

## Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum

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[1] Olivine is an important host of hydrogen in the Earth's upper mantle, and the OH abundance in this mineral determines many important physical properties of the planet's interior. To date, natural and experimentally hydrated olivines have been analyzed by uncalibrated spectroscopic methods with large ( $\pm 100\%$ ) uncertainties in accuracy. We determined the hydrogen contents of three natural olivines by <sup>15</sup>N nuclear reaction analysis and used the results to calibrate the common infrared (IR) spectroscopic method for quantitative hydrogen analysis of olivine. OH content (expressed as parts per million H<sub>2</sub>O by weight) is 0.188 times the total integrated absorbance of the fundamental OH stretching bands in the 3750–3100 cm<sup>-1</sup> region. The results indicate that an upward revision of some previous determinations by factors of between 2 and 4 is necessary. The most hydrous naturally occurring mantle-derived olivine analyzed to date contains 240 ppm wt. H<sub>2</sub>O. Retrospective application of this calibration to experimentally hydrated olivines may be limited by spectral differences in some cases and by the previous use of nonpolarized IR spectra. *INDEX TERMS*: 1025 Geochemistry: Composition of the mantle; 3670 Mineralogy and Petrology: Minor and trace element composition; 3934 Mineral Physics: Optical, infrared, and Raman spectroscopy; 8124 Tectonophysics: Earth's interior—composition and state (old 8105); 8162 Tectonophysics: Evolution of the Earth: Rheology—mantle; *KEYWORDS*: mantle, infrared, water, defect, hydrogen, spectroscopy

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### 1. Introduction

[2] Mineralogical models of the upper mantle based on seismic velocity measurements, on phase equilibrium experiments, and on the compositions of meteorites and mantle xenoliths indicate that Mg-rich olivine is the most abundant phase in the upper mantle and therefore of great importance in dictating the physical properties of this region. Water is believed to be a critical factor in the internal dynamics of the terrestrial planets through its effect on melting temperature, viscosity, and diffusive mass transfer in rocks. It is now recognized that hydrogen is incorporated in trace to minor amounts in most rock-forming minerals of the Earth's crust and upper mantle, including olivine, which may constitute the dominant hydrogen reservoir in depleted upper mantle material [Bell and Rossman, 1992]. The effects of small amounts of hydrogen on the

physical properties of olivine-rich rocks have been reviewed by Kohlstedt *et al.* [1996], who also examined the extent to which a hydrous component is incorporated in olivine and its high-pressure polymorphs over a pressure range corresponding to the Earth's crust, upper mantle, and transition zone [Bai and Kohlstedt, 1993; Kohlstedt *et al.*, 1996]. These papers and the studies cited therein indicate an important role for olivine in the dynamic evolution of planetary interiors.

[3] Fourier transform infrared (FTIR) spectroscopy is currently the most sensitive technique for quantifying OH in olivine and has the added advantages of providing site-specific information, detecting the presence of contaminant H, nondestructiveness, microbeam capability, and a high degree of analytical precision. However, because of the lack of an independent calibration for OH in olivine, its accuracy when applied to that mineral is in question. Previous FTIR results are typically of satisfactory precision and therefore have yielded important information on relative OH abundances in natural and experimental samples of olivine [Miller *et al.*, 1987; Mackwell and Kohlstedt, 1990; Bell and Rossman, 1992; Bai and Kohlstedt, 1992, 1993; Libowitzky and Beran, 1995; Kohlstedt *et al.*, 1996; Jamtveit *et al.*, 2001; Matveev *et al.*, 2001].

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[4] Other techniques applied to hydrogen analysis in olivine include secondary ion mass spectrometry (SIMS) [Kurosawa *et al.*, 1992, 1993, 1997; Koga *et al.*, 2003] and elastic recoil detection analysis (ERDA) [Sweeney *et al.*, 1997, 1998]. The former has been calibrated with H<sup>+</sup>-implanted olivines and yields results broadly similar to those derived from FTIR studies. ERDA-determined concentrations of hydrogen in olivines are considerably higher than those obtained by either SIMS or FTIR. A nuclear magnetic resonance (NMR) study of hydrogen in synthetic olivine [Kohn, 1996] has also yielded higher hydrogen concentrations, which Keppler and Rauch [2000] have argued is due to surface contamination. These discrepancies indicate the need for well-calibrated olivine standards.

[5] Translation of IR absorbances to quantitative estimates of OH abundance in olivine has, to date, relied on a generic calibration derived from the relationship between IR absorption intensity and wave number of O-H stretching bands of molecular water in certain compounds and water and OH groups in glasses [Paterson, 1982]. This calibration was not intended to be an accurate calibration for OH analysis in minerals (with the possible exception of water in quartz) but has been routinely used on the (often unstated) understanding that no better alternative is available. The original data show considerable scatter from the linear fit that represents the calibration, with deviations up to 150% from the best fit line.

[6] An alternative summary of the relationship between absorption frequency and molar absorptivity, based on data for OH groups in stoichiometrically hydrous minerals alone, was proposed by Libowitzky and Rossman [1997]. This curve produces values of the integrated molar absorptivity that are 20–30% lower than those obtained by the Paterson [1982] calibration, with the difference varying slightly as a function of wave number. Calibration of the molar absorptivity for different minerals containing OH with weak hydrogen bonds shows variations of up to a factor of 3 [Bell *et al.*, 1995].

