

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: ϵ_i (the integrated molar absorption coefficient in units of cm⁻² per mol H₂O/L) = 246.6(3753 - ν) (ν = 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, manganite, mozartite, 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 μ m), 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 Göttinger 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

anisotropic crystals (Libowitzky and Rossman 1996a) and the investigated wavenumber region, the instrumental parameters were varied between tungsten or global light source, CaF₂ or KBr beam-splitters, LiIO₃ crystal polarizer (extinction ratio > 10⁴:1) or AgBr gold-wire grid polarizer (extinction ratio > 10²:1), MCT, InSb, or DTGA detector, resolution 2 or 4 cm⁻¹. In some cases, where only crystal fragments smaller than 100 μm were retained, a Nic-Plan FTIR microscope with a 15×/0.58 N.A. Cassegrain objective was used. Isotropic samples were measured in unpolarized light.

The preparation of extremely thin, oriented single-crystal samples was described in Libowitzky and Rossman (1996b) and Nyfeler et al. (1997). In all cases the deviation of the prepared slabs from the principal directions was considered to be less than ± 5°. The sample thickness (*t*), which ranged from 2 to 23 μm, was determined by different methods. Thicker slabs were measured on multiple spots with a Mitutoyo electronic micrometer. All slabs were measured under an optical microscope with slab orientation parallel to the stage, measuring the thickness with the micrometer in the focus mechanism through the sample with compensation for the refractive index and directly between sample surface and carrier; optical measurements were also made with slab orientation perpendicular to the stage, using the eyepiece reticule and a stage micrometer scale for calibration. In addition, weak absorption bands of thick samples (whose thickness can be easily and accurately measured) were compared with those of thin samples to confirm the thickness of the latter. However, because of limitations in the various techniques, errors up to 20% may be present in the thinnest samples.

Band intensities (either peak heights, *A*, or areas, *A_i*) were easily obtained, because the background could be treated as a flat line in most cases (which is different from the more difficult situation of trace H in minerals, e.g., Bell et al. 1995). The integrated intensities and mean band energies were obtained from peak fitting using the PeakFit program (Jandel Scientific). In cases of more than one peak, the area-weighted average of the peak positions was used. Even though the weighted mean wavenumber has no physical meaning (in contrast to the energies of the single bands that are related to the hydrogen bond strengths, coordination effects, and so forth), it proved appropriate for the present purpose of calibration. An example of background selection, measured peak area, and calculated weighted mean band energy is shown for analcime in Figure 1. The high energies of the observed bands are in good agreement with the very weak hydrogen bonds of the H₂O molecules in the wide cages of the analcime structure (Ferraris et al. 1972). However, minerals with strong hydrogen bonds, e.g., mozarite (Nyfeler et al. 1997) and pectolite (Hammer et al. 1998), provide additional difficulties. Because of the very broad OH stretching band at low energies, the accuracy of the peak position is limited to ± 200 cm⁻¹. In addition, superposition of this broad band with other lattice fundamentals

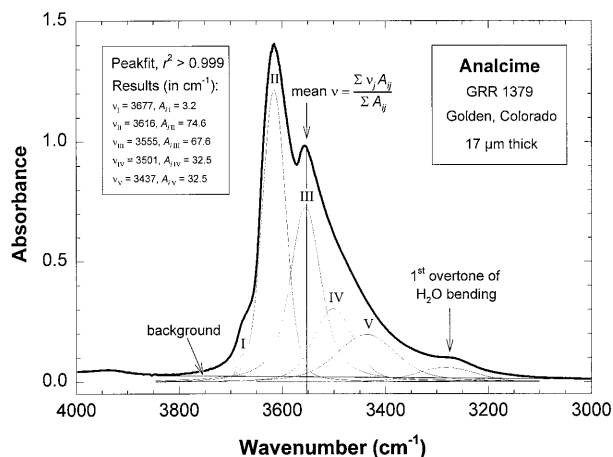


FIGURE 1. The infrared absorption spectrum of a 17 μm thick analcime slab showing the stretching vibrations of the H₂O molecules. In addition to the background line and the weighted mean wavenumber, the component bands from peak-fitting are indicated by thin lines.

or overtones introduces an uncertainty of ± 10% in the intensity measurements.

