

Analytical Methods for Measuring Water in Nominally Anhydrous Minerals

George R. Rossman

*Division of Geological and Planetary Sciences
California Institute of Technology
Pasadena, California, 91125-2500, U.S.A.
e-mail: grr@gps.caltech.edu*

INTRODUCTION

Decades of work have shown that trace- to minor-amounts of hydrous components commonly occur in minerals whose chemical formula would be normally written without any hydrogen, namely, the nominally anhydrous minerals (NAMs). When the concentrations of the hydrous components are several tenths of a percent by weight or higher, a variety of analytical methods such as weight loss on heating, X-ray cell parameters, X-ray structure refinement, Karl-Fischer titrations, or even careful electron microprobe analyses can be used to establish their concentrations (e.g., Aines and Rossman 1991). However, for most NAMs, accurate determinations with these common analytical methods prove difficult if not impossible. For this reason, infrared (IR) spectroscopy has become, and remains, the most widely used method to detect and analyze hydrous components (OH or H₂O) in minerals and glasses because it is both highly sensitive and can be done rapidly with a commonly available, modestly priced instrument and at dimensions of just a few tens of micrometers. A change in the electric dipole occurs when the OH bond in either water and hydroxyl ions vibrate. This motion has a resonance coupling with electromagnetic radiation generally in the 3500 cm⁻¹ region of the infrared spectrum. In addition, bending motions of the water molecule, and overtones and combination of these motions produce absorption in the infrared.

Under favorable conditions, namely a sharp band in a single orientation, just a few nanometers equivalent thickness of a hydroxyl species such as an amphibole can be detected in an otherwise anhydrous mineral such a pyroxene (Skogby et al. 1990). Routinely, detection limits of a few to tens of ppm wt of H₂O in a mineral can be detected and often quantitatively determined. The overtone and combination modes of OH and H₂O behave in predictable fashion in minerals (Rossman 1975) so that the two species can usually be separated from each other.

Infrared spectra, however easily obtained, are not rigorously self-calibrating, so independent methods of analysis have been necessary to calibrate the spectroscopic work. A couple general correlations of IR band intensity with the absorption energy have proven useful, if approximate. Various absolute hydrogen extraction methods have proven highly useful for purpose of rigorous calibration. More recently, nuclear methods that rely upon specific resonant reactions with the hydrogen nucleus or nuclear scattering specific to hydrogen have gained importance and have provided critical absolute calibrations of the infrared spectra. Secondary Ion Mass Spectroscopy (SIMS) for hydrogen is still in the early stages of development but once calibrated, and with established protocols, should play an ever-expanding role in the future. NanoSIMS promises to bring hydrogen analyses to ever finer spatial dimensions but will require significant effort before it can be regarded as an accurate analytical technique for small concentrations of hydrogen. The purpose of this chapter is to review the various methods that have been used to analyze hydrous components in the NAMs.

ANALYTICAL METHODS

Early infrared studies

Much of the early interest in OH in minerals came from the study of synthetic minerals used in the electronics industry. Quartz, in particular, was an important phase used for frequency control in telecommunications and radio circuits. Consequently, much effort was directed towards the understanding of factors that influenced the efficiency and cost of these devices. Water in quartz was one of the most important factors. The OH bond is dipolar with a partial negative charge on the oxide ion and a partial positive charge on the hydrogen ion. Thus, the vibrations of the OH bond coupled well to infrared radiation and infrared spectroscopy quickly became the tool of choice to study OH in both natural and synthetic minerals. An important early study was conducted by Kats and Haven (1960) who used deuteration to demonstrate which bands in the complex quartz spectrum in the 3000 to 4000 cm^{-1} region originated from ^1H as opposed to overtone or combination bands of the quartz vibrational spectrum that appeared in the same region. Once the OH vibrations were positively identified, Kats (1962) performed a comprehensive study of OH in quartz and identified which of the sharp band absorptions in the 3000-3600 cm^{-1} region are due to O-H stretching vibrations. Kats further showed that most of the absorptions are primarily due to the presence of Al^{3+} substitution for Si^{4+} with charge compensating cations (such as H^+ , Li^+ , Na^+) in defects in the crystal.

Other studies were taking place at Bell Labs in the United States where elastic properties and dielectric loss in synthetic quartz was related to H defects (King et al. 1960; Dodd and Fraser 1965, 1967). In these studies, the relationship between infrared absorption, and hydroxyl and water defects in quartz was also being established. During these times, Brunner et al. (1961) concluded that H enters defects in clear, natural quartz in the form of OH ions and estimated the amount of H as 10^{18} per cc (corresponding to about 15 ppm H_2O wt). These early estimates showed that small amounts of hydrous components could have a large impact on the physical properties of the host phase. As work on synthetic quartz progressed, studies of quartz also used natural samples and ultimately, the results were reported in the mineralogical literature through the work of Dodd and Fraser (1965).

Simultaneously, interest in the low concentrations of water in ring silicate minerals was generated by infrared (Schreyer and Yoder 1964; Wood and Nassau 1967; Farrell and Newnham 1967) and NMR (proton nuclear magnetic resonance) (Pare and Ducros 1964; Sugitani et al. 1966) studies of beryl that demonstrated that water molecules occur in the *c*-axis channels. The NMR work showed that the water molecules were in motion and the IR studies showed that the water molecule existed in two independent crystallographic orientations in the crystal.

In Austria, in the late 1960's and early 1970's, Beran and Zemann obtained the IR spectra of a number of minerals such as titanite, kyanite, axinite, titanium oxides, cassiterite (Beran 1970a,b,c,d; Beran and Zemann 1969a,b, 1971) and demonstrated that they had structurally bound, crystallographically oriented OH groups. These studies demonstrated that polarized infrared radiation could establish the orientation of the OH groups in minerals and demonstrated that trace amounts of hydroxyl occur broadly in a number of nominally anhydrous minerals.

A couple of significant motivations to develop quantitative understanding of the H-content of nominally anhydrous minerals appeared in the early 1970's. Martin and Donnay (1972) suggested that hydrogen may be stored as OH groups in minerals in the deep earth, and Wilkins and Sabine (1973) initiated a broad effort to determine the amount of hydrous components in a variety of minerals by combining infrared absorption with independent water analysis (P_2O_5 electrolytic coulometry). Although we now recognize that many of the analyses of Wilkins and Sabine included alteration products and water in micro-inclusions, they did set the quantitative stage for further detailed studies.

Another major impetus to the study of water in the nominally anhydrous minerals came from the studies of the rheological properties of, first, quartz (Griggs and Blacic 1965; Kirby and McCormick 1979), and then olivine (Mackwell et al. 1985). To study how water weakens minerals, it was necessary to know both the chemical species of the hydrous components that enter nominally anhydrous minerals, and to know their absolute concentrations.

Quantitative IR methods

The determination of the concentration of OH or H₂O in an “anhydrous” mineral depends upon accurate measurement of the infrared spectrum and ultimately on an independent calibration. Infrared spectra are intrinsically not self-calibrating. A number attempts have been made to develop generic calibrations. These often may be good as an initial estimate of the water concentration, but, for many systems, have been shown to be inadequate for precise work. Thus, mineral-specific calibrations have been developed. Once such calibrations are established and properly published, they can be used by other labs worldwide, even if an in-house standard is not available.

