

LETTER

Tetrahedral disorder in fibrolitic sillimanite: Comparison of ^{29}Si NMR and neutron diffraction data

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ABSTRACT

In this paper ^{29}Si MAS NMR data for fibrolitic sillimanite from Pays de Leon, France, are presented that demonstrate that the sample has no significant Si-Al disorder within the double tetrahedral chains. This confirms previous findings of essentially complete short-range order in this mineral. However, a recently published neutron powder diffraction study of the same sample showed significant disorder (18%) among ^{14}Si and ^{14}Al . The only structure model that is consistent with both data sets is one of chain disorder, in which the relative positions of Si and Al from double chain to double chain are partially randomized without affecting the ordered Si-O-Al tetrahedral linkages. The entropic and energetic consequences of chain disorder are very small relative to those of normal random site disorder.

INTRODUCTION

Disorder among ^{14}Si and ^{14}Al in fibrolitic sillimanite has been suggested as an explanation both for discrepancies among different sets of experimental phase-equilibrium data, and for natural occurrences of the mineral in apparent disequilibrium with other assemblages. As reviewed recently (Bish and Burnham, 1992; Kerrick, 1990), direct structural evidence for such disorder has generally been negative. In the former paper, however, two of us presented new evidence from Rietveld analysis of powder neutron diffraction data for significant disorder (18%) in a fibrolitic sillimanite sample from Pays de Leon, Brittany, France. We reported that about 9% of the ^{14}Si sites are occupied by Al and vice versa. However, because diffraction techniques cannot distinguish between short and intermediate or long-range disorder, the energetic and entropic significance of these findings were unclear. In particular, it was uncertain whether the observed disorder involves a random mixing of Si and Al on tetrahedral sites or some kind of chain or stacking disorder. Here we present new data from ^{29}Si NMR spectroscopy on the same sample of fibrolitic sillimanite studied previously (Bish and Burnham, 1992) that rules out random site

mixing and constrains the mechanism for long-range order considerably.

EXPERIMENTAL

The fibrolitic sillimanite sample (Harvard University Mineralogical Museum no. 109970) was carefully characterized and described in detail previously (Bish and Burnham, 1992). Fibers appear optically to be about 10–50 μm in diameter and at least 0.5 mm long, but it is not clear that each fiber is a single crystal. Electron microprobe data showed that the sample has very close to ideal stoichiometry; contents of impurity phases (muscovite, chlorite, and quartz) were well below the 1% level. NMR spectra were collected on the same batch of material prepared for neutron diffraction, using a Varian VXR 400S spectrometer at a Larmor frequency of 79.45 MHz. A Varian MAS probe with a 7-mm rotor was used, with a spinning rate of about 6 kHz; 1.5- μs pulses (with an rf tip angle of 30°) were repeated every second. The Fe content of the sample (about 0.2 wt%) allowed this unusually rapid data collection but apparently did not broaden the peak significantly. Spectra obtained with longer delays had identical peak shapes but lower signal to noise ratios. A

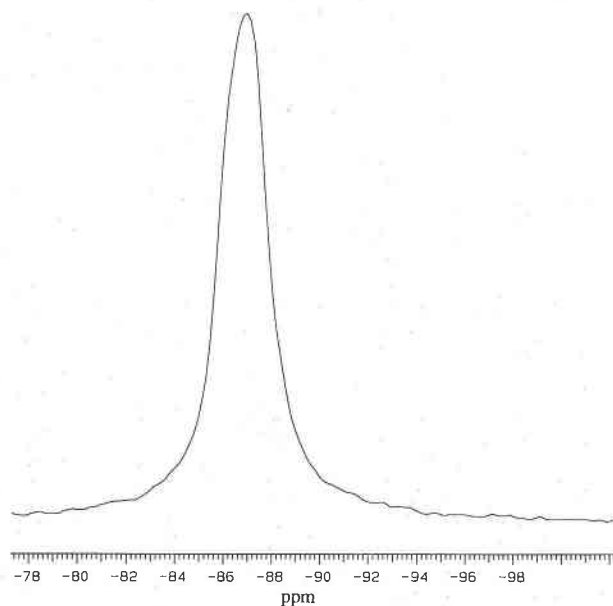


Fig. 1. The ^{29}Si MAS NMR spectrum for fibrolitic sillimanite. Chemical shift is relative to external tetramethylsilane.

typical spectrum is shown in Figure 1. Simulations of the effects of disorder on peak shapes, as described below, are shown in Figure 2.