The H₂O concentrations (*c*) and densities (*D*) of the minerals were computed from their formulae or obtained from Klein and Hurlbut (1993). In the case of hydrogrossular the data from Rossman and Aines (1991) were used. The basic relationship between IR intensity and concentration is given by the Beer-Lambert law, $A_i = c \cdot t \cdot \epsilon_i$, where ϵ_i is the (integrated) molar absorption coefficient, which is the important constant for calibration. The unit is "L/(mol·cm)" for the linear, and "L/(mol·cm²)" for the integrated case. However, great care must be taken with respect to the "mol" in the unit. In some cases [e.g., Paterson (1982), Skogby and Rossman (1991), Rossman and Aines (1991)] ϵ_i was expressed in "cm⁻² per mol H (or OH)/L", in other cases [e.g., Beran et al. (1993) and Bell et al. (1995)] the unit "cm⁻² per mol H₂O/L" was employed. For obvious reasons, the latter, which is also used throughout the present paper, provides molar absorption coefficients twice as large as the former. When H concentrations are expressed as their H₂O equivalent, the water concentration is given by: c (wt% H₂O) = A_i (cm⁻¹) · 1.8/[*t* (cm) · *D* (g/cm³) · ϵ_i (cm⁻² per mol H₂O/L)].

Furthermore, it is important to use total intensities, i.e., the sum of absorbances in all three orthogonal polarization directions of a crystal, (Libowitzky and Rossman 1996a). As a consequence, ϵ_i values for garnets in this paper are three times as large as those published in Rossman and Aines (1991) and Bell et al. (1995) where only one direction was used.

RESULTS AND DISCUSSION

A summary of quantitative IR results on the ten hydrous minerals used is given in Table 1. The first correlation plot of integrated intensity (normalized per centi-

TABLE 1. Quantitative data for the IR calibration of the water content in hydrous minerals

| Mineral | H ₂ O (wt%) | D (g/cm ³) | Mean ν (cm ⁻¹) | ϵ (l/mol-cm) | ϵ_i (l/mol-cm ²) | A/t (cm ⁻¹) | A _i /t (cm ⁻²) |
|------------------|------------------------|------------------------|--------------------------------|-----------------------|---------------------------------------|-------------------------|---------------------------------------|
| Pectolite* | 2.70 | 2.80 | 1000 | 540 | 730 000 | 2270 | 3 083 000 |
| Mozartite† | 4.40 | 3.65 | 1500 | 308 | 486 000 | 2750 | 4 333 000 |
| Manganite‡,§ | 10.25 | 4.30 | 2650 | 412 | 244 000 | 10 100 | 5 975 000 |
| Diaspore‡,§ | 15.00 | 3.40 | 2950 | 606 | 249 000 | 17 170 | 7 058 000 |
| Goethite§ | 10.10 | 4.35 | 3100 | 604 | 174 000 | 14 750 | 4 253 000 |
| Lawsonite | 11.50 | 3.10 | 3300 | 510 | 110 000 | 10 080 | 2 183 000 |
| Hemimorphite# | 7.50 | 3.45 | 3490 | 300 | 66 000 | 4310 | 954 000 |
| Dehyd. Hemi.** | ~3.25 | ~3.45 | 3560 | 1124 | 50 000 | 7000 | 309 000 |
| Analcime†† | 8.15 | 2.25 | 3552 | 240 | 36 000 | 2450 | 371 000 |
| Hydrogrossular‡‡ | 12.20 | 3.15 | 3635 | 210 | 22 000 | 4490 | 468 000 |

* Hammer et al. (1998). # Libowitzky and Rossman (1997).
† Nyfeler et al. (1997). ** Libowitzky et al. (1997).
‡ Kohler et al. (1997). †† This paper.
§ Libowitzky (1996). ‡‡ Rossman and Aines (1991)—mean of samples 1329 and 1358.
|| Libowitzky and Rossman (1996b).

meter of thickness) vs. H₂O concentration is presented in Figure 2. Even though this type of plot gives a good calibration line in single-mineral systems, e.g., grossular-hydrogrossular (Rossman and Aines 1991), Figure 2 shows almost random scattering. This behavior primarily results from different strong hydrogen bonds in different minerals that have different sensitivities to IR radiation (expressed by varying ϵ values). A minor reason for the scatter in Figure 2 is also found in different mineral densities.

