Short-range order in synthetic aluminous tremolites: An infrared and triple-quantum MAS NMR study

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ABSTRACT

Fourier-transform infrared spectra (FTIR) were recorded on a series of synthetic amphiboles along the join Ca_1.8Mg_5.2Si_8O_22(OH)2–Ca_1.8(Mg_4.2Al)(Si_7Al)O_22(OH)2. The spectra were fitted by up to six component bands by optimization and non-linear least-squares techniques. 27Al MAS NMR and triple-quantum (3Q) MAS NMR spectra were recorded for the synthetic amphibole Ca_1.8(Mg_4.8Al_0.4)(Si_7.6Al_0.4)O_22(OH)2. The fitted FTIR and NMR spectra show that VIAl occurs at the M2 site and at the M1 or M3 sites; by analogy with previous crystal-structure refinement results on natural amphiboles, VIAl occupancy of M2 and M3 is presumed. The fine structure present in the FTIR spectra indicates that they are also affected by NNN (next-nearest-neighbor) interactions. There are two types of NNN arrangements: (1) SiSi or SiAl at adjacent T1T1 dimers; (2) permutation of Mg/Al over M2M2M3 sites. Discounting those arrangements unlikely on bond-valence grounds, there are two arrangements that give rise to five distinct bands in the infrared spectra. There are two principal conclusions: (1) infrared spectra of amphiboles in the principal OH-stretching region can be affected significantly by NNN effects; (2) the small number of bands due to NNN effects indicates that amphiboles show strong short-range order.

INTRODUCTION

The composition of calcic amphiboles, and the Al content in particular, has great potential in geobarometry of igneous and metamorphic processes. Both field evidence and experimental work suggest that Al content is correlated with the physical conditions (P and T) of amphibole formation (e.g., Spear 1981; Hammarstrom and Zen 1986; Hollister et al. 1987). This, together with the fact that amphiboles are ubiquitous in many geological environments (Hawthorne 1983), has prompted increased attention directed toward a more quantitative definition of Al solubility in both natural (Holland and Richardson 1979; Tribollet and Audren 1988; Kohn and Spear 1990; Mader and Berman 1992) and synthetic amphiboles (Jenkins 1988, 1994; Cho and Ernst 1991; Smelik et al. 1994). Two main problems have been encountered in these studies: (1) identifying the exchange reactions responsible for Al incorporation in the amphibole structure; in calcic amphiboles, there is general consensus in considering the tschermak substitution as the main mechanism whereby one divalent cation and one Si are replaced by Al in both octahedral and tetrahedral coordination. (2) Thermodynamic modeling has been largely based on mixing models which did not take into account possible patterns of long-range order (LRO) and short-range order (SRO) involving substituting cations over non-equivalent sites. Most thermodynamic analyses have considered activity models based solely on Mg/Al ordering at M2 and Si/Al ordering at T1. Recent crystal-structure work has shown that these mixing models are inadequate. Long-range ordering patterns of Al in amphiboles are now quite well understood (Oberti et al. 1995a, 1995b), but we still know very little about SRO of Al. Infrared spectroscopy has potential with respect to SRO characterization in silicates, and there has been considerable effort recently to develop procedures to quantify SRO in synthetic amphiboles (Della Ventura 1993; Della Ventura et al. 1996a, 1996b, 1998; Hawthorne et al. 1996a, 1996b, 1997).

Here, we report Fourier-transform infrared (FTIR) and magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic studies of synthetic aluminous tremolites along the tremolite-tschermakite join, and show that IR spectroscopy in the OH-stretching region is a valuable tool in understanding particular features of Al incorporation in calcic amphibole.