RESULTS AND DISCUSSION

Only a single, symmetrical peak is present in the ^{29}Si spectra, with a maximum at -86.8 ppm and a full width at half maximum of 2.3 ppm. These data are similar to previous results (Kerrick, 1990; Mägi et al., 1984; Smith et al., 1983). The first of these references also includes a spectrum of a fibrolitic sillimanite sample, and the author concluded that there was no evidence for random, short-range Si-Al disorder in the mineral. We fully concur with that finding. However, the observation of significant disorder in the Pays de Leon sample by means of neutron diffraction requires that the restricted meaning of the conclusions from the NMR data be discussed in detail.

The spectrum of sillimanite is quite sensitive to random tetrahedral disorder and, because of the ideal stoichiometry, is relatively simple to interpret. In the fully ordered structure, there is only a single Si site. As shown in Figure 3a, one O atom of the Si tetrahedron (O_c) is shared with ^{41}Al in the adjacent chain only; each of the two O atoms labeled O_b is shared with one ^{41}Al atom along the chain and one ^{61}Al ; the fourth, nonbridging, O atom (O_a) is shared with two ^{61}Al atoms (as is the analogous O, O_b , in the Al tetrahedron). Because of the presence of three bridging O atoms, the Si site in the ordered structure can be designated $Q^3(3\text{Al})$. An exchange of a Si and an Al within the double tetrahedral chain (in violation of strict order) affects the first neighbor connectivities of not one, but three Si sites, converting one to a $Q^3(1\text{Al})$ site and two to $Q^3(2\text{Al})$ sites. At the same time,

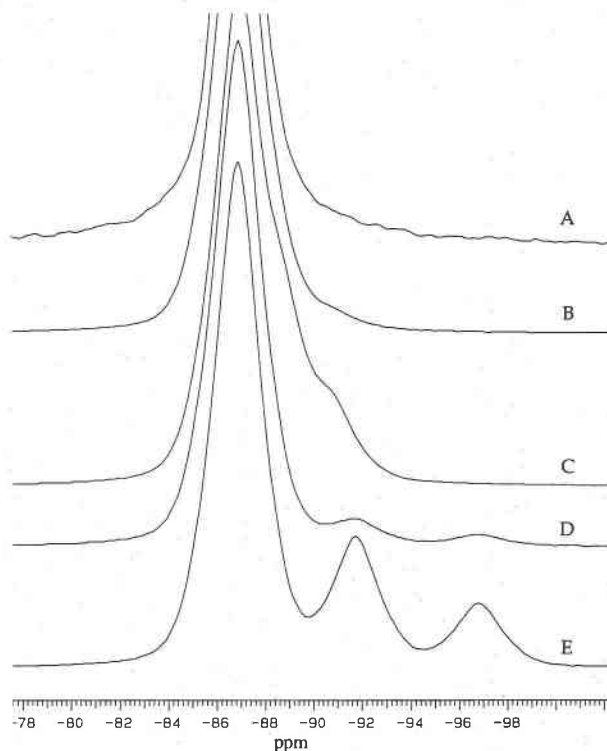


Fig. 2. Experimental (A) and simulated (B-E) ^{29}Si MAS NMR spectra for fibrolitic sillimanite. (A) Same spectrum as in Fig. 1; (B) simulation assuming 2% occupancy of Si site by Al and vice versa (4% disorder), with a 2-ppm change in chemical shift ($\Delta\delta$) for each Si neighbor replaced by Al. Note asymmetry to more negative δ ; (C) $\Delta\delta = 2$ ppm and 18% disorder; (D) $\Delta\delta = 5$ ppm, 4% disorder; (E) $\Delta\delta = 5$ ppm, 18% disorder. Simulations were made assuming a 50% Lorentzian, 50% Gaussian shape, and a peak width similar to that of the observed peak.

two Al-O-Al linkages are formed. Given the correlations between the number of Al neighbors and ^{29}Si peak position that are well known from studies of framework and sheet silicates (Engelhardt and Michel, 1987), this kind of disorder should produce two extra peaks at chemical shifts more negative than the main peak, with a 2:1 area ratio. If the extent of the disorder were great enough, a third peak for $Q^3(0\text{Al})$ might also be produced at even lower frequency (Kerrick, 1990). The positions of these extra peaks cannot be calculated exactly because they depend on the (unknown) details of the way in which the structure locally relaxes around the defects created. However, in framework and sheet silicates a reduction by one in the number of Al neighbors typically results in a change in peak position ($\Delta\delta$) by 5 ppm (Engelhardt and Michel, 1987). This effect may be less for substitutions along the chain in sillimanite, because it could be diluted by the relatively strong bond to ^{61}Al . An estimate for the sillimanite structure quoted by Kerrick (1990) suggests that the change could be only 2 ppm. Even if extra peaks generated by disorder are not resolvable, however, they

should be apparent as shoulders or asymmetry in the main peak toward more negative chemical shifts.

