^{29}Si MAS NMR systematics of calcic and sodic-calcic amphiboles

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ABSTRACT

We report the compositional systematics of the ^{29}Si MAS NMR spectra of richterite, $^{[A]}(Na,K,Rb)_1(Na,Ca,Sr)_2Mg_5Si_8O_{22}(OH,F)_2$; pargasite, $NaCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2$; and fluor-edenite, $NaCa_2Mg_5Si_7AlO_{22}F_2$. $^{[A]}$Na causes (1) splitting of T1 into two sites, while leaving T2 unsplit, and (2) the Q^3 chemical shift to be 2.5 to 3 ppm less negative than Q^3 when the A site is empty as in tremolite and magnesiohornblende. The preferential splitting of T1 is explained in terms of ordering of the A cation at A*m*. The effects of M4 and A-site chemistry upon the richterite spectra aid the assignment of peaks for pargasite and fluor-edenite. The long-range ordering of Al and Si over T1 and T2 sites in fluor-edenite synthesized at 2 kbar, and 1000 °C, and pargasite synthesized at 1 kbar, and 930 °C has been calculated from their ^{29}Si MAS NMR spectra assuming that Al avoidance operates. The extent of long-range order is calculated from the intensities of the $Q^2(2Al)$, $Q^2(1Al)$, and $Q^2(0Al)$ peaks. An equation is derived that allows the extent of long-range Al-Si order to be calculated from ^{29}Si MAS NMR spectra of amphiboles. The spectrum of fluor-edenite is consistent with all $^{[4]}$Al being at T1 with maximal short-range disorder within the constraints of Al avoidance. The pargasite spectrum is more complex, because there is a probable peak coincidence of $Q^2(1Al)$ and $Q^3(2Al)$ at -82 ppm that must be considered. The presence of a $Q^3(0Al)$ peak in the pargasite spectrum indicates unambiguously that some long-range disorder exists, and this implies that $Q^3(2Al)$ groupings also occur. The calculated extent of long-range disorder in pargasite is $55 \pm 10\%$. This value is consistent with the single-crystal X-ray data of Oberti et al. (1995a) for natural amphiboles extrapolated to $^{[4]}$Al = 2 apfu at 900 °C. The different long-range Al-Si ordering behavior of flour-edenite and pargasite is explained in terms of the bond-valence requirements of O4. At high temperatures, configurational entropy becomes an important stabilizing factor, and structural distortion around O4 in pargasite and hornblende allows Al into T2, provided that O4 is coupled to Al at an adjacent M2 site, as in pargasite. The results for fluor-edenite, which has no $^{[6]}$Al, show that the low O4 bond-strength sum of the $^{T2}Al^{M2}Mg^{M4}Ca$ configuration cannot be accommodated by sufficient structural relaxation, even at 1000 °C. Coupling between Al at M2 and T2 is an important control on Al-Si long-range order-disorder.