Site-specific infrared O-H absorption coefficients for water substitution into olivine

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ABSTRACT

There are four ways by which OH− commonly substitutes into olivine, namely those associated with (1) Si vacancies, (2) Mg vacancies, (3) Ti, or (4) trivalent cations. The four mechanisms, which we label [Si], [Mg], [Ti], and [triv], respectively, may each be fingerprinted by their characteristic O-H stretching modes in the infrared spectrum. We show by comparing the integrated intensities of these characteristic infrared peaks against total water content analyzed by secondary ion mass spectrometry, obtained for a suite of synthetic olivines plus one natural olivine, that the different substitution mechanisms require different absorption coefficients (k). For [Ti], we find k = 0.18 ± 0.07, identical to the value previously obtained from natural olivines in which the water was mainly associated with [Ti] defects. Values of k for [Si] and [triv] are 0.57 ± 0.04 and 0.18 ± 0.05, respectively; that for [Mg] is too small to be accurately determined (0.03 ± 0.03). The values of k for [Ti] and [Si] defects differ by a factor of three even though their average wavenumbers are virtually the same. The [Ti] and [triv] defects, on the other hand, have very similar absorption coefficients at significantly different wavenumbers. This highlights the inadequacy of using wavenumber-dependent calibrations for olivine and presumably for NAMs in general. Different substitution mechanisms have their own crystallographic environments that determine their absorption coefficients. The large variation in absorption coefficients within a single mineral emphasizes the importance of distinguishing the substitution mechanism if meaningful quantitative results are to be obtained from infrared spectroscopy.

Keywords: Nominally anhydrous minerals, olivine, infrared spectroscopy, secondary ion mass spectrometry, extinction coefficients

INTRODUCTION

The variety and complexity of the infrared spectra of olivine associated with O-H stretching modes attest to the great number of ways by which hydroxyl (OH−, colloquially called “water”) can reside in this nominally anhydrous mineral (e.g., Beran and Putnis 1983; Miller et al. 1987; Libowitzky and Beran 1995; Matsuk and Langer 2004). However, four substitution mechanisms, each identified from their characteristic bands in the infrared absorption spectrum, stand out as being commonly observed in natural mantle-derived olivine and in synthetic forsteritic olivine synthesized at mantle temperatures and pressures. These substitution mechanisms are associated with Si vacancies, Mg vacancies, octahedral Ti, and trivalent cations, which hereafter we label as [Si], [Mg], [Ti], and [triv]. The Kröger-Vink notation for these defects is: [Si] = (4H)X0, [Mg] = (2H)X0, [Ti] = (TiX+)Y0, (2H)X0, and [triv] = {[(Me3+)X0(H)Y0], respectively. Potentially, deconvoluting the infrared spectrum into the integrated absorption bands for each mechanism could yield the amounts of water substituting by that mechanism, but to obtain this information requires that the absorption coefficient for each mechanism be known. By contrast, methods of analysis as such secondary ion mass spectrometry (SIMS) give total water content, irrespective of the substitution mechanism, and thus provide no information on how the water is incorporated. For olivine and probably other nominally anhydrous minerals (NAMs), such information is needed to assess at what stage of the mineral’s history the water was acquired—for example, whether the water was present at the time of the original crystallization of the host rock, or was added subsequently by hydrothermal activity. Here we obtain infrared absorption coefficients specific to each substitution mechanism by determining total water by SIMS and relating this to the infrared spectra of olivine specimens containing the four major types of OH-related defects in different proportions.

The four major substitution mechanisms for water in olivine have the following characteristics:

(1) [Si]. Four H atoms charge-balance a Si vacancy in a tetrahedral site by being bound to O atoms at the apices of the tetrahedron, producing the stoichiometry MgH2O (Lemaire et al. 2004; Walker et al. 2007). This mechanism produces O-H absorption peaks between 3630 and 3400 cm−1, the most prominent of which are at 3613, 3580, 3567, and 3480 cm−1. The identification of these absorption peaks as related to Si vacancies follows their appearance in olivine from a silica-deficient environment and is supported by ab initio calculations (Walker et al. 2007). On the other hand, Kudoh et al. (2006) and Smyth et al. (2006) attributed the same set of IR peaks to Mg vacancies,

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