[7] Another problem in previous determinations of OH in minerals has been the use of unpolarized light in absorption spectroscopy intended for quantitative purposes. Libowitzky and Rossman [1996] have illustrated some of the pitfalls of this procedure, which introduces nonsystematic errors into quantitative analysis. We reiterate here that a constant crystallographic orientation of the sample with respect to the beam axis is not a sufficient condition for reproducible quantitative analysis of optically biaxial crystals, as errors may be introduced by the efficiency of the polarizer, thickness of the sample, and nature of the absorption spectrum in the two vibration directions being sampled. In certain cases these effects may fortuitously be minor, but rigorous quantitative analysis by this method demands determination of the absorption spectrum of light polarized in all three principal vibration directions of the optical indicatrix.

[8] In order to address this problem, we analyzed the hydrogen concentration of three spectroscopically well-characterized mantle-derived olivine megacrysts by <sup>15</sup>N nuclear reaction analysis (NRA), which yields absolute hydrogen concentration values and, thus, water concentration values. We use the results to calibrate the integrated IR absorbance of the OH bands. We then compare this calibration with that of Paterson [1982] as applied to both

polarized and unpolarized olivine spectra and examine the implications for the OH contents of natural and experimentally hydrated olivines.

## 2. Analytical Methods

### 2.1. Samples

[9] The study forms part of an ongoing project to refine the quantitative analysis of trace quantities of hydrogen in minerals, in which a number of different minerals have been analyzed to date [Hammer *et al.*, 1996; Maldener *et al.*, 2001, D. Endisch *et al.*, manuscript in preparation, 2002]. The samples (Table 1) were chosen to span a range of IR absorbance and, most importantly, to provide a large (~5 × 5mm) surface that was free of any cracks or imperfections that might host contaminant hydrogen. Most mantle-derived olivine samples are cut by numerous fractures that are separated by volumes of unaltered material. The samples used here are exceptional in containing large volumes of olivine that appears homogeneous and unaltered. In some cases (notably in GRR1012-2), a slight turbidity is apparent in these regions, which may be due to submicroscopic inclusions. Sample compositions, determined by electron microprobe at Caltech, are given in Table 2.

### 2.2. <sup>15</sup>N NRA

[10] The NRA measurements were performed using the <sup>15</sup>N technique [Lanford, 1978] that is based on the nuclear reaction <sup>1</sup>H(<sup>15</sup>N,αγ)<sup>12</sup>C. They were conducted at the accelerator laboratory of the Institut für Kernphysik, Frankfurt am Main, with a <sup>15</sup>N<sup>2+</sup> beam delivered by the 7-MV Van de Graaff accelerator. The apparatus used has been specially designed for the analysis of low hydrogen concentrations in mineral samples. A detailed description of the experimental design can be found in the work of Endisch *et al.* [1994]. Salient aspects include a Pb-shielded bismuth germanate (BGO) scintillation detector with an anticoincidence counting system for reduction of cosmic ray background, with the sample holder placed in an ultra-high-vacuum chamber. Further modifications [Maldener and Rauch, 1997] that include accurate sample positioning by Rutherford backscattering and sample surface cleaning by ion sputtering have improved the ability to measure hydrogen in very low-hydrogen materials.

[11] Despite the extensive measures employed to minimize background hydrogen, a finite background or blank level may contribute to the amount of hydrogen measured. Due to the evolving methods of background reduction, the absolute background contribution to each analysis may vary somewhat. In the most recent set of procedures, analysis of anhydrous silica glass and a silicon wafer place this estimate at 2 ± 2 ppm H<sub>2</sub>O.

### 2.3. IR Spectroscopy

[12] IR spectra were determined at Caltech on a Nicolet 60SX spectrometer fitted with an air-spaced Glan-Foucault-type LiIO<sub>3</sub> prism polarizer producing linearly polarized IR radiation of high polarization purity. We used the sample preparation and spectrometric techniques for biaxial minerals described by Miller *et al.* [1987] and Bell *et al.* [1995]. For the two GRR samples, a single determination in each polarization was made. Homogeneity as well as uncertainties

**Table 1.** Sample Details and Analytical Results

Sample Number	KLV-23	GRR1012-2 <sup>a</sup>	GRR1695-2
Locality	Kaalvallei kimberlite, S. Africa	Kimberley, S. Africa	Black Rock Summit, Nevada
Color	dark brown	brownish-green, slightly turbid	brownish-green, clear
H <sub>2</sub> O (ppm by weight)	140 ± 20	220 ± 20	16 ± 5
Hydrogen/10 <sup>6</sup> Si (atomic)	2320 ± 330	3600 ± 330	270 ± 80
IR integ/cm (α + β + γ)	122 + 149 + 401 = 672 ± 15	155 + 258 + 748 = 1161	6.8 + 9.4 + 55.3 = 71.5
IR integ/cm (unpol) βγ	202	427	37

<sup>a</sup>Harvard University Mineral Museum sample 12531.

introduced by the preparation and orientation method was tested in KLV-23 by acquiring spectra on four oriented fragments. The following convention and terminology is adopted to relate the crystallographic, morphological, and optical directions: [100] = **E**||*a*, 4.76Å = γ, [010] = **E**||*b*, 10.23Å = α, [001] = **E**||*c*, 5.99Å = β where **E** is the vibration direction of the electric vector, *a*, *b*, and *c* are crystallographic axes, α, β, and γ are the principal directions of the optical indicatrix, and the values in angstroms are unit cell dimensions in the given crystallographic directions.

