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 TiO2, Cr2O3, V2O5, 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 Ni2+, Co2+, and Zn2+ 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

INTRODUCTION

Wadsleyite (β-Mg2SiO4) is a phase of very broad geochemical significance and is considered to be the fourth most abundant silicate phase in the Earth (after bridgmanite, olivine, and ringwoodite). The total mass of wadsleyite in the mantle may be more than four times the mass of the crust. High-pressure mineral-physics studies (Bolfan-Casanova et al. 2000; Demouchy et al. 2005; Kohlstedt et al. 1996) show that transition-zone minerals at average mantle temperatures have significantly higher water solubility (on the order of 1 wt% under realistic T and P conditions and as much as 3 wt% at upper mantle minerals (less than 0.1–0.2 wt%), and as the ascending ambient mantle rises out of the high-water-solubility transition zone into the low-solubility upper mantle above 410 km, it may undergo dehydration-induced partial melting (Bercovici and Karato 2003). Unlike olivine, wadsleyite can also incorporate significant amounts of trivalent cations at both tetrahedral and octahedral sites (Bolfan-Casanova et al. 2012; Smyth et al. 2014). Therefore, minor element substitution in wadsleyite may have played a significant role in the chemical evolution of the bulk silicate Earth. Substitution of hydrogen and transition metal cations in wadsleyite can influence the depth of wadsleyite-olivine boundary and may result in hydrous melting at the interface between the transition zone and upper mantle (Woodland and Angel 1998; Kawamoto et al. 1996; Inoue et al. 2010; Deon et al. 2011; Bercovici and Karato 2003; Bolfan-Casanova et al. 2012).

Wadsleyite has the spineloid III crystal structure (Akaogi et al. 1982) that is based on a cubic-close-packed array of oxygen anions. The structure (see Fig. 1) is nominally orthorhombic (space group Imma), but can be slightly monoclinic (space group I2/m) with a β angle up to 90.4° (Smyth et al. 1997). Wadsleyite has three symmetrically distinct divalent octahedral sites: M1 (4a position, point symmetry 2/m), M2 (4e position, point symmetry mm), and M3 (8g position, point symmetry 2), one tetrahedral site T (8h position with point symmetry m), and four distinct oxygen positions: O1 (4e position, point symmetry mm), O2 (4e position, point symmetry mm), O3 (8h position, point symmetry m), and O4 (16g general position). The tetrahedral sites form SiO4 dimers and are unusually large with one of the longest Si-O distances of any pure silica tetrahedron (>1.70 Å). The polyhedral volume of the tetrahedron at one atmospheric pressure is about 4% larger than that of forsterite (Smyth and Bish 1988) and therefore may be expected to partition trivalent transition metals from olivine. The O2 position is the bridging oxygen of the Si2O7 group and is also bonded to one M2, so it is overbonded. By contrast, O1 is bonded to five Mg, but not to Si, and is thus underbonded. Therefore, the non-silicate O1 is a

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