The well-established Beer-Lambert law is used to determine the concentration of hydrous species in a mineral from the infrared spectra:

$$Absorbance = \epsilon \times c \times t \quad (1)$$

This relates *Absorbance* (A), the band height in the region of interest (corrected for baseline), c , the concentration of hydrous species expressed in moles of H₂O per liter of mineral, and t , the thickness of the path (in cm) through which the measurement is made where ϵ is a mineral-specific calibration factor. In the classical chemical applications, the sample is in solution, so only one measurement is made. In the case of anisotropic solids, it is necessary to make the measurement in multiple directions (Libowitzky and Rossman 1996). Typically, linearly polarized light would be used and measurements would be made along the three principal extinction directions, X , Y , and Z . In this case, the intensities would be summed so A becomes $A_X + A_Y + A_Z$ (where A_X is the absorbance obtained with light polarized in the X direction, etc.). This approach tends to work best with phases that have one or a small number of narrow bands in the OH region. It also requires knowledge of the density of the mineral to convert from moles per liter to weight percent (or ppm) water.

For most minerals, it is usually more useful to use a modified version of the Beer-Lambert law that uses integrated band areas rather than band heights. Band heights can vary depending on both the quality of the polarizer in the instrument and on the spectroscopic resolution of the instrument whereas band areas are less dependent on these parameters. The band height measured by the *Absorbance* is replaced by the total integrated area of bands in the region of interest $Absorbance_{total}$ (also written as Abs_{total} or A_{total}). The concentration, c , remains expressed as moles of H₂O per liter of mineral. In this case, the absorption coefficient, ϵ , is replaced by the integral molar absorption coefficient, I , in units of L/(mol·cm²). When c is expressed as ppm H₂O by weight, the absorption coefficient becomes the integral specific absorption coefficient (I' , ppm⁻¹·cm⁻²). The absorption coefficient for each species of hydrogen is found by determining the concentration, c , by an independent, absolute method and measuring Abs_{total} from polarized IR spectra in the three principal optical directions (X , Y , and Z) for the mineral of interest. For an orthorhombic mineral such as olivine:

$$Abs_{total} = \frac{1}{t_a} \int_{\nu_1}^{\nu_2} Abs_a d\nu + \frac{1}{t_b} \int_{\nu_1}^{\nu_2} Abs_b d\nu + \frac{1}{t_c} \int_{\nu_1}^{\nu_2} Abs_c d\nu \quad (2)$$

Here, the equation specifies measuring the integrated area of an orthorhombic crystal with light polarized in the E_{lla} , E_{llb} , and E_{llc} directions between the appropriate wavenumber limits of the OH bands, ν_1 and ν_2 . For lower symmetry crystals (monoclinic, and triclinic)

$Abs_{total} = \int Abs_x + \int Abs_y + \int Abs_z$, and for a uniaxial crystal (hexagonal or tetragonal) $Abs_{total} = 2\int Abs_{\perp c} + \int Abs_c$ (e.g., Libowitzky and Rossman 1996). To be comparable to measurements on lower symmetry crystals, an isotropic crystal would need to have $A_{total} = 3\int Abs_a$.

Paterson's method. If the absorption frequency and intensity of a unit concentration of OH were a constant, then a single calibration of the OH spectrum would be all that is needed to conduct quantitative analysis with IR spectroscopy. Unfortunately, that is not the case. First of all, while the fundamental stretching vibration of a free (gaseous) hydroxide ion occurs at 3555.59 cm^{-1} (Lutz 1995), the OH stretching frequency in a mineral commonly can occur over a range of several hundred wavenumbers and can vary by nearly 2000 cm^{-1} . A variety of studies (Nakamoto et al. 1955; Bellamy and Owen 1969; Novak 1974) showed that for a variety of chemical elements, the stretching frequency of an X-H bond in an X-H...Y hydrogen bonded system is a function of the X-Y distance. This includes O-H bonds. These authors derived empirical fits to experimental data that mathematically expressed this relationship. The second observation of interest is that the infrared absorption intensity of a unit concentration of OH in a solid is obviously not constant. Paterson (1982) confirmed that the strength of the OH absorption in the 3600 to 3000 cm^{-1} region was frequency dependent. From the calibrations available for various substances, he presented a single empirical calibration line that related the OH intensity to band position that could be applied as a first approximation for determining the amount of OH in a variety of substances such as silicate glasses, quartz, and various forms of water. This was the first generic calibration specifically designed for the study of hydrous components in minerals and glasses.

Paterson demonstrated that the intensity of an OH band (normalized to a unit concentration of H_2O) increases when the band occurs at lower wavenumbers (stronger hydrogen bonding). This trend has been used by a number of authors to estimate the OH content of various minerals. Subsequent work has shown that determinations based on Paterson's trends are a reasonable first estimate, but that accurate determinations do require mineral-specific calibrations.

Paterson's method first assumes that if a crystal is being measured, it is in a known crystallographic orientation. To determine the concentration of hydroxyl groups in the sample, the integrated absorbance is determined by integration of the infrared spectra over the region dominated by the stretching vibrations due to O-H bonds, typically from approximately 3750 to 3000 cm^{-1} . The integral molar absorption coefficient (I) is scaled to reflect the higher intrinsic intensities of bands at lower wavenumbers (stronger H-bonds) through the equation:

$$I = \gamma \times 150 \times (3780 - \nu) \quad (3)$$

where ν is the wavenumber and gamma (γ) is a factor to take account of the anisotropy of the crystal based on an assumption that O-H bonds are oriented in a single direction. The OH concentration is then calculated from a Beer-Lambert law relationship:

$$\text{Concentration}_{\text{OH}} = \frac{1}{(150 \times \gamma)} \int \frac{A(\nu)}{(3780 - \nu)} d\nu \quad (4)$$

assuming that the data are scaled for 1 cm sample thickness.

Although uncertainties in this calibration were thought by Paterson to be about 30%, it has been widely adopted, partly in the hope that it would eliminate the need for more involved polarized light observations with multiple crystallographic directions. However, the studies of Libowitzky and Rossman (1997) and Bell et al. (2003) show that it can result in non-systematic underestimates of hydrogen concentrations. Examples of mineral specific calibrations that fall far from the trend are documented, particularly those that involve nominally anhydrous minerals with low concentrations of OH. As examples, the pyrope analyzed by Bell et al. (1995) departs from the Paterson trend by nearly a factor of three, the nuclear reaction analysis

of olivine by Bell et al. (2003) departs by more than a factor of two (Fig. 1) and the SIMS analysis of both olivine and orthopyroxene (Koga et al. 2003) show that the Paterson trend also underestimates their OH concentrations.

Libowitzky and Rossman's revision. Libowitzky and Rossman (1997) presented an updated version of the correlation of Paterson (1982). They measured polarized IR absorption data from single crystal minerals that contained stoichiometric water contents in the form of either OH or H₂O. These data were used to construct a calibration curve for the intensity of the infrared absorption as a function of the band energy. Specifically, integrated molar absorption coefficient, ϵ_i (in units of cm⁻² per mole_{H₂O}/liter), was evaluated as function of the mean wavenumber of the OH stretching band (in units of cm⁻¹). The result in Figure 2 shows that an increase in the hydrogen bonding leads to a decrease in the energy of the OH stretching energy which, in turn, is associated with an increase in the intensity of absorption. The form of the correlation is

$$\epsilon_i = 246.6 \times (3752 - \nu) \quad (5)$$

where ν is the mean wavenumber of the OH stretching band.