[13] The background correction is not well constrained and is a potential source of inaccuracy in the IR analysis of olivine. Backgrounds are commonly curved because OH fundamental stretching absorptions lie adjacent to the broad-tailed overtones of Si-O vibrations. In addition, scattering due to imperfect surface polish and imperfections within the crystal (which vary from one sample to another) may result in sloped backgrounds with an absorption proportional to  $\nu^4$ . Unsatisfactory as it may seem, operator choice of baseline is important, especially for low-OH samples. We have attempted to minimize baseline curvature before integration, by manually subtracting out the curved baseline. This has been done in two ways that give comparable results. In the first method, the spectrum outside the region of OH absorption was fit with the sum of a Gaussian band centered at a low wave number (representing the tail of Si-O overtone absorptions) and a  $\nu^4$  function (to correct for absorption due to scattering). The sum of these two curves was then subtracted from the sample spectrum, leaving the OH bands on a relatively flat baseline. A second method is to use the interactive software on the FTIR to fit a continuous smooth background over the entire range. These two methods were also checked against spectra derived by subtracting the polarized spectra of anhydrous, or very OH-poor, olivine from the sample spectra.

[14] Following subtraction of the synthetic baselines, the area under the OH peaks was integrated using a homemade computer routine. Because the baseline subtraction is imperfect, there is commonly a small degree of baseline curvature or irregularity in the residual spectrum, particularly evident for samples with low OH content. This makes setting rigid limits for integration inappropriate, and subjective judgment is required. Despite the subjectivity, the results are consis-

tent and agreement between different operators is typically within 5%. This precision of analysis with subjective choice of integration limits has in many trials proved superior to the setting of rigid arbitrary integration limits. For sample KLV-23, a maximum wave number of 3750 cm<sup>-1</sup> was chosen because this sample contains a minor absorption band at 3708 cm<sup>-1</sup> (Figure 3b) that is probably due to microscopic inclusions of a sheet silicate. This will contribute to the hydrogen analyzed by NRA.

#### 2.4. Calibration of IR Spectroscopic Analysis of OH in Olivine

[15] Our approach for determining the OH concentration from the IR spectrum in the OH region in olivine is to determine the integrated area under the OH absorption bands and to calibrate this area with the NRA results. We obtain three spectra on each sample, with incident light polarized along *a*, *b*, and *c* axes. After the appropriate baselines are subtracted, the integrated areas of the three individual absorption spectra are normalized to a unit thickness and added together to obtain a “total” integral absorbance,  $Abs_{tot}$ :

$$Abs_{tot} = 1/t_a \int_{\nu_1}^{\nu_2} Abs_a dv + 1/t_b \int_{\nu_1}^{\nu_2} Abs_b dv + 1/t_c \int_{\nu_1}^{\nu_2} Abs_c dv, \quad (1)$$

where the thicknesses of the three slices are given by  $t_a$ ,  $t_b$ , and  $t_c$  and  $Abs_a$  is the integrated absorbance in the **E**||*a* direction, etc. For the purposes of our work, the unit of thickness to which data are normalized is 1.00 cm and the region of integration is usually from 3750 to 3100 cm<sup>-1</sup> but may vary in specific cases as required by the shape of the spectrum (discussed above).

[16] The concentration of OH (expressed as moles of H<sub>2</sub>O per liter of olivine) is calculated from  $Abs_{tot}$  using the Beer-Lambert law by correlating the NRA-determined water contents with  $Abs_{tot}$  (equation (2)):

$$c_{H_2O} = Abs_{tot}/I, \quad (2)$$

where  $I$  is the integral molar absorption coefficient.

**Table 2.** Composition of Olivine Samples in wt.% Determined by Electron Microprobe<sup>a</sup>

Sample	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO	NiO	Total	Fo
GRR1695.2	0.02	48.14	0.09	40.21	n.d.	0.21	0.02	0.03	0.17	11.87	0.27	101.0	87.9
GRR1012.2	0.02	50.51	0.01	40.82	0.02	0.03	0.03	0.02	0.11	8.76	0.37	100.7	91.1
KLV-23	0.03	47.47	0.05	40.32	n.a.	0.08	0.03	0.02	0.11	12.27	0.40 <sup>b</sup>	100.8	87.3

<sup>a</sup>n.a., not analyzed; n.d., not detected.

<sup>b</sup>NiO content estimated by analogy with similar olivines from the Monastery kimberlite (Moore [1986]).

[17] In principle, this equation could be combined with the density-composition relationship,  $\rho(X_{fo})$ , for olivine to yield the following equation for determination of hydrous components in olivine:

$$c_{H_2O}(\text{in ppm H}_2\text{O by weight}) = k\rho(X_{fo})Abs_{tot}/I, \quad (3)$$

where  $X_{fo}$  is the proportion of the forsterite component and  $k$  is a calibration constant arising from the conversion of the units moles per liter to parts per million of water molecules by weight.

