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A multinuclear NMR study of synthetic pargasite—Discussion

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INTRODUCTION

Welch et al. (1994) characterized synthetic pargasite, $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$, by multinuclear NMR and infrared spectroscopic methods. Their work focused on two aspects of ordering in amphiboles: (1) $^{[4]}$Al ordering over the T1 and T2 sites, and (2) $^{[6]}$Al ordering over the M1, M2, and M3 sites. It is the second aspect of their work that I wish to consider here. Crystal-structure refinement (Robinson et al., 1973) had assigned $^{[6]}$Al to the M2 site in natural pargasite. Infrared spectroscopy (Raudsepp et al., 1987) shows that $^{[6]}$Al must occur at the M1 or M3 site (or both) in synthetic pargasite. Welch et al. (1994) showed by comparison of ^{27}Al MAS NMR and CP MAS spectra that $^{[6]}$Al occurs at M2 as well as at M1 or M3 (or both) in synthetic pargasite. However, Welch et al. (1994) also compared their ^{27}Al MAS NMR spectrum with a series of models for local ordering over the M1, M2, and M3 sites and concluded that $^{[6]}$Al occurs at the M2 and M3 sites. However, their preferred model predicted a peak-intensity ratio of 2:1, whereas the observed ratio was 1:1; they stated that this discrepancy arose because Mg and $^{[6]}$Al are not randomly distributed over all three (2M2 + M3) sites, with the rider that there may be random mixing of Mg and $^{[6]}$Al within the M2 and M3 sites. I wish to suggest that their models of local order over the M1, M2, and M3 sites are inappropriate; an alternative set of models is more realistic from a crystal-chemical viewpoint and is more consistent with the infrared and ^{27}Al MAS NMR spectra.

LOCAL ORDERING OF $^{[6]}$Mg AND $^{[6]}$Al

Welch et al. (1994) assumed that Mg and $^{[6]}$Al can take up all geometrically possible local configurations and that the probability of them doing so can be calculated on the basis of random mixing. I suggest that this is extremely unlikely on bond-valence grounds. Table 1 shows the bond valence incident to O3 for all local configurations suggested by Welch et al. (1994). The sum of the bond valences incident at O3 should equal the formal valence of the O3 anion. For the configuration Mg_3OH, the bond-valence sum is 1.0 vu, consistent with the high frequency (3711 cm^{-1}) of the analogous OH-stretching band in the infrared spectrum. For the configuration Mg_2AlOH, the bond-valence sum is 1.16 vu. This is somewhat higher than the ideal value of 1.0 vu, but this is accommodated by a weakening of the O3-H bond as indicated by the lower frequency (3678 cm^{-1}) of this configuration in the infrared spectrum; in addition, minor bond-length adjustments around the O3 anion can help compensate for this increase in incident bond valence. For the configurations $MgAl_2OH$ and Al_3OH, the incident bond-valence sums are 1.33 and 1.50 vu, respectively, too large for the amphibole structure to accommodate by local structural relaxation; these local configurations will not occur.

TABLE 1. Bond valence incident at O3 for all local 2M1 + M3 arrangements suggested by Welch et al. (1994)

Local arrangement	Incident bond valence to O3
Mg Mg Mg	$\frac{1}{3} \times 3 \times 1.00$ vu
Mg Mg Al	$\frac{1}{3} \times 2 \times \frac{1}{2} = 1.16$ vu
Mg Al Al	$\frac{1}{3} + 2 \times \frac{1}{2} = 1.33$ vu
Al Al Al	$\frac{1}{2} \times 3 = 1.50$ vu

The infrared spectra of pargasite (Raudsepp et al., 1987; Welch et al., 1994) show two bands at 3711 and 3678 cm^{-1}; both sets of authors assigned these bands to the local configurations Mg_3OH and Mg_2AlOH. Any bands due to $MgAl_2OH$ or Al_3OH configurations would occur at significantly lower frequencies; the spectra of both Raudsepp et al. (1987) and Welch et al. (1994) show no sign of such bands.

AN ALTERNATIVE ORDERING MODEL

Given that the configurations $MgAl_2OH$ and Al_3OH do not occur, any model of local $^{[6]}$Al ordering in pargasite should reflect this fact; the models of Welch et al. (1994) assume that such local configurations are possible, and hence these models are inappropriate. Table 2 shows probabilities of local configurations given that the $MgAl_2OH$ and Al_3OH configurations do not occur and that there is no long-range ordering. All possible ordering schemes give either one or two peaks. Given that the relative peak intensities can be affected by long-range ordering, all two-peak models may be considered compatible with the infrared and ^{1}H MAS NMR spectra. Thus the MAS NMR study of Welch et al. (1994) does not resolve the question of Al ordering over the M1, M2, and M3 sites in synthetic pargasite.

TABLE 2. Probabilities of local ordering patterns around O3 in end-member pargasite

Model	Sites	Mg_3OH	Mg_2AlOH
1 site	M3	0.00	1.00
2 site (a)	2M1	0.00	1.00
2 site (b)	2M2	1.00	0.00
3 site (a)	2M1 + M3	0.00	1.00
3 site (b)	2M2 + M3	0.67	0.33
4 site	2M1 + 2M2	0.50	0.50
5 site	2M1 + 2M2 + M3	0.40	0.60

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A multinuclear NMR study of synthetic pargasite—Reply to Hawthorne

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