The results in Figure 2 show that the revised calibration produces ϵ_i values about three-quarters of those of Paterson (1982). Measurements of minerals with stoichiometric OH are difficult to obtain. Their OH intensities are so high that crystals must be prepared very thin (perhaps as thin as 2 μ m). Such preparations are difficult to near impossible; and when successful, the determination of their thickness to a high degree of accuracy is difficult.

Figure 1. Comparison of the results of the calibration developed by Bell et al. (2003) using Nuclear Reaction Analysis and the OH analysis method of Paterson (1982), as applied to polarized (solid circle) olivine spectra. Modified after Fig. 6 of Bell et al. (2003).

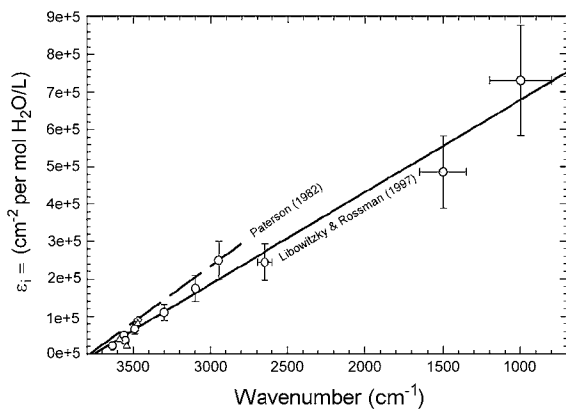
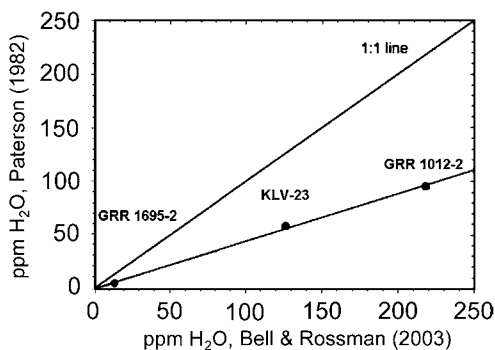


Figure 2. The correlation of the integrated molar absorption coefficient of OH stretching vs. wavenumber. Circles are experimental data points for stoichiometric minerals. The correlation of Paterson (1982) is shown for comparison. This means that if all things are equal, the Paterson trend underestimates the OH content. From Libowitzky and Rossman (1997).

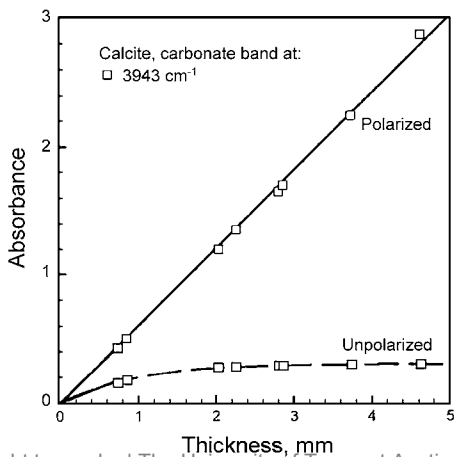
In a related effort, Libowitzky (1999) evaluated correlations specific to minerals between the frequency of the O-H stretching vibration and the length of the oxygen-oxygen distance and the H...O distances in the O-H...O hydrogen bond. Effectively, the shorter these distances are, the lower becomes the energy of the O-H stretch. Because the intensity of the OH band is related to the energy of the vibration (Libowitzky and Rossman 1997), such correlations provide some degree of a predictive estimate about the intensity of an OH absorption that arises from a particular site in a crystal.

Use of unoriented grains. Asimow et al. (2006) present a method that allows multiple, randomly oriented grains of a mineral to be used to determine the total absorbance. In their method, the spectra of oriented sample of the phase of interest must already exist. Then, the spectra of three different randomly oriented crystals are measured, and the orientations of the grains are determined via methods such as electron backscatter diffraction (EBSD) or from the silicate overtone bands in the infrared spectra. They demonstrated that such methods result in angular errors of typically only 6 degrees and provide a surprising good determination of the OH content of the phase.

Polarizer considerations. A linear polarizer must be used in the infrared beam of conventional spectrometers to obtain the total absorbance of anisotropic crystals. Commonly, the polarizers are made of a fine, parallel wire grid deposited on an infrared-transparent substrate such as CaF₂ or KRS5 (a thallium bromide iodide). These polarizers have wide acceptance angles and are readily available, but have only moderate polarization ratios. Crystal polarizers of a design similar to calcite polarizers used in the visible wavelength region are also available, but often have a narrow range of wavelengths over which they function. Lithium iodate covers a wide wavelength range and has a very high polarization ratio, but is hydroscopic and no longer readily available.

Libowitzky and Rossman (1996) discussed the principles of quantitative absorbance measurements of anisotropic crystals and paid particular attention to the influence of the quality of the polarizers upon the results. First, they showed that the use of unpolarized radiation with an anisotropic crystal could not produce quantitatively accurate results. The Beer-Lambert law demands that the height of an absorption band will scale with the thickness of the sample. Figure 3 demonstrates how the spectrum taken with linearly polarized radiation follows the law. It also shows that unpolarized spectra do not scale according to the law. This means that unpolarized spectra should not be used to calibrate the infrared spectrum of OH

Figure 3. Comparison of the intensity of a carbonate overtone band in the calcite spectrum taken with well-polarized and unpolarized radiation. The experiment that used different thickness of calcite to test the Beer Lambert law shows that unpolarized spectra are not appropriate to quantitatively measure anisotropic crystals. From Libowitzky and Rossman (1997).



in an anisotropic standard, and cannot be used to accurately determine the concentration of OH in an anisotropic unknown. The more highly anisotropic the sample is, the more problematic this issue will become. Libowitzky and Rossman also showed that the intensity of an absorption band of an anisotropic crystal is highly dependent upon the polarization ratio of the polarizers (Fig. 4) which means that if band heights are used to calibrate the infrared spectra, results can vary significantly from lab to lab if the appropriate in-lab standards are not available.

Baselines issues. Figure 5 shows that strongly rising, non-linear baselines may be an intrinsic part of the spectrum in the OH region. These baselines commonly arise from Fe^{2+} and may arise from silicate overtones in thick samples. A major, subjective source of uncertainty in IR measurements of OH in minerals remains the choice of the baseline.