In order to assess the sensitivity of the NMR spectra to random disorder, we have simulated spectra with a variety of assumptions about peak widths and the effect of changing numbers of Al neighbors on peak positions (Fig. 2). It is clear that the 18% disorder observed by neutron diffraction would be obvious with $\Delta\delta$ of either 2 or 5 ppm. As little as 2% disorder would still be easily detectable for $\Delta\delta = 5$ ppm, but would produce a just-detectable asymmetry for $\Delta\delta = 2$ ppm.

We conclude therefore that the disorder observed in this sample by neutron diffraction is not primarily the result of random mixing on tetrahedral sites: we observe no evidence for Si sites with anything but the ordered pattern of Al neighbors. However, the topology of the sillimanite structure allows for a different type of disorder that is consistent with both the neutron diffraction and the NMR data. We propose that chain disorder is present in which Si and Al alternate perfectly in the tetrahedra of each double chain, as in the ordered structure, but the relative positions of Si and Al tetrahedra from chain to chain, controlled by the *b*- and *n*-glide planes of the space group of the ordered structure (*Pbnm*), become somewhat randomized in the partially disordered structure. The ordered space group relationship is destroyed if one double chain is offset along [001] by $\frac{1}{2}c$ relative to its neighbors (Fig. 3b). Random offsetting of tetrahedral double chains by $\frac{1}{2}c$ yields an average structure that appears Al-Si disordered to diffraction experiments. Yet because the double tetrahedral chains are not directly attached to each other, there are no changes in the number or type of first neighbor cations for any Si site, and changes in intertetrahedral bond angles are also negligible. The ^{29}Si NMR spectrum therefore appears to be unchanged from that of ordered sillimanite. Because the offset of one double chain coherently displaces all Si and Al tetrahedra in the chain from their ideal long-range positions, the 9% reversed occupancy observed for the Pays de Lyon fibrolitic sillimanite implies that 9% of the chains are offset. The short-range structural effect of such chain disorder is probably limited to minor distortions of the intervening Al octahedra. The disordering might arise from stacking faults, either parallel to (100) that locally interrupt the *b*-glide relation or parallel to (010) that interrupt the *n*-glide relation (Bish and Burnham, 1992; Lefebvre and Paquet, 1983). Or, the disorder could arise from individual random chain offsets, rather than from organized planar defects. Given that in this sample only 9% of the chains must be offset to incorrect positions, it is possible that diffraction coherency would be less likely to be retained across stacking faults than between randomly offset chains. Our experiments cannot, however, distinguish between these two possibilities.

As in standard treatments of site disorder, the ideal configurational entropy due to chain disorder is obtained by enumerating distinct configurations. In contrast to random site mixing, however, the contribution of double-

