^{29}Si MAS NMR study of diopside–Ca-Tschermak clinopyroxenes: Detecting both tetrahedral and octahedral Al substitution

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ABSTRACT

We have studied short-range cation ordering across the diopside ($CaMgSi_2O_6$)-Ca-Tschermak pyroxene ($CaAl_2SiO_6$) (Di-CaTs) solid solution in samples synthesized at 1400 °C and 2 GPa, for 24 hours. Peak positions in ^{29}Si MAS NMR spectra are sensitive to Al substitution, both in the corner-sharing NN tetrahedral sites on the single chain and in one of the three NN octahedral M1 sites. The substitution of Al for Mg on M1 causes the [29]Si chemical shift to be shielded by about the same magnitude as the deshielding caused by substitution of Al for Si in NN tetrahedra, causing severe peak overlap among central peaks. Two pairs of the unique local environments have very similar chemical shifts, leaving only four peaks resolved in the spectrum, for which six site assignments have been made.

^{29}Si MAS NMR peak intensities for end-member CaTs are consistent with 70% of the Si in the tetrahedral chain being locally ordered into alternating [4]Al-O-Si-O-[4]Al linkages, although space group *C*2/*c* would suggest that Si and Al are long-range disordered over the tetrahedral chain. CaTs clearly violates Löwenstein's (1954) Al-O-Al avoidance principle, with 0.175 Al-O-Al linkages per formula unit (based on six O atoms per formula unit), as calculated from observed ^{29}Si MAS NMR peak intensities. For intermediate members of the solid solution, site populations have been modeled using a random distribution model (RD), an Al-O-Al avoidance model (AA) and a modified AA model which couples the cation distribution between the tetrahedral and octahedral sites (AAOC). The RD model fits the ^{29}Si MAS NMR peak intensities poorly. The AA and AAOC models fit the ^{29}Si NMR data well to at least 75% CaTs, suggesting that diopside-rich Di-CaTs clinopyroxenes obey Löwenstein's Al-O-Al avoidance principle. For compositions >75% CaTs, observed cation distributions deviate considerably from that predicted by Al-O-Al avoidance, indicating formation of Al-O-Al linkages. The AAOC model yields an improved fit to the observed ^{29}Si MAS NMR intensities, particularly near $Di_{50}CaTs_{50}$, implying the presence of [4]Si-O-[6]Mg and [4]Al-O-[6]Al couples. This suggests the presence of short-range ordering on both tetrahedral and octahedral sites in Di-CaTs pyroxenes.

The high sensitivity to octahedral Al substitution observed in these chain silicates is not observed by ^{29}Si MAS NMR of more-polymerized silicates, such as framework and sheet structures. Thus, ^{29}Si MAS NMR of pyroxenes has potential to reveal tetrahedral-octahedral cation coupling and octahedral cation ordering information, which is potentially important for geothermobarometry of aluminous pyroxenes.