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Transition metals in the transition zone: Crystal chemistry of minor element substitution in wadsleyite

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Abstract

As the most abundant solid phase at depths of 410–525 km, wadsleyite constitutes a large geochemical reservoir in the Earth. To better understand the implications of minor element substitution and cation ordering in wadsleyite, we have synthesized wadsleyites coexisting with pyroxenes with 2–3 wt% of either TiO_2, Cr_2O_3, V_2O_3, CoO, NiO, or ZnO under hydrous conditions in separate experiments at 1300 °C and 15 GPa. We have refined the crystal structures of these wadsleyites by single-crystal X-ray diffraction, analyzed the compositions by electron microprobe, and estimated M3 vacancy concentration from *b*/*a* cell-parameter ratios. According to the crystal structure refinements, Cr and V show strong preferences for M3 over M1 and M2 sites and significant substitution up to 2.9 at% at the tetrahedral site (T site). Ni, Co, and Zn show site preferences similar to those of Fe with M1≈ M3 > M2 > T. The avoidance of Ni, Co, and Fe for the M2 site in both wadsleyite and olivine appears to be partially controlled by crystal field stabilization energy (CFSE). The estimated CFSE values of Ni^{2+}, Co^{2+}, and Zn^{2+} at three distinct octahedral sites show a positive correlation with octahedral occupancy ratios [M2/(M1+M3)]. Ti substitutes primarily into the M3 octahedron, rather than M1, M2, or T sites. Ti, Cr, and V each have greater solubility in wadsleyite than in olivine. Therefore these transition metal cations may be enriched in a melt or an accessory phase if hydrous melting occurs on upward convection across the wadsleyite-olivine boundary and may be useful as indicators of high-pressure origin.

Keywords: Wadsleyite, transition metals, X-ray diffraction, cation ordering