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Aluminum substitution in stishovite and $MgSiO_3$ perovskite: High-resolution ^{27}Al NMR

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ABSTRACT

Aluminum is an important minor constituent of a number of high-pressure mantle silicates in which it substitutes for octahedrally coordinated silicon. In several cases, its solid solution may be linked to the presence of oxygen vacancies; in others, to charge balance with H^+. Here we present new data from high-resolution, high-field (18.8 Tesla) ^{27}Al NMR of aluminous stishovite and of a non-stoichiometric perovskite with nominal composition $MgSi_{0.95}Al_{0.05}O_{2.975}$. For the stishovite, we characterize the local structure of the symmetrical, octahedral site for Al. These results, combined with $^{27}Al\{^1H\}$ REDOR NMR, are consistent with hypothesized H^+ charge balance, although the presence of a significant fraction of randomly distributed oxygen vacancies could remain undetected. As in a recent previous study of a related perovskite composition, the observed ratio of Al at symmetrical octahedral B sites to that of Al at large, central A sites is about 2:1, indicating the presence of oxygen vacancies to account for charge neutrality in this phase. Such vacancies are not preferentially associated with the Al octahedra, however, suggesting a random distribution in the structure.

Keywords: High-pressure studies, perovskite, stishovite, NMR spectroscopy, crystal structure, phase equilibria