The equation of state of wadsleyite solid solutions: Constraining the effects of anisotropy and crystal chemistry

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ABSTRACT

A quantitative knowledge of the equation of state of wadsleyite solid solutions is needed to refine thermodynamic and thermoelastic models for the transition zone in Earth’s upper mantle. Here we present the results of high-pressure single-crystal X-ray diffraction experiments on two crystals of slightly hydrous iron-bearing wadsleyite with Fe/(Mg+Fe) = 0.112(2), Fe3+/ΣFe = 0.15(3), and 0.24(2) wt% H2O up to 20 GPa. By compressing two wadsleyite crystal sections inside the same diamond-anvil cell, we find a negligible influence of crystal orientation on the derived equation of state parameters. Volume and linear compression curves were analyzed with finite strain theory to demonstrate their mutual consistency for the Reuss bound indicating quasi-hydrostatic stress conditions. The results on the here-studied wadsleyite crystals are incorporated into a multi-end-member model to describe the equation of state for wadsleyite solid solutions in the system Mg2SiO4-Fe2SiO4-MgH2SiO4-Fe3O4. For the hypothetical ferrous wadsleyite end-member, Fe2SiO4, we find a substantially larger bulk modulus than expected by extrapolating currently accepted trends. The multi-end-member equation of state model may serve as a basis for the calculation of phase equilibria and the interpretation of seismic observations regarding the transition zone.

Keywords: Wadsleyite, transition zone, equation of state, solid solution, diamond-anvil cell

INTRODUCTION

In most models for Earth’s upper mantle, wadsleyite, β-(Mg,Fe)2SiO4, is assumed to be a major phase in the transition zone (Ringwood 1991; Frost 2008; Stixrude and Lithgow-Bertelloni 2011). The steep increase in seismic velocities around 410 km depth has been attributed to the phase transition of olivine, α-(Mg,Fe)2SiO4, to wadsleyite (Bina and Wood 1987; Ringwood 1991; Agee 1998). Seismological observables related to the 410 km discontinuity such as the magnitude, depth, and depth interval of the velocity and density increase (Shearer 2000; Houser 2016) serve as anchor points to constrain the mineralogical, chemical, and thermal state of the upper mantle (Katsura et al. 2010; Wang et al. 2014; Chang et al. 2015; Zhang and Bass 2016).

In addition to iron-magnesium substitution (Ringwood and Major 1970; Frost 2003), nominally anhydrous wadsleyite can incorporate substantial amounts of hydrogen (Smyth 1994; Inoue et al. 1995) in the form of hydroxyl groups (McMillan et al. 1991; Young et al. 1993). Moreover, wadsleyites with Fe2+/2Fe up to 96% have been synthesized under oxidizing conditions (Smyth et al. 1997; McCammon et al. 2004). Both hydrogen and ferric iron expand the stability field of wadsleyite to lower pressures and affect the pressure interval of the phase transition (Wood 1995; Smyth and Frost 2002; Frost and Dolejš 2007; Frost and McCammon 2009). To describe phase equilibria and to model seismic properties of wadsleyite, we need to know the equation of state (EOS) for wadsleyite solid solutions spanning the range of relevant compositions as captured by the system Mg2SiO4-Fe2SiO4-MgH2SiO4-Fe3O4.

The variation of individual EOS parameters as a function of wadsleyite crystal chemistry has been addressed in previous studies, and certain trends have been established. Both iron and hydrogen incorporation expand the unit cell at ambient conditions but have opposing effects on the density (Finger et al. 1993; Holl et al. 2008; Mao et al. 2008b). While the incorporation of hydrogen clearly enhances the compressibility of wadsleyite (Holl et al. 2008; Mao et al. 2008b; Ye et al. 2010; Chang et al. 2015), the bulk modulus appears to be insensitive to iron-magnesium exchange when directly comparing experimental values determined with different techniques and based on different EOS assumptions (Wang et al. 2014; Chang et al. 2015). Only a few studies addressed the combined effect of iron and hydrogen on the EOS of wadsleyite, indicating that iron slightly counteracts the reduction of the bulk modulus due to hydrogen incorporation (Mao et al. 2011; Chang et al. 2015; Mao and Li 2016).

Although ferric iron was shown to stabilize wadsleyite at lower pressures and to broaden the 410 km discontinuity (Frost and McCammon 2009), little is known about the effect of the Fe3+ cation on the elastic properties of wadsleyite. Hazen et al. (2000b) deduced a negligible effect of ferric iron on the compression behavior from their high-pressure single-crystal X-ray diffraction study on Fe2.33Si0.67O4, a member of the low-pressure spinel-lloid III solid-solution series (Woodland and Angel 1998, 2000; Koch et al. 2004). This solid-solution series is isostructural with wadsleyite and spanned by the coupled substitution of octahedral Mg2+ and Fe2+ cations and tetrahedral Si4+ by ferric iron (Woodland and Angel 1998; Hazen et al. 2000b; Woodland et al. 2012). The fact that in many studies on the EOS of iron-bearing wadsleyites the amount of ferric iron has not been assessed could...