[18] In many practical situations (such as the limited compositional range for mantle olivines of  $FO_{80}$ - $FO_{95}$ ), the error introduced by compositional uncertainty (<5% relative) is likely to be significantly less than the combined uncertainty in  $I$  and  $Abs_{tot}$ . In this case, it may be assumed that the term  $k\rho(X_{fo})/I$  in equation (3) is a constant, yielding the following simplified expression:

$$c_{H_2O}(\text{in ppm H}_2\text{O by weight}) = \text{constant} \times Abs_{tot}. \quad (4)$$

[19] It has been recognized that the calibration constant tends to decrease with increasing wave number, so that a more rigorous expression for complex spectra spanning a range of absorption frequencies is

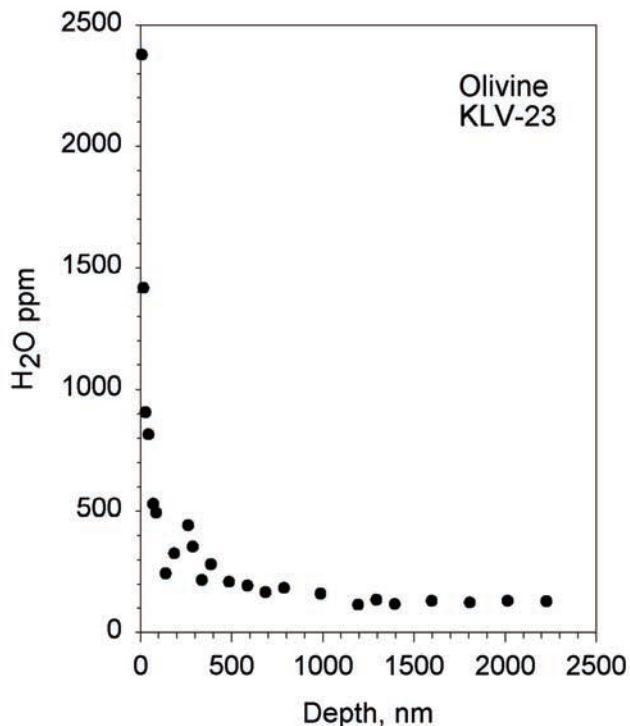
$$c_{H_2O} = 1/t_a \int_{\nu_1}^{\nu_2} [Abs_a/\epsilon(\nu)]d\nu + 1/t_b \int_{\nu_1}^{\nu_2} [Abs_b/\epsilon(\nu)]d\nu + 1/t_c \int_{\nu_1}^{\nu_2} [Abs_c/\epsilon(\nu)]d\nu. \quad (5)$$

[20] Most previous estimations of the OH content of olivines followed the method of *Paterson* [1982], which used data from hydrous materials to determine a linear functional form for  $\epsilon(\nu)$ . This approach has the advantage of applicability to very different spectra. In this study, restricted to naturally hydrous olivine, the spectra are similar and the use of either constant  $\epsilon$  or its integral equivalent,  $I$ , is justified. This is considered a more precise calibration method for quantitative analysis (as long as the spectra are similar) because it is specific to olivine. The point is illustrated in the work of *Libowitzky and Rossman* [1997] by the scatter outside analytical uncertainty about the best fit calibration lines. Thus we suggest the use of equation (4) to calculate water concentrations from IR absorbances and proceed to determine the value of the constant in that equation.

### 3. Results

#### 3.1. NRA Analysis

[21] A typical NRA profile for a relatively OH-rich olivine (KLV-23, 120 ppm  $H_2O$ ) is shown in Figure 1. High hydrogen concentrations occur at the sample surface, with counts decreasing as the comparatively hydrogen-poor interior is penetrated with higher-energy ions. The concentration profile levels off at depths of 1–2  $\mu\text{m}$  to a value that represents the intrinsic hydrogen content of the olivine. The transition region between the hydrogen-rich surface and the OH-poor interior varies between samples and is probably



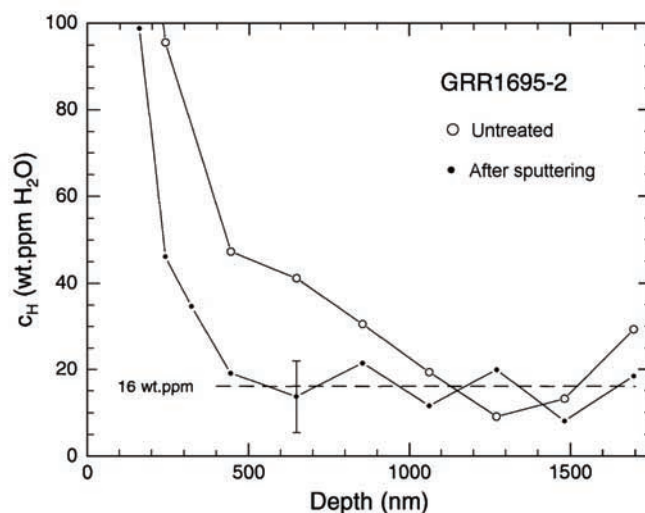
**Figure 1.**  $^{15}\text{N}$  nuclear reaction analysis depth profile of hydrogen in olivine megacryst KLV-23. The depth profile is generated by progressively increasing the energy of incident  $^{15}\text{N}^{2+}$  ions, with the result that they penetrate to increasing depths in the olivine matrix before their kinetic energy is reduced to that of the resonant nuclear reaction with hydrogen.

caused by a region of subsurface damage where surface hydrogen penetrates partially into the sample interior. Some hydrogen-diffusion during analysis from the surface layer into the sample may also occur. The resonance energy of the nuclear reaction has a Lorentzian energy distribution with an effective depth resolution of  $\sim 10$  nm, which also contributes a small degree of “spillover” from the surface hydrogen into the interior. In OH-poor olivines (Figure 2), the gamma ray count rate does not level off at depth but begins to rise at  $>1500$  nm to create a U-shaped pattern. This is due to high-energy, off-resonance interactions with surface hydrogen that assume relatively greater importance when the intrinsic hydrogen content is low. This effect may be greatly reduced by ion sputtering to reduce the surface hydrogen layer [*Maldener and Rauch*, 1997]. Figure 2 illustrates the effect of the surface sputtering treatment on the measured hydrogen content of a low-OH olivine (sample GRR1695-2).

