INTRODUCTION

Pyroxenes are major constituents of the Earth’s crust and upper mantle to depths of 400 km. They occur in a wide variety of geological settings, both igneous and metamorphic. Their wide stability range and chemical variability make them potentially important indicators of the temperature and pressure conditions of formation. Aluminum-bearing pyroxene can be used to calibrate geothermometers and geobarometers.

29Si 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 (CaMgSi2O6)-Ca-Tschermak pyroxene (CaAl2SiO6) (Di-CaTs) solid solution in samples synthesized at 1400 °C and 2 GPa, for 24 hours. Peak positions in 29Si 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 29Si 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.

29Si 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 C2/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 29Si 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 29Si MAS NMR peak intensities poorly. The AA and AAOC models fit the 29Si 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 29Si MAS NMR intensities, particularly near Di80CaTs20, 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 29Si MAS NMR of more-polymerized silicates, such as framework and sheet structures. Thus, 29Si 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.

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The presence of aluminous components, such as jadeite (NaAlSi2O6), Ca-Eskola (Ca0.5⁺Al0.5Si2O6), and Ca-, Mg-, Fe-, Cr-, and Ti-Tschermak pyroxenes (CaAl2SiO6, MgAl2SiO6, FeAl2SiO6, CaCrAlSiO6, CaTiAl2O6, respectively), is generally correlated with elevated pressures of formation. Tschermak pyroxenes are useful in numerous geobarometers involving both orthopyroxenes (e.g., Carswell 1991; Taylor 1998) and clinopyroxenes (e.g., Putirka et al. 1996; Nimis and Ulmer 1998; Yoshino et al. 1998; Nimis 1995, 1999). A complication that arises in attempting to calibrate or apply these geobarometers is the potential for cation ordering to displace reactions. Configurational entropy and enthalpy accompanying cation disorder in aluminous pyroxenes influences their stability and displaces P-T equilibria. Therefore, determination of the cat-