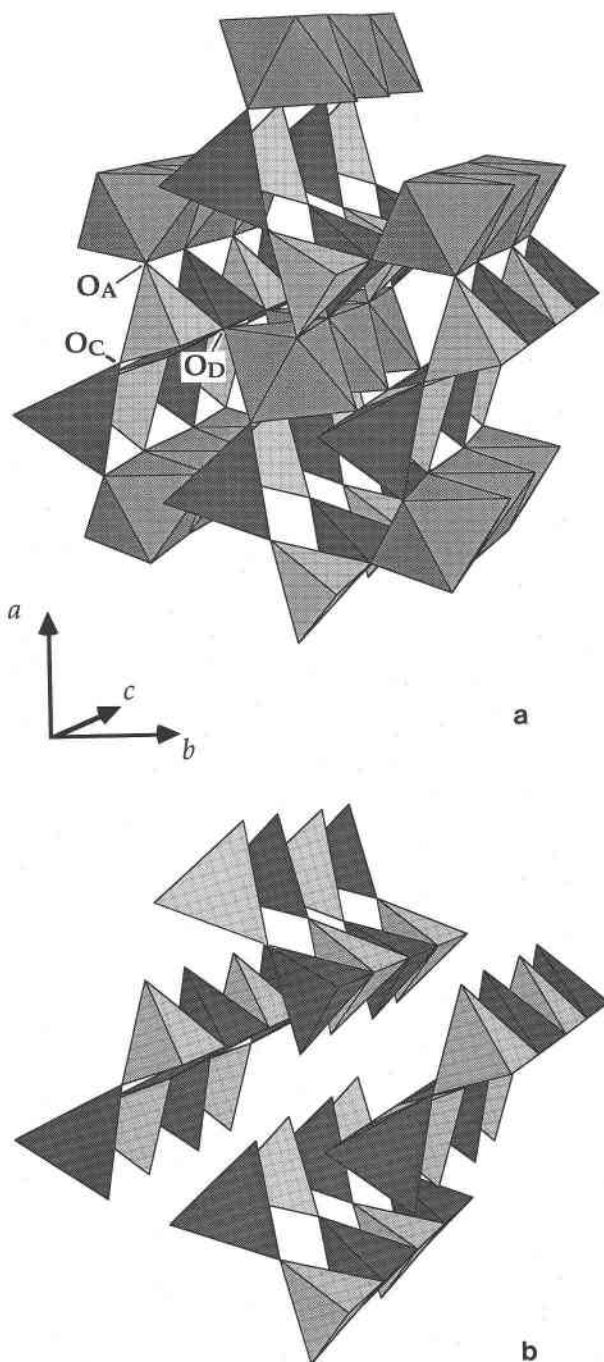


Fig. 3. (a) Perspective view of the sillimanite structure, space group *Pbnm*. Four double tetrahedral chains are shown, in which Si and Al alternate (light and dark tetrahedra). These chains are indirectly linked through parallel intervening Al octahedral chains. Crystallographically distinct O atoms are labeled. (b) Same view of sillimanite structure as in a, showing only double tetrahedral chains. Here, the uppermost chain is offset along the *c* axis by $\frac{1}{2}c$, illustrating chain disorder. Note that intertetrahedral linkages are not modified.

chain disorder to configurational entropy depends on the number of double chains per mole of fibrolitic sillimanite, which depends on the crystal shape (Allen and Burnham, 1992; Thompson, 1981). Configurational entropy due to chain disorder is given by

$$S_{\text{config}} = -kn \sum_i N_i \ln N_i$$

where k is the Boltzmann constant, n is the total number of double chains per mole of sillimanite, and N_i is the fraction of double chains with position i . The number of distinguishable positions for each double chain is two, namely the correct space group position and its opposite, which is translated $\frac{1}{2}c$ relative to the correct position. Because the number of formula units per unit cell for sillimanite is four and there are two double chains per unit cell, the maximum number of chains per mole of sillimanite is 0.5 mole, which would be obtained by a flat crystal one unit cell thick in the c direction. The contribution to configurational entropy from complete chain disorder in such an absurdly shaped crystal would be $-\frac{1}{2}R \ln(\frac{1}{2})$ per mole of sillimanite, or 2.88 J/mol·K. A roughly equant crystal with the same number of unit cells along a , b , and c will contain about 4×10^{15} chains per mole. Complete chain disorder in this case would give S_{config} on the order of 10^{-8} J/mol·K. In a crystal elongated along c with only 18% chain disorder, S_{config} is even less significant, particularly in comparison with any estimate based on random site disorder. Thus, the thermodynamic driving force for the structure to undergo the observed amount of chain disorder with increasing temperature is virtually nonexistent. If the energy effect is also very small, the likelihood of chain disorder is most closely related to circumstances of growth, with rapid growth most conducive to such disorder.

CONCLUSIONS

Neutron powder diffraction analysis and ^{29}Si NMR spectroscopy of the same sample of fibrolitic sillimanite yield results that are mutually consistent only for a structure model involving partial disorder of tetrahedral dou-

ble chains with Si-Al order in the sillimanite structure. This is the first well-documented example of such chain disorder in a silicate, although its occurrence has also been suggested in vesuvianite (Allen and Burnham, 1992) and may well occur in other silicates having unlinked tetrahedral chains containing both Al and Si. Ca-Tschermak's pyroxene is a very likely candidate. The thermodynamic effects of such disorder are minuscule compared with those of normal site disorder. These results illustrate the significantly added value of interpretations from combined experiments that examine independently the long-range (diffraction) and short-range (NMR) attributes of a structure.

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