[22] Hydrogen concentrations, expressed in parts per million  $H_2O$  by weight, are reported in Table 1. The uncertainties reported are based on counting statistics and also include uncertainties in stopping cross section of the  $^{15}\text{N}$  ions and in gamma ray detection efficiency.

#### 3.2. IR Spectroscopy

[23] Olivine IR spectra are shown in Figures 3a–3c and are similar to previously published spectra [*Miller et al.*, 1987; *Bell and Rossman*, 1992]. The dominant absorption in



**Figure 2.**  $^{15}\text{N}$  nuclear reaction analysis profiles of hydrogen in the low-OH olivine GRR1695-2. The effect of cleaning the sample surface (originally a polished surface) by sputtering is shown. The error bar reflects uncertainty based on counting statistics for an individual determination at a specific depth. The reported concentration derives from averaging values over the “flat” section of the depth profile.

all three polarizations is between  $3650$  and  $3450\text{ cm}^{-1}$ . The spectra contrast somewhat with synthetically hydrated olivine from the study of *Bai and Kohlstedt* [1992] (Figure 4), which has a significant contribution of OH absorption at lower wave numbers, but are generally similar to the high-OH olivines produced in experiments by *Kohlstedt et al.* [1996]. *Matveev et al.* [2001] proposed that the two broad groups of OH bands in olivine derive from different substitutional mechanisms and their relative intensities are a reflection of silica activity.

[24] In two of our samples, there is a minor, but distinct contribution from high wave number absorptions (between  $3650$  and  $3750\text{ cm}^{-1}$ ). In sample KLV-23, the absorption peak for this component occurs at  $3708\text{ cm}^{-1}$  (Figure 3b). The very high absorption frequency implies non-hydrogen-bonded OH, which is not a common characteristic of OH in olivine and other nominally anhydrous minerals. We believe this is likely due to inclusions of a sheet silicate. Although not due to olivine, this material is also present in the NRA and is therefore included within the IR integration limits.

[25] Integrated absorbances derived from the spectra are reported in Table 1. An estimate of the uncertainty of these measurements is provided by the reported uncertainty for sample KLV-23, which is based on the analysis of the four oriented fragments of this sample.

### 3.3. Correlation of Results and IR Calibration

[26] Our results are reported in Table 1 and presented in Figure 5, which shows a good correlation between the IR intensities and the water content determined with the NRA method. A linear regression of the data in Figure 5 gives a slope of  $0.188 \pm 0.012$  and an intercept of  $6 \pm 9\text{ ppm H}_2\text{O}$ . Substituting these values in equation (4) gives the following calibration equation:

$$\text{H}_2\text{O}(\text{in ppm by weight}) = 0.188A_{\text{stot}}. \quad (6)$$

[27] Using olivine densities calculated from the composition data in Table 2 according to the work of *Fisher and*

*Medaris* [1969], this translates to a value for  $I$  [equation (2)] of  $28,450 \pm 1830\text{ L mol}^{-1}\text{ cm}^{-2}$ .

