Quantitative analysis of H-species in anisotropic minerals by unpolarized infrared spectroscopy: An experimental evaluation

YANGYANG QIU1, HAOTIAN JIANG1, ISTVÁN KOVÁCS2, QUN-KE XIA3, AND XIAOZHI YANG1,*,††

1State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China
2Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1112 Budapest, Hungary
3Institute of Geology and Geophysics, School of Earth Sciences, Zhejiang University, Hangzhou 310027, PR China

ABSTRACT

Attempts have been made to use unpolarized infrared analyses on unoriented anisotropic crystals of nominally anhydrous minerals to determine H contents, rather than using the more demanding polarized techniques that are more accurate (given that a reliable calibration is available). In this context, different approaches have been either empirically or theoretically proposed for the quantification; however, the involved accuracy has not been systematically documented by experimental work of both polarized and unpolarized analyses. In this study, we present a careful evaluation of experimentally grown, gem-quality OH-bearing olivine, clinopyroxene, and orthopyroxene single crystals. The samples were prepared for polarized and unpolarized infrared analyses, and the obtained spectra were used to estimate the H2O contents. We show that, regardless of the applied protocol, a single unpolarized determination is inadequate for quantitative analysis and the uncertainty could be up to ~80%. The unpolarized method of Paterson (1982), by considering the linear absorbance intensity either through a single analysis or by averaging the data from multi-grain analyses, commonly underestimates the H2O content, by a factor of up to ~6. The other unpolarized calibration method by using the averages of integrated absorbances of unoriented grains is in general of good accuracy, mostly within ±25% even for analyses on 2 grains (with perpendicular indicatrix sections), and the accuracy is even better if as many as 10 gains of random orientations are involved, e.g., within ±10%. Therefore, the latter method may be safely applied to quantify H in anisotropic minerals if a reasonable number of randomly oriented grains are chosen for the analyses. However, the uncertainty is non-systematic, and both underestimates and overestimates of H are possible depending upon orientation. These results provide a basis for quantifying H-species in anisotropic minerals and for documenting the quantitative effect of H on the physical properties of the host phases.

Keywords: OH groups, quantitative analysis, unpolarized spectroscopy, infrared spectroscopy, nominally anhydrous minerals; Water in Nominally Hydrous and Anhydrous Minerals

INTRODUCTION

The importance of water for the origin and evolution of life on Earth and even the Earth itself makes it an intriguing topic in Earth science. Water in the Earth is rarely present as H2O molecules (e.g., as seen in the oceans), but is most abundant in the form of hydrogen (H) incorporated in the lattice of various minerals of the planet’s interior. In the past decades, H in nominally anhydrous minerals, the dominant constituents of the crust and mantle, has received increasing interest due to the widespread recognition of the disproportionate importance of even trace amounts of H in governing Earth’s geochemical evolution, geophysical properties, and geodynamics (Keppler and Smyth 2006; Yang et al. 2014a; Demouchy and Bolfan-Casanova 2016; Peslier et al. 2017; Xia et al. 2017). In particular, partial melting, element partitioning, ionic diffusion, mechanical strength, and electrical conductivity could be affected by small amounts of H in the host minerals (e.g., Inoue 1994; Righter and Drake 1999; Mei and Kohlstedt 2000; Regenauer-Lieb et al. 2001; Hier-Majumder et al. 2005; Huang et al. 2005; Green et al. 2010; Kovács et al. 2012; Yang et al. 2011, 2012; Yang 2012a, 2012b). The effect of H on these aspects, as well as the partitioning, distribution, and storage of water inside the Earth is closely linked to its amount and speciation types of which the latter is related to the incorporation mechanism. Hydrogen is structurally present in several forms such as OH groups, molecular H2O, and molecular H2 (Keppler and Smyth 2006; Yang et al. 2016), and OH groups in nominally anhydrous minerals have attracted particular interest, because the formation involves modification of silicate matrix of the host structure (e.g., by breaking strong Si-O bond and/or creating vacancies). Therefore, the key in many cases is to determine the concentration and species of H accurately.

Fourier-transform infrared (FTIR) spectroscopy is a very powerful technique, and it remains the most widely applied method, for probing H in nominally anhydrous minerals because of its extreme sensitivity to H, inexpensive costs, and non-destructive analyses. Also, it can be easily carried out in situ on very small sample domains and distinguishes readily different types of H-species such as OH groups, inclusion H2O, molecular H2, and organic hydrogen. Moreover, information on the orientations of H in the host structure and on the lengths of...