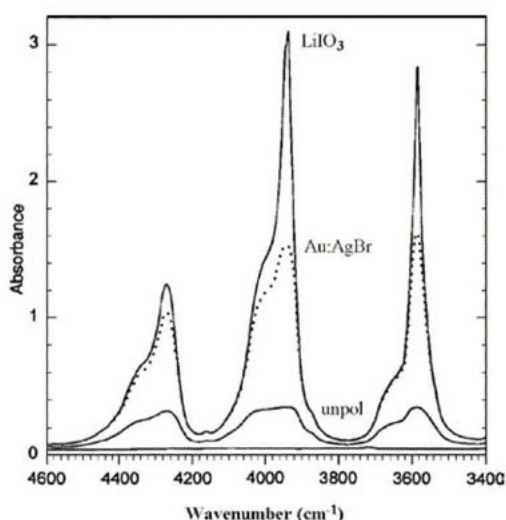
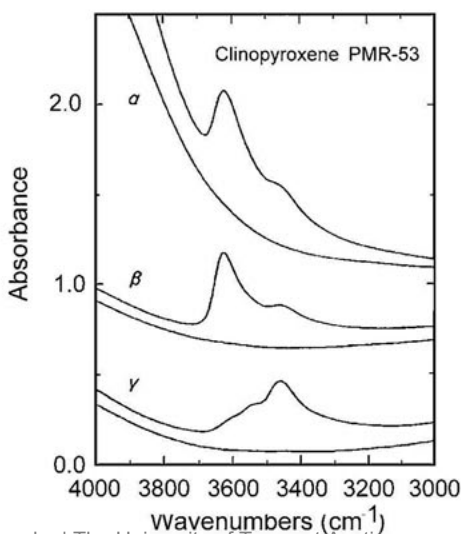


Figure 4. The intensity of absorbance depends on the quality of the polarizer used for the measurement. Here, the spectrum ($E \perp c$) of three bands in the calcite spectrum was obtained with a high efficiency polarizer (LiIO_3), a lower efficiency wire-grid polarizer (gold wire on AgBr), and without polarization. Modified after Figure 6 of Libowitzky and Rossman (1996).

Figure 5. Infrared spectra of a clinopyroxene that show the baseline remaining after the crystal is fully dehydrated. Contributions from ferrous iron cause the rising baseline towards the long wavenumber side. From Bell et al. 1995, Figure 1.



Comments on terminology. The terminology for spectroscopic units has not been consistent in the literature. Chemical terminology, the source of these terms, has evolved, and geoscience has had to modify some of the standard terms for anisotropic materials. Table 1 presents a compendium of terminology taken from the web site of the International Union of Pure and Applied Chemistry. In addition, the currently preferred terminology is compared to other terminology found in the literature.

Mineral specific calibrations

While the generic calibrations developed by Paterson (1982) and later refined by Libowitzky and Rossman (1997) are useful first approximations, they are not necessarily accurate. There is no principle of science that demands that the infrared absorption intensity of all OH bonds be the same, or that the intensity of all OH bonds vary smoothly with the O-H...O hydrogen bond distance. Unpublished work by this author has shown that the intensity of other bonds such as C-O (carbonyl) and C-N (cyano) can vary by orders of magnitude. Thus, there is the need for mineral-specific calibrations. A variety of experimental methods, discussed in the following sections, have been used over the years to independently determine the amount of hydrous components in minerals. As is often the case in the history of development of analytical methods for trace components, early attempts suffered from large (and often

Table 1. Selected terminology used in quantitative spectroscopy of minerals.

<i>Absorbance</i> = $\log(I_0/I)$
directly measured by the instrument
<i>Attenuation coefficient</i>
Analogous to the absorption coefficient, but differs from it because it accounts for the diffusion of radiation that includes absorption as well as scattering and luminescence. Formerly, it was called the extinction coefficient, a term that is now discouraged.
<i>linear absorption coefficient</i>
= Absorbance divided by the optical path length
<i>molar absorption coefficient</i> = ϵ
= molar absorptivity in earlier literature
= linear absorption coefficient divided by the amount concentration
<i>amount concentration</i>
= molarity in prior literature
commonly expressed in units of moles per liter
<i>integral molar absorption coefficient</i>
I (in units of cm^{-2} per $\text{mol}_H/\text{liter}$).
ϵ_i (in units of cm^{-2} per $\text{mol}_{H_2O}/\text{liter}$).
(note that the mols of H = mols OH)
<i>Integral absorbance</i> (not defined by IUPAC)
Integrated absorbance
$Abs_{tot} = \frac{1}{l_1} \int_{\nu_1}^{\nu_2} Abs_1 d\nu + \frac{1}{l_2} \int_{\nu_1}^{\nu_2} Abs_2 d\nu + \frac{1}{l_3} \int_{\nu_1}^{\nu_2} Abs_3 d\nu$
Absorbance _{total}
Δ
Integrated-Abs _{tot}

unrecognized) backgrounds, and the inability to separate the contributions of the hydrogen in the host phase from hydrogen contained in inclusions, cracks, and alteration products.

Thermogravimetric methods

Thermogravimetric analysis (TGA) is a commonly used analytical method to determine the amount of mass lost from a sample during heating. It involves simultaneously heating and weighing a sample to produce a weight-loss vs. temperature curve. It is frequently used to determine water of hydration in minerals with more than trace quantities of water. The method has also been applied to water loss from nominally anhydrous minerals but with limited success.

Early attempts to determine the H-content of garnets used the TGA method (Aines and Rossman 1984a) and coupled the results of this method with infrared spectra of the same samples. We now recognize that many of the earlier thermogravimetric methods over-estimated the water content of the NAMs due to the inclusion of contaminating water that remained trapped on the surface of the ground samples, even after the sample was "dried" by heating to over 125 °C prior to analysis.

TGA was used to determine the water content of nepheline from Bancroft, Ontario (0.36 wt% H₂O), and from Mt. Somma, Italy (0.17 wt% H₂O) (Beran and Rossman 1989). Because these minerals have comparatively large water contents, the error introduced by the TGA method is small compared to what it may be when minerals with a few hundred ppm or less are analyzed by this method. The results of this method were also used to calibrate the infrared spectra of nepheline.

While TGA analyses are conventionally conducted on ground samples, step heating experiments on slabs of single crystals used for infrared experiments demonstrate how difficult it can be to fully dehydrate a sample. Controlled heating experiments that were accompanied with infrared spectra of OH bands indicated that temperatures of about 1400 °C are needed to fully dehydrate slabs of some silicate minerals (sillimanite: Beran et al. 1989). Similar experiments with slabs of single crystal zircon indicated that OH is tightly held. Some OH persists in zircons even after the crystals are heated at 1500 °C (Woodhead et al. 1991). Ilchenko and Korzhinskaya (1993) also conducted step-heating experiments on kimberlitic zircon crystals and found that OH ions were only partially removed after heating to 1300 °C.

P₂O₅ cell coulometry

P₂O₅ cell coulometry is based on the principle that water released during the thermal decomposition of a sample can react with P₂O₅, a non-conductor, and turns it into H₃PO₄, an electrical conductor. The amount of H₃PO₄ formed can be determined by the amount of electric current (coulombs) necessary to reverse the hydration reaction. One of the more popular commercial models used in mineral analysis was the DuPont moisture evolution analyzer (MEA). It consisted of a thermal decomposition chamber that led to a column containing a pair of closely spaced, P₂O₅-coated, Pt wire electrodes wound in a helical fashion. A dry nitrogen flow would carry the released water vapor into the electrodes where electrical current would flow between the wires whenever the P₂O₅ reacted with the water. A known mass of a stoichiometrically hydrated material was used to calibrate the system.

The moisture evolution analyzer found use in some of the earlier analyses such as Wilkins and Sabine (1973) study, and the Aines and Rossman (1984) calibration of garnets.

In practice, these systems had to be used regularly to prevent the P₂O₅ columns from going bad, and proved difficult for many users to regenerate once the columns did degrade. Because blanks with this method are typically several tens of micrograms of H₂O, samples of at least a few hundred milligrams are required for the analysis of the nominally anhydrous minerals. (Aines and Rossman 1984).

