Effect of iron and trivalent cations on OH defects in olivine

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ABSTRACT

Hydrogen incorporation in olivine involves many OH defects, which will control the hydrogen solubility at mantle conditions. Several of these OH defects are identified from the investigation of forsterite (the olivine Mg end-member). We study here the effect of Fe2+, Fe3+, Al3+, and Cr3+ on OH defects to improve our understanding of the hydrogen speciation in natural olivine. Low-temperature infrared spectra (~194 °C) are collected on synthetic and natural olivines. These spectra are then interpreted in the light of the theoretical determination of the structural, vibrational, and infrared spectroscopic properties of Fe-related OH defects, using first-principles calculations based on density functional theory. The presence of Fe2+ changes the cationic environment around the fully protonated vacancies in forsterite, leading to a slight modification of their infrared signatures. In particular, the presence of Fe2+ in an octahedral site adjacent to a hydrogarnet-type defect is likely responsible for the additional bands observed at 3599 cm–1 and around 3520–3550 cm–1 in Fe-doped olivines. Results show that the OH bands between 3310 and 3380 cm–1 are associated with the presence of trivalent cations. Specifically, two bands at 3323 and 3358 cm–1, commonly observed in natural olivine, are associated with the substitution of Mg2+ by Cr3+ while two similar bands at 3328 and 3353 cm–1 are associated with the substitution of Mg2+ by Fe3+. The presence of these defects and the “titancinohumite” defect in natural olivine clearly underlines the prominent role of trace elements on the hydrogen incorporation in lithospheric olivine.

Keywords: Olivine, OH defect, iron, chromium, aluminum, IR spectroscopy, ab initio calculations, DFT

INTRODUCTION

The estimate of the amount of hydrogen stored in the olivine of the lithospheric and asthenospheric mantle (i.e., down to 410 km deep) is a key issue for understanding the internal cycle of this element. Attempts to constrain the hydrogen concentration in olivine from experimental solubility measurements may have been so far insufficient to accurately address this question (e.g., Bai and Kohlstedt 1992; Kohlstedt et al. 1996; Lemaire et al. 2004; Zhao et al. 2004; Smyth et al. 2006; Grant et al. 2007a; Litasov et al. 2007, 2009; Withers and Hirschmann 2008; Bali et al. 2008; Otsuka and Karato 2011; Withers et al. 2011; Férot and Bolfan-Casanova 2012; Kovács et al. 2012; Gaetani et al. 2014; Demouchy and Bolfan-Casanova 2016). The main reason for this possible inaccuracy lies in the fact that the incorporation of hydrogen into olivine is controlled by many mechanisms that are not clearly identified in most experimental studies. The evaluation and efficiency of different experimental approaches are strongly dependent on the correct identification of OH defects. Without this knowledge, the risk of mixing the respective contributions of various defects and incorporation reactions that control their solubility is high. This identification is essential to ensure that the incorporation mechanisms reproduced in the laboratory are the same as those observed in natural samples, and thus to determine the dominant incorporation mechanisms (e.g., Mosenfelder et al. 2006; Gaetani et al. 2014).

Early solubility models in olivine were based on the assumption that the solubility is controlled by a single defect composed of two protons in an octahedral Mg vacancy (e.g., Kohlstedt et al. 1996; Zhao et al. 2004; Mosenfelder et al. 2006; Bali et al. 2008). Increasing pieces of evidence indicate that this defect is, in fact, a minority point defect. As evidenced by experiments performed under varying silica activities the protonation of Mg vacancies leads to broad infrared absorption bands in the range 3150–3250 cm–1, while the protonation of Si vacancies produces narrow infrared bands above 3480 cm–1 (e.g., Lemaire et al. 2004; Berry et al. 2005; Kovács et al. 2010). Bond valence method (Donnay and Allmann 1970; Brown and Altermatt 1985) provides a simple explanation for this observation. In olivine, each O atom forms interatomic bonds with one Si4+ atom and three Mg2+ atoms, compensating for 1 and ⅓ valence units (v.u.), respectively. In octahedral Mg2+...