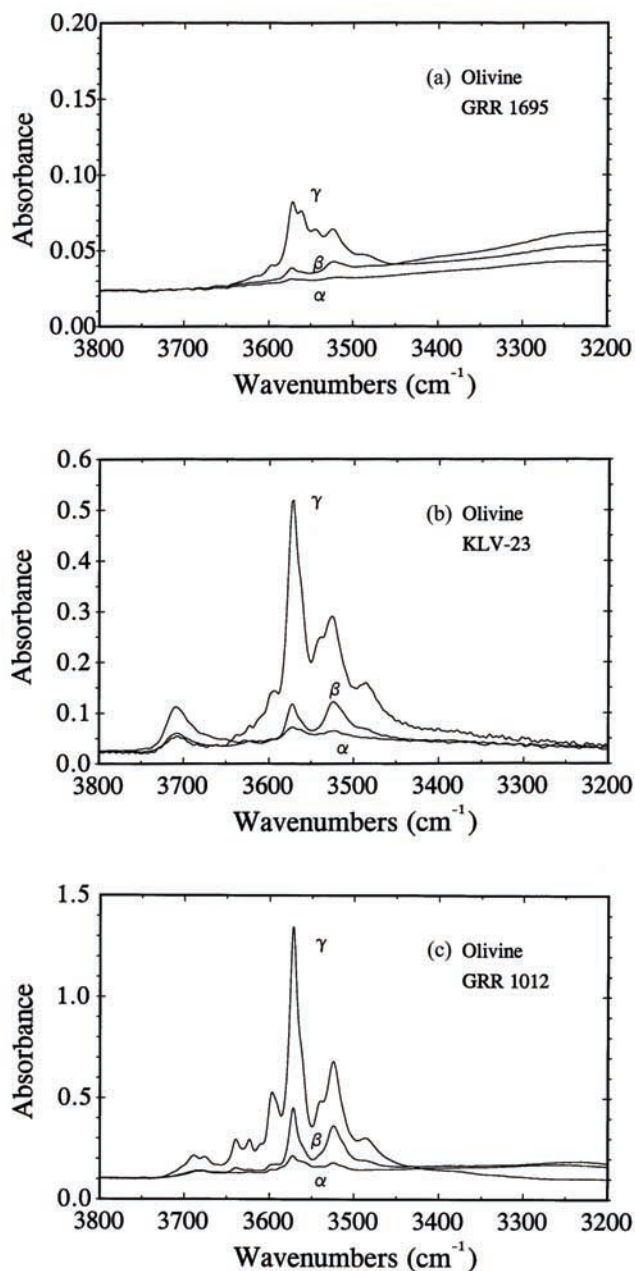
## 4. Discussion

### 4.1. Comparison With Previous Estimates

[28] The integrated molar absorptivity ( $I$ ) for olivine of  $28,450 \pm 1830\text{ L mol}^{-1}\text{ cm}^{-2}$  is comparable with previous calibrations of nominally anhydrous minerals, lying between values of  $38,300 \pm 300$  determined for clinopyroxene [*Bell et al.*, 1995] and  $I/\gamma$  of  $20,000$ – $22,000$  for garnets [*Rossmann and Aines*, 1991; *Bell et al.*, 1995].

[29] Both the measurement and the calibration methods significantly influence the results of OH analysis in olivine by IR spectroscopy. The most commonly applied calibration is that proposed by *Paterson* [1982], which is a generic calibration based upon the spectra of water in glass, quartz, and solvents. Previous IR-based determinations of OH in olivine use this calibration, except that of *Bell and Rossmann* [1992], who used preliminary, unpublished NRA data on olivine KLV-23, which give results very similar to those presented here.

[30] Measurement methods have varied in their use of polarized or unpolarized radiation and in the choice of crystal orientation. As discussed by *Libowitzky and Rossmann* [1996], rigorous quantitative analysis of anisotropic materials involves summing absorption intensities from polarized spectra in all three vibration directions. In practice, however, unpolarized radiation has been commonly used where quantitative analysis is intended. *Paterson* [1982] introduced the orientation factor,  $\gamma$ , which allows an approximation of the full three-dimensional absorption intensity from measurements in a single orientation. In a commonly used application, the value  $\gamma = 0.5$  is used to convert unpolarized measurements in a single crystal orientation to a quantitative estimate of OH. The use of both the unpolarized radiation and the orientation factor can introduce error into the spectroscopic analysis.

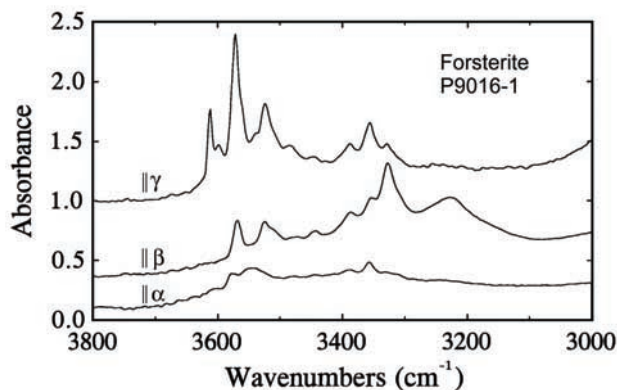


**Figure 3.** Polarized IR spectra of olivine samples (a) GRR1695-2, (b) KLV-23, and (c) GRR1012-2 normalized to 1-mm sample thickness.

**4.1.1. Polarized Radiation Studies**

[31] Figure 6 illustrates a comparison between the OH concentrations determined with the present calibration and those derived by applying the *Paterson* [1982] calibration function with  $\gamma = 1$  in each polarization direction. A regression of the data indicates that, on average, the present calibration yields OH concentrations in olivine that are higher by a factor of 2.3.

[32] We emphasize, however, that subjective differences in the choice of baseline and interval for integration can yield significant differences in integrated absorbances and hence OH content. This error is likely to be especially significant at low OH content and in low-absorption

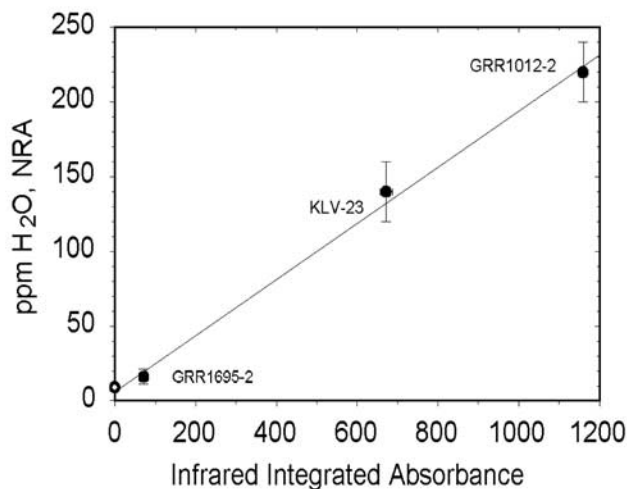


**Figure 4.** Polarized IR spectra of an experimentally hydrated olivine (P9016-1) from the study of *Bai and Kohlstedt* [1993] illustrating the presence of prominent additional bands at wave numbers less than  $3450\text{ cm}^{-1}$ .

