Ab initio study of water speciation in forsterite: Importance of the entropic effect

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ABSTRACT

In this ab initio study, we expand previous investigations of charge-balanced hydrous Mg ((2H)\textsubscript{X}) and Si ((4H)\textsubscript{X}) defects in forsterite, the Mg end-member of olivine, to address the relative stability of these two defects. First, we systematically search for (2H)\textsubscript{X} configurations to find possible defect states; second, we include the contribution of vibrational energy and defect configurational entropy in the calculation of formation energies of both defects; third, we address the effect of pressure and temperature simultaneously on their relative stability. Based on these considerations, we demonstrate that hydrous Mg defects ((2H)\textsubscript{X}) can be stabilized with respect to hydrous Si defects ((4H)\textsubscript{X}) at relevant mantle conditions and that configurational entropy and vibrational free energy play key roles in this stabilization. Our results reveal that water speciation in olivine is influenced by temperature and pressure. As mantle physical and chemical properties may be affected by the speciation of water in olivine, application of experimental results to the mantle should account for the temperature- and pressure-dependent changes in water speciation.

Keywords: Hydrous defects, olivine, nominally anhydrous minerals, ab initio calculations, thermodynamics; Water in Nominally Hydrous and Anhydrous Minerals

INTRODUCTION

A feature unique to our planet is that over 70% of its surface is covered by liquid water, which is an essential factor of its habitability. Over the decades, it has become evident that water is not only present at Earth’s surface, but is also stored in large quantities in its interior (Martin and Donnay 1972; Bell and Rossman 1992; Smyth 1994; Kohlstedt et al. 1996; Bolfan-Casanova 2005). Recently, a ringwoodite inclusion in diamond revealed that the mantle transition zone is at least locally “wet” with near 1 wt% H\textsubscript{2}O (Pearson et al. 2014). Plate tectonics is responsible for the deep-Earth water cycle, carrying hydrous minerals and water-bearing sediments into the mantle via subduction. Water then returns to the surface by magmatic degassing beneath mid-ocean ridges and oceanic islands (Peacock 1990; Ohtani 2005). Most of the water in Earth’s surface today might come from the degassing of the Earth’s mantle through volcanism shortly after the Earth formed (Rubey 1951).

Water is transported into the mantle during subduction chiefly as hydroxyl groups in hydrous silicate minerals (Peacock 1990; Ohtani 2005; van Keken et al. 2011; Nishi et al. 2014). As most hydrous minerals are not stable along the normal mantle geotherm, water delivered to the convecting mantle is believed to be stored chiefly as hydrous defects (hydroxyl point defects) in minerals that do not contain hydrogen in their stoichiometric formulas. These so-called nominally anhydrous minerals (NAMs) include olivine, pyroxene, and garnet (Bell and Rossman 1992). Though present in modest concentrations, these defects dramatically influence the physical and chemical properties of their hosts, including the electrical conductivity (Karato 1990; Wang et al. 2006; Yoshino and Katsura 2013) and viscosity (Carter and Ave’lalamment 1970; Chopra and Paterson 1984; Karato et al. 1986; Mei and Kohlstedt 2000a, 2000b), the latter having a strong effect on mantle processes such as convection. Water also decreases the solidus temperature of mantle rocks and, consequently, the extent and composition of partial melting (Kushiro 1972; Green 1973; Hirose 1997).

To understand the influence of water on mantle properties, the mechanisms of water incorporation in olivine, the most voluminous mineral in the upper mantle, must be clarified. In the past few decades, this problem has been addressed by various methods, for example, IR spectroscopy (Bai and Kohlstedt 1992, 1993; Matveev et al. 2001; Lemaire et al. 2004; Berry et al. 2005; Smyth et al. 2006; Kudoh et al. 2006; Hushur et al. 2009; Kovács et al. 2010; Otsuka and Karato 2011; Ingrin et al. 2013; Balan et al. 2014; Tollan et al. 2017; Blanchard et al. 2017), Raman spectroscopy (Bolfan-Casanova et al. 2014), NMR spectroscopy (Kohn 1996; Xue et al. 2017), and theoretical calculations (Wright and Catlow 1994; Brodholt 1997; Haiber et al. 1997; Braithwaite et al. 2002, 2003, Walker et al. 2006, 2007; Umemoto et al. 2011). Several water incorporation mechanisms in olivine have been proposed. Among them, the most likely ones are the formation of hydroxyl groups (OH\textsuperscript{−}) associated...