Figure 3 shows the correlation between ϵ_i and the wavenumber of the OH stretching bands. Using moles of H₂O per liter instead of weight percent, this plot is independent of mineral densities. The ten data points on the plot can be fitted with a regression coefficient $r^2 \approx 0.98$, giving the function ϵ_i (cm⁻² per mol H₂O/L) = 246.6[3753 - ν (cm⁻¹)], where ν is the mean wavenumber of the stretching band. The correlation confirms the increase of the molar absorption coefficient with decreasing band energy, which was also expressed by the trend of Paterson (1982). However, in comparison with Pater-

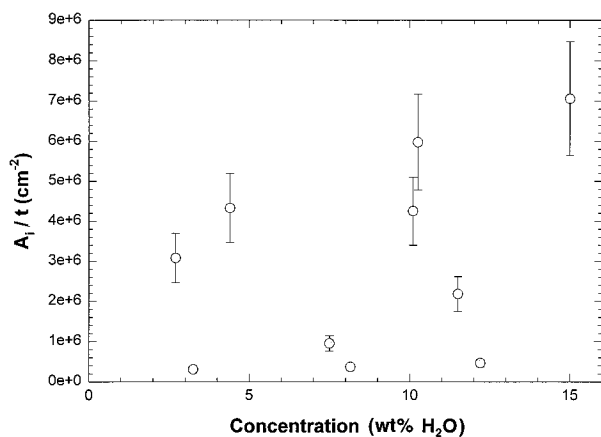


FIGURE 2. Integrated intensity (A_i) of the OH stretching fundamentals (normalized to 1 cm sample thickness) vs. water concentration in weight percent of H₂O.

son's line, the slope of the present regression line is smaller. (Note that Paterson (1982) used "cm⁻² per mol H/L" instead of "cm⁻² per mol H₂O/L".) Nevertheless, the origin of both curves between 3750 and 3800 cm⁻¹ is similar. The present calibration line also shows that the ϵ_i vs. wavenumber relation is valid over a wide range of OH stretching fundamentals, thus covering all hydrogen bond lengths from O-H...O > 3.4 to 2.45 Å. Diagrams that express the correlation between H bond lengths and OH stretching energies were published by several authors, e.g., Nakamoto et al. (1955), Novak (1974), and Mikenda (1986).

Comparing of the present calibration line (Fig. 3) with previous IR studies of hydrous minerals (if they also obeyed the conditions for quantitative measurement), good agreement is obtained with the values on staurolite

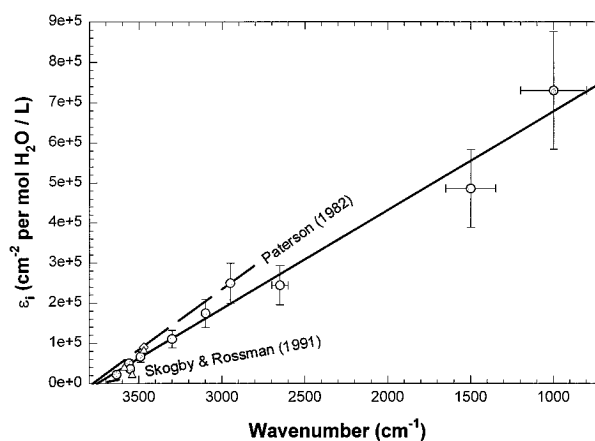


FIGURE 3. Correlation of the integrated molar absorption coefficient (ϵ_i) of OH stretching bands vs. wavenumber. Shaded circles mark the ten hydrous minerals used to establish the correlation. The trends of Paterson (1982) and Skogby and Rossman (1991), the short line between 3700 and 3600 cm⁻¹, are also shown for comparison. Open symbols represent other data from literature: diamond = staurolite (Koch-Müller et al. 1995); triangles (with increasing ϵ_i) = pyrope, clinopyroxene, and orthopyroxene (Bell et al. 1995).

(Koch-Müller et al. 1995). The calibration line on amphiboles (Skogby and Rossman 1991) is also introduced in Figure 3. Because the latter authors presented their data on the basis of concentrations expressed as OH, their values were completely redetermined from the original IR data. Their trend shows lower values than the present correlation line, and the slope is shallow in comparison with that of the present paper (Fig. 3). This is, however, in good agreement with the experience that IR band intensities in amphiboles can usually be directly related (without correcting for different band energies) to site occupancies (Della Ventura et al. 1996). Thus it seems that the variations of OH band energies in amphiboles depend more on cation coordination effects than on hydrogen bond lengths and strengths. Moreover, these cation effects can be considered a source of inaccuracy in all data points of the plot.