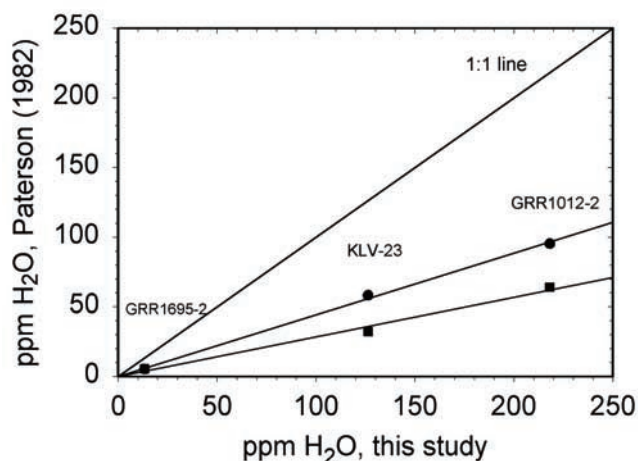
polarization directions, where the height of signal intensity above ambiguously interpretable baseline variations is minimized.

**4.1.2. Unpolarized Measurements**

[33] Experimental studies [e.g., *Mackwell et al.*, 1985; *Mackwell and Kohlstedt*, 1990; *Bai and Kohlstedt*, 1992, 1993; *Kohlstedt et al.*, 1996] have commonly used unpo-



**Figure 5.** Calibration relating the IR OH absorption intensities to absolute OH concentration (expressed as parts per million  $\text{H}_2\text{O}$  by weight) determined by  $^{15}\text{NRA}$ . Solid circles are olivine analyses. The absorption intensity is the sum of the total integrated absorption due to OH between  $3750$  and  $3100\text{ cm}^{-1}$  in the three polarizations, as discussed in the text and given by equation (1). Uncertainty shown for KLV23 represents  $1\sigma$  derived from the analysis of four separate oriented fragments. Origin of the uncertainty in  $\text{H}_2\text{O}$  content is discussed in the text. The open circle represents an anhydrous blank determination at an intermediate stage of experimental development and illustrates a possible contribution to the higher OH samples. The line shown is a linear regression of the olivine data and excludes the blank determination.



**Figure 6.** Comparison between the calibration developed in this study and the OH analysis method of *Paterson* [1982], as applied to polarized (solid circle) and unpolarized (solid square) olivine spectra. In the polarized case, the values are calculated according to equation (5), with the form for  $\epsilon(\nu)$  as given by *Paterson* [1982], and  $\gamma = 1$  for all three polarization directions. For the unpolarized case, OH concentrations were derived for each sample from a single nonpolarized IR spectrum in the  $\beta$ - $\gamma$  plane (i.e., beam parallel to [010]), with  $\gamma = 0.5$ . Regression of the two data sets, constrained to pass through the origin, indicates that OH concentrations determined by the calibration presented here are, on average, 2.3 and 3.5 times the concentrations derived from the *Paterson* [1982] calibration for the polarized and unpolarized cases, respectively.

larized radiation on oriented crystal plates in combination with the *Paterson* calibration to determine hydrogen concentration in olivine. Unfortunately, as explained by *Libowitzky and Rossman* [1996], it is not possible to consistently recover quantitatively accurate water contents from unpolarized data. However, in order to gain an approximate idea of the implications of the present calibration for quantitative interpretation of these experimental studies, we compare (Figure 6) our new calibration results with estimates of OH using unpolarized [010] spectra and the *Paterson* [1982] function with  $\gamma = 0.5$ . The linear fit to the data indicates that the unpolarized method applied to our samples underestimates absolute OH content by a factor of 3.5 on an average.

[34] One contribution to this discrepancy derives from setting  $\gamma = 0.5$ . This choice of the orientation factor is made on the assumption that no OH absorption occurs aside from that in the  $\beta$ - $\gamma$  plane. In fact, the data in Table 1 indicate that 10–18% is contributed from the  $\alpha$  direction. However, it appears that this is a minor source of error and that the error deriving from the use of unpolarized radiation is greater. Because unpolarized methods have been widely applied, there is an understandable desire to be able to relate such measurements to the polarized results. Unfortunately, there is no theoretical basis for a consistent relationship, and differences are expected to relate to many different factors, including the nature of the spectrum, the thickness of samples, the degree of detector saturation, and the degree of polarization anisotropy induced by individual spectrometer optical systems.

[35] Thus, while our polarized and unpolarized IR spectra used in the *Paterson* [1982] calibration yield OH contents that differ by a factor of  $\sim 1.5$ , the expectation from theoretical considerations is that this factor may differ for other samples and measurement conditions. Unfortunately, the extent of variability in this factor for commonly used experimental conditions is presently unknown.

## 4.2. Potential Sources of Error in the Calibration

### 4.2.1. Other Forms of Hydrogen in Olivine

[36] In the IR aspects of this study, we have focused on hydrogen bonded to O. This is believed on the basis of the IR spectra to be present as OH (hydroxide) groups. The IR spectra indicate that no detectable hydrogen is present as  $H_2O$  in inclusions. Other forms of hydrogen could, in theory, occur in olivine. Any chemical form of hydrogen will be included in the NRA, so that hydrogen undetected by IR would result in an erroneous calibration of the OH absorption bands. *Freund* [1984] and *Freund and Oberheuser* [1986] interpreted a feature near  $4200\text{ cm}^{-1}$  in the IR spectrum of Zabargad olivine as an absorption band attributable to molecular  $H_2$ , but provided no further experimental evidence supporting that assignment. We have been unable to find such a band in that material and regard the occurrence of  $H_2$  in olivine as presently unconfirmed. Should this or other chemical species of hydrogen without O-H bonds in olivine be quantified in future, the present calibration would require adjustment accordingly, resulting in a calibration that produced lower hydrogen contents than did the IR analysis, i.e., closer to the calibrations of *Paterson* [1982] and *Libowitzky and Rossman* [1997].

