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Hydration-driven stabilization and volume collapse of grain boundaries in Mg_2SiO_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_2O) 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_2SiO_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_2O 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