The present calibration was obtained from stoichiometric hydrous minerals. The question remains, whether this trend applies to the determination of water in nominally anhydrous minerals. Bell et al. (1995) accurately determined molar absorption coefficients for pyrope garnet, clino-, and orthopyroxene. Whereas the pyroxenes (which also contained the highest trace amounts of water) are close to the calibration line (Fig. 3), the garnet is off by a factor of three. One possibility is that the water content of only 55 ppm in this garnet was determined inaccurately, but recent studies using nuclear reaction analysis confirmed the previous results (Endisch et al., in preparation). Another possibility might be that the trace quantities of H atoms are not exclusively present as hydrous species (but for example as molecular H_2) or that they are involved in strongly hydrogen bonded units (causing a flat, broad, low-energy band) and thus were invisible in the IR spectra of that investigation. More likely, the spectroscopic properties of H in low-concentration point defects may differ from those of stoichiometric components in hydrous minerals. The misfit of the kyanite data (Beran and Göttinger 1987) is probably caused by inaccurate water determinations on inclusion-bearing samples (A. Beran, personal communication).

Most of the stretching vibrations of trace OH in minerals are observed in the high-energy region between 3700 and 3200 cm^{-1} . As can be seen from Figure 3, this high-energy end of the regression line ($> 3500 cm^{-1}$), which shows the lowest ϵ_i values, is also the most sensitive part of the calibration, i.e., small absolute deviations from the line cause strong relative deviations. From the present data the question remains open, whether the calibration continues as a straight line towards 3753 cm^{-1} (Fig. 3) or if it bends slightly down to a somewhat lower value (as is suggested by the highest-energy data point of the present data and by the values recalculated from Skogby and Rossman 1991).

Finally, we must emphasize that only integrated intensities can be used for general calibration purposes. Figure 4, which is similar to Figure 3, uses ϵ values that were extracted from linear intensities (note the different unit).

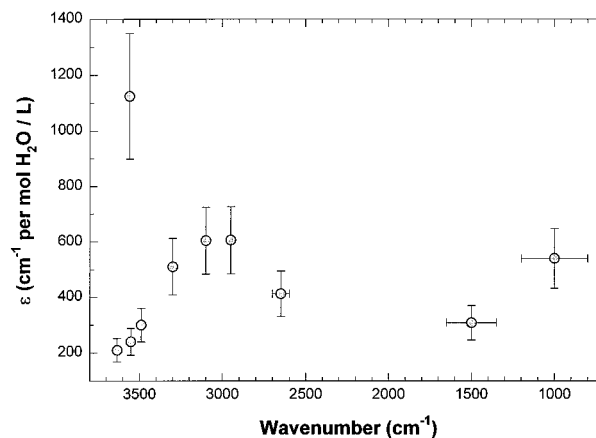


FIGURE 4. Linear molar absorption coefficient (ϵ) of OH stretching vibrations vs. wavenumber showing a generally poor correlation.

It is evident that the scattering in Figure 4 does not give a useful correlation. This behavior is also reasonable from theoretical considerations. Whereas integrated intensities contain all bands, independent of whether they are separated or overlapping, peak heights can only be obtained on well-resolved bands. Linear intensities also may be strongly temperature dependent, whereas integrated intensities commonly have little temperature dependence. However, among similar systems, which always show well resolved, comparable bands, linear intensities can be used (Libowitzky and Rossman 1996a).

The present calibration for water in minerals seems applicable to a wide spectrum of oxide and silicate minerals. According to the analytical limitations mentioned above, the regression is reliable to 10–20%. Nevertheless, differences beyond these limits were encountered in pyrope garnet (Bell et al. 1995, see above). Because large groups of hydrous minerals like acid phosphates, arsenates, sulfates, and so forth were not investigated, a recommendation for these minerals cannot be given. Additional work is necessary to further refine the calibration line and to test its applicability to other mineral groups. Nevertheless, different structures do not seem to cause randomly different molar absorption coefficients. Rather, the different structures drive the hydrogen bonding, and because most of the O-H vibration is in the proton motion, the hydrogen bond strength (correlated with the wavenumber of the band) determines the molar absorption coefficient instead of the remaining structure.

Finally, we note that prior quantitative work based upon the trend of Paterson (1982) is largely confirmed, but only in those cases where the proper experimental conditions defined by Libowitzky and Rossman (1996a) were used.

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