Effect of iron and trivalent cations on OH-defects in olivine

MARC BLANCHARD[1], JANNICK INGRIN[2], ETIENNE BALAN[1], ISTVÁN KOVÁCS[3], ANTHONY C. WITHERS[4]

[1] Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7590, Muséum National d'Histoire Naturelle, UMR IRD 206, 4 place Jussieu, F-75005 Paris, France

[2] UMET, UMR CNRS 8207, Université de Lille1, Bât. C6, 59655 Villeneuve d'Ascq, France

[3] Geological and Geophysical Institute of Hungary, Budapest, Stefánia street 14, H-1143, Hungary

[4] Department of Earth Sciences, University of Western Ontario, London, ON, Canada N6A 5B7

Hydrogen incorporation in olivine involves many OH-defects that will control the hydrogen solubility in mantle conditions. Several of these OH-defects are clearly identified essentially from the investigation of the olivine Mg end-member. We study here the effect of Fe^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} on OH-defects in order to improve our understanding of the hydrogen speciation in natural olivine. Low-temperature infrared spectra are collected on synthetic and natural olivines, and are interpreted in 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 Fe^{2+} changes the cationic environment around the fully protonated vacancies in pure forsterite, leading to a slight modification of their infrared signatures. In particular, the presence of Fe^{2+} in an octahedral site neighbor of the 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 clearly 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 Mg^{2+} by Cr^{3+} while two similar bands at 3328 and 3353 cm^{-1} are associated with the substitution of Mg^{2+} by Fe^{3+}. The presence of this defect and the "titanoclinohumite" defect in natural olivine clearly underlines the prominent role of trace elements on the hydrogen incorporation in the lithospheric olivine.