Hydrogen extraction with uranium reduction methods

Hydrogen manometry. Hydrogen manometry has long been a standard and generally reliable method to determine the water content of samples. In this method, several hundred milligrams to gram quantities of samples are weighed into a metal (Mo, or Pt) crucible, and first degassed under vacuum and low heat to drive off the adsorbed moisture. The sample crucibles are then heated with an induction furnace to liberate the bound water while under vacuum. The volatiles (H_2 and H_2O) are converted to just water and trapped and separated from the condensable and non-condensable gases by distillation in cryogenic traps. The water vapor is next passed over a hot furnace containing uranium metal (Bigeleisen et al. 1952) to reduce the water to molecular hydrogen. Alternatively, zinc has been used to reduce water (Michel and Villemant 2003). The hydrogen is then moved by a mercury-piston Toepler pump into a calibrated chamber in which the volume of hydrogen can be measured at a known pressure. From the $PV = nRT$ relationship, the absolute amount of hydrogen can be determined.

The system can be calibrated by known amounts of water, or by dehydration of minerals or compounds with known, stoichiometric water contents. For minerals with very low hydrogen contents such as the nominally anhydrous minerals, significant blank corrections must be applied that correct for degassing from the crucibles (Bell et al. 1995). Errors have been reported to be much less than 1% with this method (Dyar et al. 1996). Additional details of the technique can be found in Holdaway et al. (1986)

This method has been used to determine the water content of minerals that are used to calibrate infrared spectra. The advantage of using this approach is that once the sample is destroyed by the hydrogen extraction procedure, its value as a calibrant remains through the calibration of the infrared spectrum which can be used to analyze additional samples of the calibrated phase that have similar spectra. Furthermore, the infrared spectrum allows re-evaluation of the calibration because the original spectrum can be compared to the spectrum of other samples re-calibrated by improved methods years later.

Early calibration efforts with hydrogen extraction (Aines and Rossman 1984) include a grossular with 0.18 wt% H_2O , and a pyrope with 0.08 wt% [that is probably overestimated based on the more recent calibration of Bell et al. (1995) that indicate about 37 ppm H_2O]; and perthite feldspar from two pegmatites (Hofmeister and Rossman 1985a,b) that had water in the 0.09 to 0.15 wt% range. More recent calibrations with lower blank contributions (Fig. 6) consist of a pyrope with 56 ppm, an enstatite with 217 ppm, and an augite with 268 ppm (Bell et al. 1995). In these experiments, large quantities of sample had to be carefully prepared, and checked to eliminate inclusions, cracks and other imperfections. The clean material was

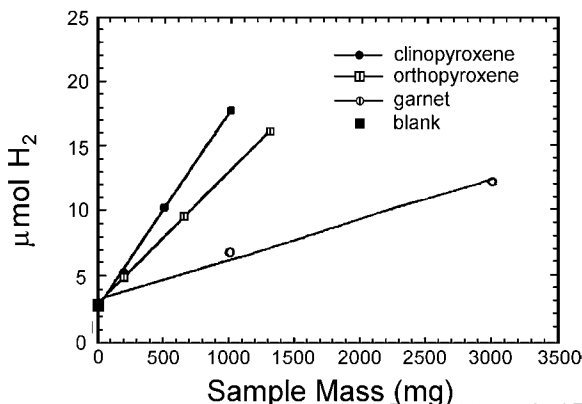


Figure 6. Quality of hydrogen extraction determination of water in garnet and two pyroxenes using aliquots of different mass to determine the water content. Figure 4 from Bell et al. (1995).

then crushed to less than 2 mm particles and the fraction less than 100 μm was discarded to minimize the effects of adsorbed water.

Continuous flow mass spectrometry. A more recent variation of the hydrogen extraction technique uses continuous flow mass spectrometry to measure the absolute amount of hydrogen released from minerals by heating (O'Leary et al. 2006). This method is a modification of the method of Eiler and Kitchen (2001) used to determine D/H isotopic ratios of picoliter quantities of hydrogen. It requires about 1/1000 the amount of hydrogen required by conventional hydrogen manometry. Samples in the range of 50 μg to 20 mg of coarsely ground minerals are heated to release hydrous components, which are collected and converted to hydrogen by reaction with uranium (as opposed to carbon in the Eiler and Kitchen paper). The hydrogen is then detected in a mass spectrometer. The system is calibrated with a few hundred micrograms of zoisite grains of known H content. This system has been used to independently calibrate a series of garnets and pyroxenes that have been previously calibrated by conventional hydrogen extraction manometry or by nuclear methods. The linearity and agreement with previous calibrations has been excellent with samples at the few hundred-ppm H_2O level and higher (Fig. 7).

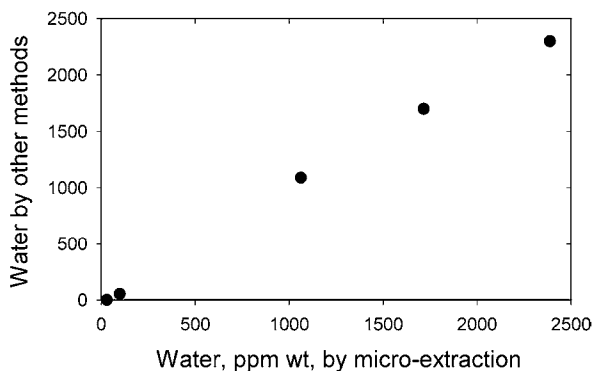


Figure 7. Comparison of the water contents determined by the new micro-extraction method compared to conventional methods (O'Leary et al. 2006).

Nuclear methods for hydrogen determination

A variety of nuclear reactions can be used to analyze hydrogen in solids (Lanford 1992). Some make use of nuclear reactions and others make use of nuclear scattering. Beams of ions accelerated to high energy can undergo a resonant nuclear reaction with the hydrogen ions in the target sample. Such methods are known either as Nuclear Resonant Reaction Analysis (NRRA), Nuclear Reaction Analysis (NRA) or Nuclear Profile Analysis (NPA) (when the hydrogen concentration is determined as a function of depth in the sample). The 6.42 MeV resonance of ^{19}F with hydrogen and the 6.385 MeV resonance of ^{15}N with hydrogen are the two that are typically used. Additional resonances of ^{19}F at 16.44 MeV and ^{15}N at 13.35 MeV can also be used (Xiong et al. 1987). In each of these reactions, the analysis depends upon the detection of gamma rays emitted from a heavier element that formed from transmutation of the ion beam from its reaction with hydrogen.

^{19}F Nuclear reaction analysis. Initially, ^{19}F was the ion of choice for analysis of hydrogen in solids. The reaction involves the interaction of ^{19}F with ^1H to yield an ^{16}O atom plus an alpha particle and a gamma ray. In the geological sciences, the 16.4 MeV resonance has found use for measuring hydration profiles in glass such as obsidian (Lee et al. 1974) and measurements of the H concentration in synthetic and natural quartz (Clark et al. 1978). Early work on analysis of H in garnets (Rossman 1990) also used ^{19}F , but found that the reproducibility needed improve-

ment. Because some accelerators can bring the ^{19}F ion to as much as 22 MeV, significant depth profiles are possible.