### 4.2.2. Spectral Variation in Olivines

[37] In this work we have made the simplifying assumption of a single value of  $\epsilon$  or  $I$ . The justification for this is that the olivine spectra we have calibrated have a similar distribution of absorption intensity as a function of wave number. However, not all olivine IR spectra conform to this distribution in the OH region. As noted above, a greater proportional contribution from low wave number ( $3100$ – $3400\text{ cm}^{-1}$ ) bands occurs in certain experimentally annealed olivines [*Bai and Kohlstedt*, 1992; *Matveev et al.*, 2001]. It is expected that such OH bands may have higher values of  $\epsilon$  than do the higher wave number bands that dominate the spectra of our samples in this study. Estimates of the magnitude of this difference may be gained from the calibrations of *Paterson* [1982] and *Libowitzky and Rossman* [1997]. These calibrations predict that absorptions near  $3300\text{ cm}^{-1}$  will have values of  $\epsilon$  that are 2.3–2.5 times greater than those of the major high wave number absorption at  $3570\text{ cm}^{-1}$ . This suggests that the present calibration applied to experimental samples dominated by a low wave number component could overestimate the OH content substantially, but requires experimental verification.

[38] We alluded above to the presence of high wave number absorptions in some of our calibration samples that we do not expect to occur as a constant component in olivine OH spectra. For the material in KLV-23 that has a peak frequency of  $3708\text{ cm}^{-1}$ , the calibrations by *Paterson* [1982] and *Libowitzky and Rossman* [1997] predict that this material may absorb IR radiation 3–4 times less efficiently than the major olivine-hosted OH component. However,

this prediction is probably exaggerated because this peak frequency is approaching the artificial singularity in these equations. Since this absorption contributes a minor proportion (~5%) of the total absorption, we expect that its effect on the calibration is negligible.

### 4.3. Implications for Mantle Water Contents

#### 4.3.1. Natural Samples

[39] The compilation of the work by *Bell and Rossman* [1992] applied a calibration of  $c_{\text{H}_2\text{O}}$  (ppm wt.) = 0.1786  $\text{Abs}_{\text{tot}}$  to new and previously published olivine data to evaluate the role of olivine as an hydrogen reservoir in the mantle. The calibration presented here implies that these estimates require upward revision by 6%. The maximum concentration measured in a natural mantle-derived olivine is 240 ppm and occurs in an Fe-rich (Fo80) megacryst from the Monastery kimberlite, South Africa (D. R. Bell et al., Abundance and partitioning of OH in a high-pressure magmatic system: Megacrysts from the Monastery kimberlite, South Africa, submitted to *Journal of Petrology*, 2002; hereinafter referred to as submitted manuscript, 2002). Recent measurements of OH in olivines from Icelandic lavas [*Jamtveit et al.*, 2001] were made using unpolarized spectra and are likely to underestimate the absolute OH content to an unspecified degree, as discussed earlier.

#### 4.3.2. Experimental Studies

[40] Experimental studies are important in predicting the OH content of olivine under expected mantle conditions. This is especially important because the ability of natural olivines to retain their original mantle OH contents has been questioned (e.g., *Mackwell and Kohlstedt* [1990]) and is currently a debatable issue (D. R. Bell et al., submitted manuscript, 2002). While it is highly desirable to apply quantitative calibration to high-pressure studies of OH solubility in olivine, the unpolarized IR measurements made in those studies make the retroactive application of the present calibration highly unreliable (see the work of *Libowitzky and Rossman* [1996] for a more extensive discussion). If the difference between polarized and unpolarized determinations of OH in olivines from the study by *Kohlstedt et al.* [1996] is the same as that determined in this study (a factor of 3.5), then the maximum reported solubility of 1510 ppm  $\text{H}_2\text{O}$  may actually correspond to an OH content of ~5300 ppm  $\text{H}_2\text{O}$ . This would mean that the upper mantle at depths approaching the transition zone could hold at least as much water as under very shallow conditions (<3GPa) where hornblende is stable. However, to reiterate what has been stated above, the variability in the ratio of polarized-derived OH concentrations to unpolarized-derived ones under the different experimental conditions employed by various workers is not known.

[41] An additional complication in application of the present calibration to experimental results is the difference in spectral characteristics. A more significant contribution from lower wave number bands to the total integrated absorption intensity is apparent in the experimental samples (Figure 4). This is particularly notable in the study of *Matveev et al.* [2001]. Apart from the intrinsic differences in absorption efficiency that are implied by the  $\epsilon(\nu)$  relationship, a changing spectral shape introduces more variability in possible choice of baseline. We therefore suggest that the present calibration is rigorously applicable only to samples

dominated by high wave number (3650–3450  $\text{cm}^{-1}$ ) OH absorptions.

## 5. Summary

[42] Differences between the present results and those using the *Paterson* [1982] calibration on the same samples illustrate and confirm the need for mineral-specific and even spectrum-specific calibrations of the IR absorption spectra for OH. The present work provides a basis for a relatively accurate analysis of natural samples, in particular, for the more hydrous, mantle-derived samples with spectra similar to those of the calibration samples. A quantitative framework for interpretation of the natural data and application of experimental results requires the use of appropriate and consistent measurement techniques and calibration of the low wave number OH component prominent in many experimental products.

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