The effect of oxygen fugacity on the olivine to wadsleyite transformation: Implications for remote sensing of mantle redox state at the 410 km seismic discontinuity

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**Abstract**

High-pressure and -temperature multi-anvil experiments were performed to test the effect of varying oxygen fugacity on the olivine to wadsleyite transformation. Two capsules, containing samples of (Fe,Mg)SiO$_3$, were placed in each experiment; the first buffered the oxygen fugacity with an assemblage of Re and ReO$_3$, whereas the second ensured the lowest possible ferric iron concentration through the presence of excess Fe metal. Measurements of coexisting olivine, wadsleyite, and ringwoodite compositions from the Fe metal saturated experiments were used to accurately determine the pressure in each experiment using established phase relations. Under the more oxidizing conditions of the Re-ReO$_3$ buffer, the stability field of wadsleyite was found to expand with respect to both the olivine and ringwoodite stability fields. Mössbauer spectroscopy measurements reveal Fe$^{3+}$/ΣFe ratios for wadsleyite buffered by Re-ReO$_3$ of 0.1–0.25, while olivine appears to be Fe$^{3+}$-free. A thermodynamic model that employs the wadsleyite end-members (Fe$^{3+}$O$_2$-Fe$_2$SiO$_4$-Mg$_2$SiO$_4$) is used to examine the effect of varying bulk mantle Fe$^{3+}$/ΣFe ratio on the depth and depth interval of the 410 km seismic discontinuity. Fe$^{3+}$/ΣFe ratios in the range 0.02–0.12 would cause the depth interval or thickness of the 410 km discontinuity to increase from ~8 to 15 km but would have very little effect on the seismically observable absolute depth. Very large bulk mantle Fe$^{3+}$/ΣFe ratios (>0.2), unrepresented in recovered mantle samples, would be required to explain recent seismic observations that the depth interval of the 410 km may be >20 km beneath certain regions. Such observations are more likely to be explained by moderate local enrichments in both ferric iron and H$_2$O in the mantle, most likely as a result of slab interaction.

Keywords: Ferric iron, multi-anvil, transition zone, seismic discontinuity

**Introduction**

The (Mg,Fe)$_4$SiO$_3$ olivine to wadsleyite transformation is considered to cause the jump in seismic wave velocity observed globally at ~410 km depth (hereinafter d410), which separates the upper mantle from the transition zone (Agee 1999). Properties of the discontinuity, such as the depth, depth interval, and sound velocity jump, can be measured using seismological techniques and are linked to properties of the mantle at these conditions (e.g., Helffrich 2000; Katsura et al. 2004). High-pressure experimental data on the petrology of the phase transformation and the elasticity of minerals involved are required to interpret these properties. The depth of d410, for example, is known to vary globally (Flanagan and Shearer 1998) and this variation is most likely principally coupled to mantle temperature variations. From knowledge of the Clausius-Clapeyron slope of the olivine to wadsleyite transition an estimate of mantle temperature and its global variation can be made from observations of the regional depth variation of d410 (Frost 2008). Similarly, it has been proposed that the depth interval over which the increase in seismic velocity takes place can provide information on the concentrations of certain components in the mantle (Wood 1995; Agee 1999). Both olivine and wadsleyite are Fe-Mg solid solutions and because Fe$^{3+}$ partitions more strongly into wadsleyite during the transformation, the transition is divariant and occurs over a pressure interval where the width of this interval is nominally constrained by the bulk Fe content of the mantle. In dry, reduced mantle this transition interval should be ~7 km, (Frost 2003) although the presence of non-transforming phases such as garnet may reduce this to ~5 km (Irifune and Ishiki 1998; Frost 2003).

In a recent study, where the frequency of waves converted at d410 were analyzed to determine the depth interval of the discontinuity, it was concluded that beneath regions of the Mediterranean the discontinuity may have a thickness of up to 30 km (van der Meijde et al. 2003). Extreme Fe enrichments in the mantle would be required to produce such a depth interval. On the other hand, any component that partitions strongly into one of the transforming phases also has the potential to broaden the transformation pressure interval. Useful information on the state of the mantle at 410 km could be extracted from seismic observations of the depth interval of d410 if the effects of important mantle components on the transformation were understood. H$_2$O, for example, partitions more favorably into wadsleyite as OH defects than in olivine, which broadens the phase transformation by stabilizing wadsleyite at lower pressures than in the dry system (Wood 1995). Experimental studies show that very large concentrations of H$_2$O (>0.5 wt%) are required to influence the depth interval of d410, mainly because the H$_2$O concentration of wadsleyite is only 2–3× that of olivine at equilibrium (Hirschmann et al. 2006; Frost and Dolejš 2007). Gudfinnsson