^{15}N Nuclear reaction analysis. The most sensitive analyses of hydrogen in minerals have been made by a nuclear resonant reaction using the ^{15}N technique (Lanford, 1978) that is based on the nuclear reaction $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$. In this method (Fig. 8), the hydrogen ions in the sample (the target) interact with a beam of ^{15}N ions and are transmuted into ^{16}O that immediately decays through alpha decay into ^{12}C in a nuclear excited state. The ^{12}C has a decay path that emits a gamma ray that is detected in the analysis. The number of ^{12}C gamma rays is proportional to the amount of hydrogen in the sample and does not depend on the chemical species of the hydrous component. A single calibration point is all that is needed to use the method for quantitative analysis of hydrogen.

The methods for mineral analysis were initially refined at Caltech and later, when the Caltech accelerator shut down, were transferred to the accelerator laboratory of the Institut für Kernphysik, Frankfurt am Main, where a beam of $^{15}\text{N}^{2+}$ ions was delivered by a 7-MeV Van de Graaff accelerator onto a sample under high vacuum. At Frankfurt, the apparatus was specially designed and modified for the analysis of low hydrogen concentrations (to 10 ppm wt) in mineral samples. A detailed description of the experimental design can be found in the works of Endisch et al. (1993, 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 (10^{-10} mbar) chamber.

The NPA method for low concentrations of H in minerals has been under development since the late 1970's. Initially, F-19 was the ion beam of choice, but with the discovery of weak, interfering reactions, the ion beam was changed to N-15. Initially, weak nuclear reactions from carbon contamination were problematic, but improved detection methods, improved instrument vacuum and trapping of carbon compounds in the sample chamber brought them down to a manageable level (Kuhn et al. 1990). Ultimately, the layer of hydrous materials on the surface of the sample became the limiting problem, but high voltage ion sputtering was able to reduce this limitation to low levels (Maldener and Rauch 1997). An additional modification described by Maldener and Rauch allowed accurate sample positioning by Rutherford backscattering.

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 was subject to some degree of variation. One of the key calibrations for olivine was established using this method (Fig. 9). In the most recent set of procedures, analysis of anhydrous silica glass and a silicon wafer placed the background estimate at 2 ± 2 ppm H_2O . In late 2004, the accelerator at Frankfurt was decommissioned and work there on hydrogen in minerals has ceased.

During the lifetime of the Frankfurt facility, the nuclear profile analysis method has been applied a variety of minerals including garnets (Rossman et al. 1988; Maldener et al. 2003), olivines (Bell et al. 2003), kyanite (Bell et al. 2004), rutile and cassiterite (Maldener et al. 2001), titanite (Hammer et al. 1996), ortho- and clinopyroxenes and zircon (Rossman et al. in prep.).

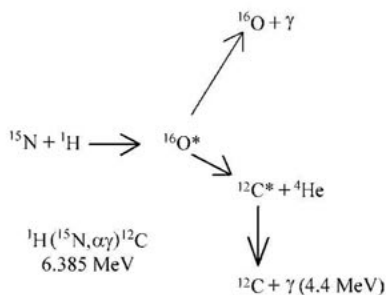


Figure 8. The nuclear reaction scheme in the ^{15}N nuclear reaction method. The reaction of ^{15}N and ^1H produce ^{16}O in a nuclear excited state. A decay path of oxygen produces ^{12}C , which comes to the ground nuclear state with the emission of a 4.44 MeV gamma ray that is the analytical signal.

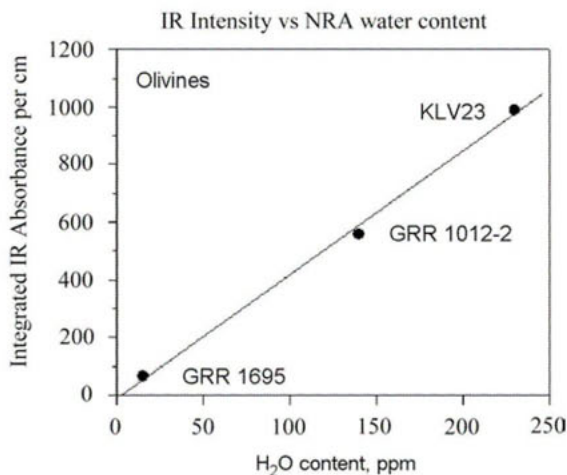


Figure 9. The olivine calibration established with ^{15}N nuclear reaction analysis. This calibration relates the total integrated absorption of the infrared spectrum to the water content determined by NRA. From Bell et al. 2003.

Other workers have used the NPA method for analysis of H in minerals and geological materials. Rauch et al. (1992) used the ^{15}N method to determine the hydration of tektite glass. Semi-quantitative hydrogen concentration depth profiles were obtained on forsterite crystals by Fujimoto et al. (1993). They treated crystals under water at different pH and temperature conditions and found that high surface hydrogen concentrations developed. Under medium to high pH conditions at 25 °C, they found that the hydrogen-rich region extended less than 20 nm into the surface while at low pH conditions; it reached as deep as 200 nm.

Elastic recoil detection analysis (ERDA). Methods based on the scattering of nuclei by protons are also used in the analysis of minerals. A particularly promising method is known as Elastic Recoil Detection analysis (Barbour et al. 1995; Sie et al. 1995). This method (Fig. 10) involves using 2 MeV $^4\text{He}^+$ ion beam that is focused on the polished surface of the sample at a low angle (15°).

Forward scattered $^1\text{H}^+$ ions that come from the hydrous component in the mineral (the recoil spectrum) are detected by a silicon ERDA detector. Because the forward scattered protons lose energy as they traverse through the thickness of the sample, their energy at the

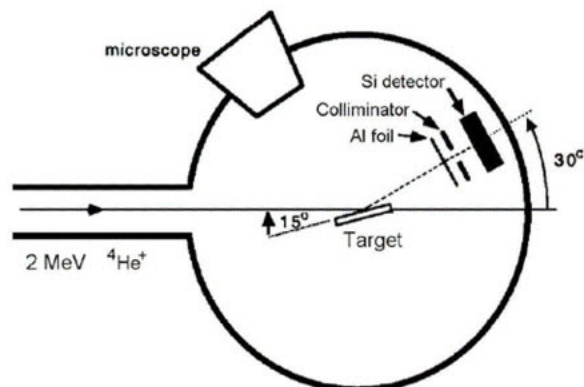


Figure 10. A diagram of a typical ERDA sample chamber where a beam of 2 MeV $^4\text{He}^+$ ions are scattered at low angles by protons in the sample. Modified after Fig. 1 of Sweeney et al. 1997.

detector is a function of the depth of interaction with the $^4\text{H}^+$ ion. Sweeney et al. (1997) used a microbeam elastic recoil detection analysis to determine the hydrogen content of minerals. With suitable calibration, a depth profile (Fig. 11) as well as the absolute H-concentration can be obtained, in principle.

In ERDA, there is a problem of H-loss due to diffusion away from the He^+ beam, but it is quantifiable and the technique is readily applicable to the analysis of H in both hydrous and nominally anhydrous minerals down to the 0.04 wt% (400 ppm wt) level. Sweeney et al. state that this detection limit is potentially improvable with better protected electronics.

Proton-proton scattering. Furuno et al. (2003) describe an application of a proton-proton elastic recoil coincidence spectroscopy to hydrogen analysis using a proton microbeam at an energy of 20 MeV. This method provides depth profiles of hydrogen over a thickness of 200 μm of silicate samples in a short time. A typical beam size is as small as $27 \times 32 \mu\text{m}$. The depth resolution is about 10 μm . The present work proves that the proton-proton elastic recoil coincidence spectroscopy is a promising method for measurements of hydrogen in mineral and rock samples with thickness up to 200 μm .

