who found that the heat capacity of sillimanite increases because of the strain fields associated with stacking faults. However, our results are not in complete agreement with Salje's or those of Cameron and Ashworth (1972), as we found no evidence of crystallite-size broadening, suggesting therefore that the strain is related to factors other than particle size reduction. The strain in fibrolite may be due to a combination of its defect structure and the partially disordered Al-Si distribution. Alternatively, as Lefebvre and Paquet (1983) showed, the observed Al-Si distribution may arise from $\frac{1}{2}$ [001] stacking faults. The O substructure of sillimanite is nearly invariant to such stacking faults, each of which reverses the sequence of Al and Si tetrahedra along c . Distinction between simple Al-Si disorder and disorder caused by $\frac{1}{2}$ [001] stacking faults would require a thorough examination of our sample by transmission electron microscopy and modeling of both possible causes of disorder. In order for the observed Al-Si disorder to be a result of such stacking faults, these defects must result in no change in coherence length in individual crystallites. Thus, any model for the observed disorder must account for the lack of change in coherence (crystallite size) and also must result in an isotropic strain field. It is not possible with the available data to differentiate between these two types of disorder, nor is it clear that stacking-fault related disorder would differ in effects significantly from simple Al-Si disorder.

Thermodynamic implications of Al-Si order-disorder

Greenwood (1972) explored a Bragg-Williams model for disordering in sillimanite. The order parameter, s , is given as

$$s = \frac{p - p_{\text{total disorder}}}{p_{\text{total order}} - p_{\text{total disorder}}} \quad (1)$$

TABLE 3. Selected interatomic distances (Å) for fibrolite

	¹⁴¹ Al	
Al1-O(A) (×2)		1.9178(7)
-O(B) (×2)		1.8692(6)
-O(D) (×2)		1.9484(5)
		1.9118(15)
	¹⁴¹ Al	
Al2-O(B)		1.7428(22)
-O(C)		1.7020(24)
-O(D) (×2)		1.7844(10)
		1.7534(35)
	¹⁴¹ Si	
Si-O(A)		1.6387(23)
-O(C)		1.5831(20)
-O(D) (×2)		1.6562(11)
		1.6336(34)

where p is the probability of finding an Al atom on a ¹⁴¹Al site and, in stoichiometric sillimanite, an Si atom on an Si site, with $p_{\text{total disorder}}$ equal to 0.5. The order parameter, s , varies from 1 for total order to 0 for total disorder. For our observed value of p of 0.91, $s = 0.82$. The enthalpy change upon partial disordering is given by Greenwood's model as

$$\Delta H_{\text{disorder}} = \Delta H^0 (1 - s^2) \quad (2)$$

where ΔH^0 is the enthalpy change for complete disordering. The disordering enthalpy, ΔH^0 , for sillimanite is not known, but estimates can be made. Navrotsky et al. (1973) carried out a calorimetric study of fibrolite from Brandywine Springs, Delaware, and argued that their high-temperature results indicated the beginnings of disordering. They derived an interchange enthalpy, ΔH_{int} , of 67 kJ/mol and pointed out that $\Delta H_{\text{int}} = d\Delta H_{\text{disorder}}/dp$ at $p = 1$, where p is as defined above. Thus $\Delta H_{\text{int}} = 4\Delta H^0$, and from their measurements $\Delta H^0 = 16.75$ kJ/mol. Carpenter (1988) reviewed various determinations of disordering enthalpies in feldspars. For albite, ΔH^0 is close to 12 kJ/mol, whereas for anorthite, ΔH^0 is approximately 16 kJ/mol. Because the ¹⁴¹Al/Si ratio in sillimanite is identical to that in anorthite (namely, 1:1), the value of about 17 kJ/mol for ΔH^0 for sillimanite, derived calorimetrically, is entirely realistic.

A much higher value for disordering energy, ~ 120 kJ/mol, has recently been calculated theoretically by Jones et al. (1990) using a newly devised split-site method that accounts for a variety of different local ¹⁴¹Al-¹⁴¹Si distributions. Bertram et al. (1990) calculated a disordering energy of 44 kJ/mol based on an energy for disordered sillimanite taken as the average of the structure energies calculated for 154 arrangements of 12 Al and 12 Si over a supercell of three sillimanite cells containing 24 tetrahedral sites. Because neither of these methods considers Boltzmann statistics, the values cannot be equated to disordering enthalpies.

Assuming a sillimanite disordering enthalpy, ΔH^0 , of 17 kJ/mol, Greenwood's (1972) Equation 26 given as

$$\Delta H^0 = RT \frac{\ln(1+s) - \ln(1-s)}{2s} \quad (3)$$

permits us to calculate a temperature of equilibration, given the order parameter s (0.82). For the Brittany fibrolite, that temperature is 1155 °C. The corresponding critical temperature, T_c , at which s becomes 0 is 1772 °C. An alternative calculation using Landau theory and assuming tricritical behavior (Carpenter, 1988, Eq. 10) yields an equilibration temperature for s of 0.82 of 847 °C. This relationship, however, yields values of s of 0.88–0.89 for equilibration temperatures of 550–500 °C, close to the Al_2SiO_5 triple-point temperature. Because no sillimanite structure analyses have yielded such degrees of disorder, either sillimanite does not exhibit tricritical behavior, or if it does, T_c must be substantially higher than 1770 °C, requiring a larger value of ΔH^0 . Landau theory will then, in turn, predict an equilibration temperature higher than 847 °C.

Both hand-specimen and optical examination of the Brittany sample show it to contain almost entirely fibrolite, with very minor quartz and secondary muscovite. The fibrolite forms rosettes or radiating crystals up to 8–10 mm long. Unfortunately the specific geologic occurrence is unknown, but the sample characteristics are similar to those of other sillimanite occurrences in synmetamorphic quartz veins cutting mica schists (J. Thompson, personal communication), whose temperatures of formation are those of sillimanite-grade metamorphism, very likely not greater than 700–750 °C. If the observed degree of disorder, $s = 0.82$, represents an equilibrium state, the fibrolite would have had to form at a much higher temperature, probably attainable only if it were a pelitic xenolith in a mafic magma. Since observation makes that possibility very unlikely, an explanation consistent with the available information is that the observed disorder was not achieved under equilibrium conditions. This conclusion lends support to Holdaway's (1971, p. 127–128) opinion that "fibrolite is . . . a metastable mineral which probably forms from the reaction of a mineral or mineral assemblage which has been made very unstable by overstepping of the equilibrium boundary."

As Greenwood (1972) and others have pointed out, partial disordering of sillimanite will have an effect on the kyanite-sillimanite and andalusite-sillimanite univariant equilibria as well as the location of the Al_2SiO_5 triple point. Following Greenwood's calculations, if a sillimanite sample with s of 0.82 were taken to 600 °C with the disorder persisting metastably, as would be likely, the excess free energy available would cause an increase in the temperature of the kyanite-sillimanite equilibrium by approximately 50 °C and its pressure by about 1 kbar. Likewise, the andalusite-sillimanite boundary would be moved upward some 200 °C and about 3.5 kbar. Displacements of this magnitude have been observed in heat capacity measurements by Salje (1986), who attributed the differences between the behavior of nonfibrous sillimanite and fibrolite to stacking faults in the latter. Our observation of partial Al-Si disorder in natural Brittany fibrolite, however, suggests that Al-Si disorder (related to stacking faults or not) may be an important factor influ-

encing experimentally observed variations in equilibria among Al_2SiO_5 polymorphs. Existence of such disorder in fibrolite will definitely alter the expected temperatures and pressures of subsequent equilibrium reactions.

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