An IR absorption calibration for water in minerals

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ABSTRACT

Using IR absorption data from polarized measurements on single-crystal minerals with stoichiometric water contents (in the form of H₂O or OH groups in the structure), a linear calibration curve ($r^2 \approx 0.98$) for water in minerals is established in the form: $\epsilon_i$ (the integrated molar absorption coefficient in units of cm⁻² per mol H₂O/L) = 246.6(3753 – $\nu$) ($\nu$ = the mean wavenumber of the OH stretching band [in cm⁻¹]). The investigated minerals include hydrogrossular, analcime, hemimorphite and its dehydrated phase, lawsonite, goethite, diaspore, manganese, mozaïrite, and pectolite. The influence of hydrogen bonding, leading to increased absorption values with lower OH stretching band energies, is confirmed. It is further shown that only the use of integrated absorbance values (band areas) results in a linear correlation with water content, whereas linear absorption data (peak heights) are not correlated. The calibration agrees with previously published quantitative IR data on staurolite and trace H in pyroxenes. It is also close to the frequently used trend of Paterson (1982). However, some of the previous calibrations of trace H in nominally anhydrous minerals, e.g., kyanite and pyrope, differ appreciably from the correlation derived from stoichiometrically hydrous minerals.

INTRODUCTION

Spectroscopic methods have been widely used in the quantitative analysis of materials. IR spectroscopy provides a sensitive tool for the detection of minor and trace amounts of H (in the form of H₂O molecules or hydroxyl groups) in minerals, glasses, and melts (Rossman 1988). However, insufficiently accurate calibration data restricted the use of the method in the field of earth sciences to semi-quantitative applications. Calibrations for H₂O contents in minerals are difficult for two reasons: (1) Minor and trace amounts of H₂O are not easily determined by other analytical methods. In addition, H₂O bound to mineral surfaces and inclusions frequently leads to inaccurate values. (2) Even though hydrous minerals contain large quantities of H₂O, which are easily analyzed by other methods, IR absorption bands are commonly so intense, that samples must be polished extremely thin (in some cases down to 2 μm), which is a difficult or even impossible task. Finally, the optically anisotropic character of most minerals requires special experimental conditions for quantitative IR spectroscopy (including the use of polarized light and single crystals) as outlined by Libowitzky and Rossman (1996a).

Nevertheless, several calibrations have now been established. One of the more frequently used in mineral spectroscopy is the trend of Paterson (1982). This calibration is based upon data on different glasses and quartz. Even though in many cases this trend proved inaccurate for precise measurements of water in minerals, the approximate relation between decreasing wavenumber and increasing integrated molar absorption coefficient was established. Newman et al. (1986) proposed a calibration of IR absorption bands for the determination of H₂O and OH in rhyolitic glasses. Whereas the former was based on integrated intensities (i.e., band areas), the latter employed linear intensities (peak heights). Problems occurred in the case of complicated bands (showing shoulders or overlapping peaks) where the use of linear intensities caused difficulties (S. Newman, personal communication). Because a unique calibration for all minerals seemed not to be feasible, different calibrations and molar absorption coefficients for single minerals or mineral groups were determined, e.g., micas (Rouxhet 1970), grossular-hydrogrossular (Rossman and Aines 1991), kyanite (Beran and Götzinger 1987), amphiboles (Skogby and Rossman 1991), pyrope, clino-, and orthopyroxene (Bell et al. 1995), titanite (Hammer et al. 1996). However, even in different members of a single mineral group (e.g., garnets), different molar absorption coefficients were encountered.

Unlike previous investigations, this paper presents a calibration exclusively based on stoichiometric, hydrous silicate, and oxide minerals that extends over a wide energy range of OH stretching fundamentals and that appears applicable to the analysis of minor and trace amounts of hydrous species in minerals.

EXPERIMENTAL METHODS

Spectra were acquired with a Nicolet 60SX FTIR spectrometer. According to the principles for measurement of