Proton beams at energies of 20 MeV can pass through several hundred micrometers with an energy loss of only a few MeV. Protons passing through a sheet of material experience proton-proton elastic recoil. Measurement of the energy-loss distribution from the proton-proton scattering events is specific for H and has a sensitivity in the ppm range (Cohen et al. 1972). A typical detection system (Fig. 12) consists of two detectors that detect scattered protons in coincidence with the recoil protons. If the detectors are the same distance from the sample, both protons arrive at detectors at the same time, but with a 90° separation. Their energy will be less than the incident beam because of energy loss that is a non-linear function of the depth of the reaction below the sample surface (Fig. 13).

This method was used by Wegdén et al. (2004) with a 2.8 MeV proton beam at Lund, Sweden. They were able to get strong signals from a synthetic pyroxene with 300 ppm water. Further development of this method demonstrated the analysis of hydrogen at the 100 of ppm H_2O concentration level (Fig. 14) and showed that surface hydration could be distinguished from the intrinsic bulk hydrogen content (Wegdén et al. 2005) where depth profiles exceeded 1 micrometer. Reichart et al. (2004) used a similar method to produce a three-dimensional image of the hydrogen distributions in a polycrystalline synthetic CVD diamond film and showed that the hydrogen atoms were concentrated along the grain boundaries.

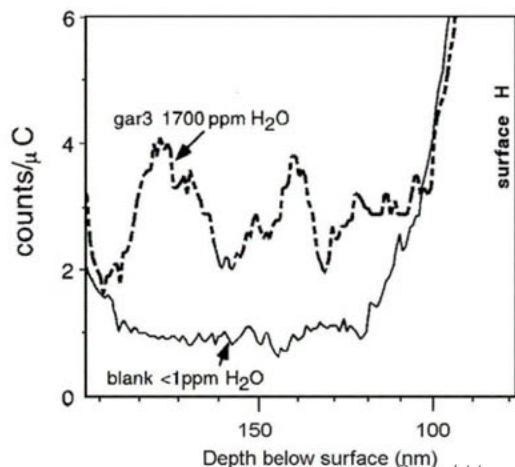


Figure 11. An ERDA profile of a grossular garnet 3-232 compared to a zero-hydrogen synthetic Al_2O_3 blank. The grossular (GRR 1386) contains 0.17 wt% H_2O as was previously determined by NMR, H-extraction and FTIR. Modified after Figure 4 of Sweeney et al. 1997.

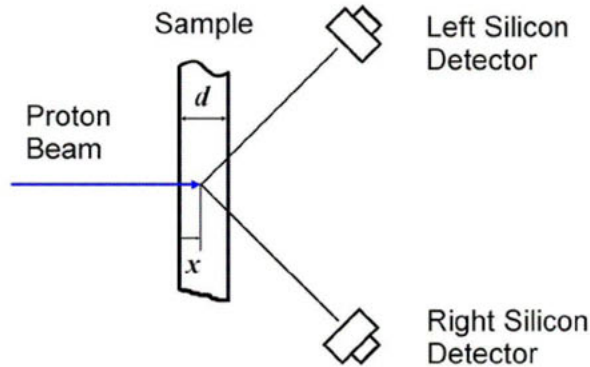


Figure 12. Schematic drawing of the detection system for p-p scattering. Modified after Furuno et al. (2003).

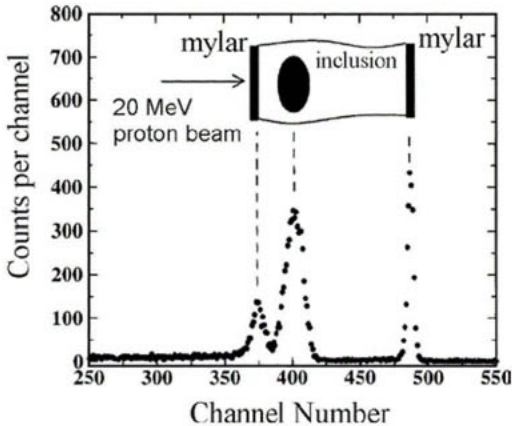


Figure 13. The results of a typical proton-proton scattering experiment on a sample containing a hydrous inclusion. Modified from Figure 4 of Furuno (2003).

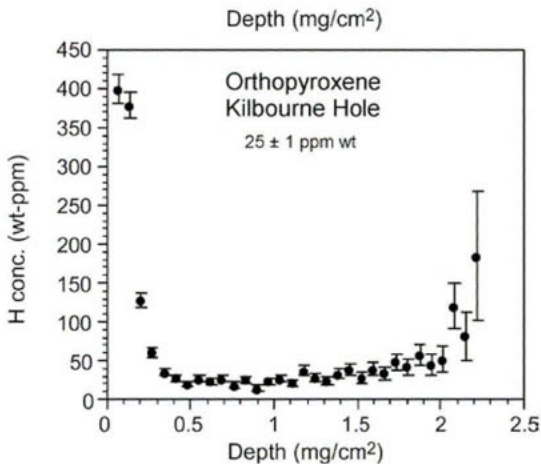


Figure 14. Depth profile of the hydrogen concentration (as H) of an orthopyroxene. (25 ppm H = 223 ppm H₂O). Modified after Figure 1 of Wegdén et al. (2005).

In each of these examples of p-p scattering, the potential of the method for geologic samples was clearly demonstrated, but as was the case of the NRA in the early 1980's, significant effort will be required before it becomes a rigorous, accurate analytical technique. Other approaches have been suggested (Wirth 1997) such as electron energy-loss spectroscopy (EELS), but have not been developed into accurate analytical methods for hydrogen in the nominally anhydrous minerals. Hopefully, geoscientists will remain associated with the nuclear physics community to bring these promising tools into the realm of a routinely useable analytical instrument.

Nuclear magnetic resonance

At first, one would think that proton nuclear magnetic resonance ($^1\text{H-NMR}$), should be an ideal method for studying H in minerals if the content of iron and other paramagnetic ions is low (less than about 0.4 wt% FeO). Although proton NMR is widely used in the chemical sciences, it has seen comparatively little application to the low concentrations of water in the nominally anhydrous minerals in part because of its low sensitivity for protons. A major challenge to the investigation of nominally anhydrous silicate minerals is overcoming or accommodating the sensitivity limits of the technique. Quantitative NMR measurements becomes difficult at H concentrations less than about 1000 ppm wt because the probe background overwhelms the sample signal unless the background is minimized through the use of pulse sequences or is somehow subtracted from the sample signal. Furthermore, the concentrations of paramagnetic transition elements are sufficiently high in most minerals that they seriously compromise or effectively eliminate the proton signal through inhomogeneous magnetic interactions. Consequently, the small amount of proton NMR conducted on minerals has been largely focused on stoichiometrically hydrous minerals and, in particular, on synthetic ones with a minimal paramagnetic component.

