Hydration-driven stabilization and volume collapse of grain boundaries in Mg$_2$SiO$_4$

forsterite predicted by first-principles simulations

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**Abstract**

Grain boundaries in mantle minerals are of critical importance to geophysical and geochemical processes of the Earth’s interior. One of the fundamental issues is to understand how the water (H$_2$O) component influences the properties of grain boundaries in silicate materials. Here, we report the results of the structure and stability of several tilt grain boundaries in Mg$_2$SiO$_4$ forsterite over the pressure range 0 to 15 GPa using density functional theory-based first-principles simulations. The results suggest greater energetic stability and hydration-driven volume collapse (negative excess volume) at zero pressure for the majority of hydrous grain boundaries relative to the anhydrous (dry) ones. All the hydrous grain boundaries become increasingly favorable at elevated pressures as the calculated hydration enthalpy systematically decreases with increasing pressure. The hydrous components at the interfacial regions are predominantly in the hydroxyl form and, to a lesser extent, in the molecular H$_2$O form. Their calculated ratio ranges from 1.6 to 8.7 among the different grain boundary configurations. Our structural analysis also reveals that the hydroxyls are bound to either both Mg and Si or to Mg only. In comparison, the molecular species are bound only to Mg sites. Besides direct oxygen-hydrogen bonding, intermolecular hydrogen bonding becomes important with compression. On the basis of our results, we suggest that local atomic rearrangements caused by dissociative adsorption of water facilitate efficient compaction of the boundary interfaces, which, in turn, results in greater relative stability of hydrous grain boundaries. This means that water prefers to be incorporated within the grain boundaries over the bulk of silicate materials.

**Keywords:** Grain boundary, forsterite, energetics, pressure, first-principles

**Introduction**

Defects that are usually present in materials in various forms influence the properties of materials to various degrees. In particular, the inter-granular regions or interfaces (i.e., grain boundaries) can act as sinks for other defects, including impurities (Hiraga et al. 2003, 2004; Karki et al. 2015). They may act as nucleation sites for corrosion, precipitation, fracture, and affect plastic deformation properties of materials (Duffy 1986; Sutton and Balluffi 1995; Yang et al. 2015; Barr et al. 2018). Additionally, they are known to provide faster pathways for ionic diffusion and electrical conduction (Van Orman et al. 2003; Hayden and Watson 2007, 2008; Dohmen 2008; Pomnier et al. 2018). The behavior and properties of grain boundaries in ceramics and minerals are of critical importance from technological and geological viewpoints.

Water, a universal solvent, can have a profound influence on various materials properties, including creep, elasticity, and melting (Hirth and Kohlstedt 1995; Henderson 2002; Asimow and Langmuir 2003; Carrier et al. 2016; Suknev 2019). The presence of hydrous components at grain boundary interfaces is likely to amplify the transport properties, such as diffusion, and electrical conductivity and influence seismic wave velocities (Karato 1990; Karato and Wu 1993). This is especially relevant for materials in subduction zones and upper mantle-transition regions where the presence of water is expected in significant amounts.

Here we choose to study hydrous grain boundaries in forsterite (Mg$_2$SiO$_4$), which is the Mg end-member of the olivine system and is a common rock-forming mineral in Earth’s upper mantle. Forsterite in its hydrated form has widely been studied (e.g., Kohn 1996; Jacobsen et al. 2008; Ye et al. 2009; Liu et al. 2018). Forsterite–water interactions are thought to be one of the key processes behind water retention during planetary accretion (Stimpfl et al. 2006; King et al. 2010). The presence of hydrous components is also considered to promote incipient melting and enhance interfacial transport at mantle conditions (Hirth and Kohlstedt 1995; Henderson 2002; Asimow and Langmuir 2003). In the study of nominally anhydrous forsterite, both OH and molecular water species were predicted to exist, with the possibility of clustered OH resembling static H$_2$O at grain boundary interfaces and non-clustered OH units as bulk point defects (Kohn 1996). Associating the hydrous components with forsterite grain boundaries is thus important with regard to mantle materials.

Investigating how H$_2$O interacts with the grain boundary and what characteristic changes occur at the atomic scale can assist us in understanding the fundamental processes that occur in grain boundaries under pressure and wet conditions. Due to the lack of atomic order at the grain boundary, the widely used two-dimensional experimental imaging techniques (e.g., transmission