Early NMR work on a nominally anhydrous mineral focused on the channel water in beryl where workers found the NMR signal from water in the channels and were able to conclude that the H-H vector was parallel to the *c*-axis (Pare and Ducros 1964; Sugitani et al. 1966; Zayarzina et al. 1969). Later work by (Carson et al. 1982) was concerned with the water in cordierite and found that the water was undergoing some kind of motion on a time scale faster than one microsecond. However, none of these studies attempted to quantitatively determine the absolute amount of water in the minerals from the NMR spectrum. Subsequent studies of beryl did distinguish between two orientations of water and determined their relative proportions (Charoy et al. 1996; Lodzinski et al. 2005).

The first attempt to examine a range of nominally anhydrous minerals (Yesinowski et al. 1988) used a method known as magic angle spinning NMR. NMR spectra of solids are usually very broad due to magnetic anisotropic interactions among components of the crystals. However, high-resolution spectra can often be obtained through a method known as "magic angle" spinning NMR (MAS-NMR). In this experiment, the sample holder is rapidly spun with its axis 54.7° with respect to the applied magnetic field. If the line shape of the non-spinning sample is dominated by inhomogeneous interactions, as it often is for minerals with low hydrogen contents, magic angle spinning produces a sharp central band as well as a set of "spinning sidebands" spaced at integer multiples of the spinning frequency. Paramagnetic metal ions in the sample can complicate the NMR experiment because they introduce additional interactions with their unpaired electron spins.

In addition to a number of stoichiometrically hydrous minerals, Yesinowski et al. (1988) examined microcline, quartz, and nepheline and grossular with ^1H MAS NMR spectra. Although the found mostly fluid inclusions, they were able to show that different hydrous species could be distinguished but determined only their relative amounts (Fig. 15).

Cho and Rossman (1993) further developed the technique for minerals and presented data on OH in grossular crystals with 0.17 to 0.31 wt% H₂O. They were able to show that in low

water-content garnets, the mode of substitution is not dominated by the hydrogarnet substitution ($\text{H}_4\text{O}_4^{4-}$), but rather by protons in pairs (Fig. 16).

Proton NMR is sensitive to just the hydrogen environment and, and is inherently quantitative. Relative amounts of various species can be determined, and, with suitable calibration, so can the absolute hydrogen content of the sample. To avoid the problem with paramagnetic components in natural samples, Kohn (1996) synthesized synthetic pyroxenes and forsterite and used NMR to study their hydrous components. He reported that they contained 0.02 to 0.24 wt% H_2O . This and a subsequent report (Kohn 1998) indicated that the concentrations of hydrous components in these fine-grained materials were much higher than any earlier study suggested.

Keppler and Rauch (2000) subsequently showed that polycrystalline materials have much higher water contents than the corresponding single crystal and suggested that the high water contents reported by Kohn (1996) were not representative of the true water content of the crystals. Contributions from hydrous species on grain boundaries, growth defects and submicroscopic fluid (or melt) inclusions are possible sources of these problems. Keppler and Rauch repeated an observation that this author's group has long recognized: "measurements [of low hydrogen content] on powders are generally not reliable, no matter which analytical method is applied." A following section discusses observations of elevated concentrations of water in mineral surfaces in more detail.

An approximately universal absorption coefficient for the infrared spectra of feldspars was determined from ^1H -MAS NMR spectra by Johnson and Rossman (2003). In this study, the spectra were used to determine the H concentration of three alkali feldspars and for the first time, eight plagioclase feldspars. To accurately measure structural H concentrations in

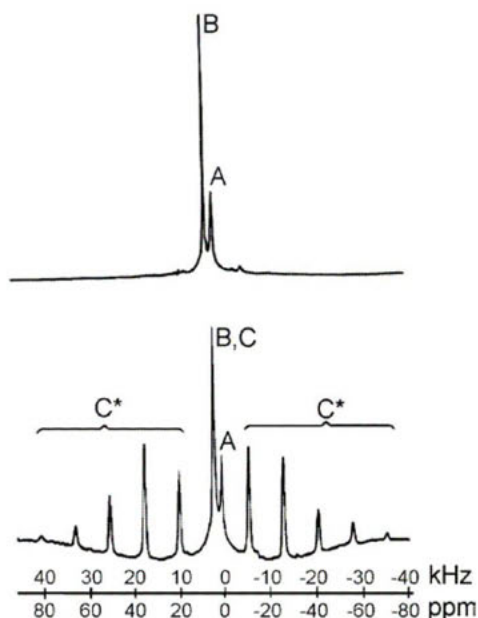


Figure 15. ^1H magic angle NMR spectra at 500 MHz of (top) microcline feldspar from Lake George, Colorado and (bottom) microcline from the White Queen Mine, Pala, California. Peak A is an organic contaminant; peak B is water in fluid inclusions; peak C is a structurally bound, isolated H_2O group; and peaks C* are the spinning sidebands of the structurally bound H_2O group. Modified after Figure 7 of Yesinowski et al. (1988).

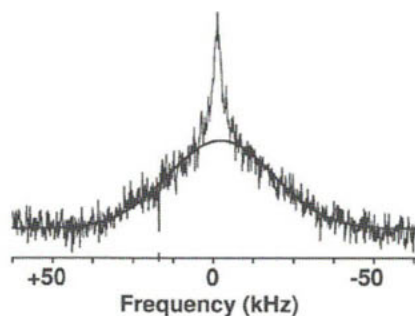


Figure 16. Proton MAS-NMR spectra of grossular from the Lelatemala Mountains, Tanzania, with 0.17 wt% H_2O showing 2 types of hydrogen. Data were obtained with 2000 scans, a 4 second delay between each scan, and a Gaussian line fit. The narrow line signal near zero kHz is from a proton either far removed from other H nuclei or is part of a mobile species within the sample. The broad band arises from pairs of protons in close proximity to each other, rather than a hydrogarnet substitution (Cho and Rossman 1993)

samples with such low H contents (<1000 ppm H₂O) it was necessary to eliminate the signal due to adsorbed water on the coarsely ground (45 to 149 μm particle size) NMR sample through a combination of sample handling protocols and background subtraction. Samples weighed about 150 mg and were spun at 12 kHz in a 500 MHz spectrometer. It was necessary to wait about 100 seconds between scans to allow the spin alignment to recover from the previous scan.

They found that their plagioclase samples contained structural OH in the range of 210-510 ppm H₂O by wt. The microclines contained structural molecular water (1000-1400 ppm H₂O) in the microcline and the Eifel sanidine sample contained only structural OH (170 ppm H₂O). An approximately linear trend is produced when the total integrated mid-IR absorbance is plotted versus the concentration of structural H determined from NMR (OH and H₂O) for both plagioclase and alkali feldspars (Fig. 17). The NMR work of Johnson and Rossman also showed that the pegmatitic and metamorphic albite samples, while transparent, contain variable (40-280 ppm H₂O) concentrations of microscopic to sub-microscopic fluid inclusions.

Xia et al. (2000) also reported using ¹H MAS NMR to calculate the water concentrations of three anorthoclase megacrysts that contained between 365 and 915 ppm H₂O. Very little additional quantitative NMR of the nominally anhydrous minerals has been presented. An earlier paper by Kalinichenko et al. (1989) reported quantitative ¹H-NMR for andalusite and sillimanite, and concluded that the OH groups are bound to Si ions at concentrations of 2.0 and 1.7 wt% H₂O, respectively. In light of other studies, it is unlikely that these values represent intrinsic OH in the phases, but more likely, represent alteration products. In other applications, NMR, in collaboration with other spectroscopic methods, has been used to study the dynamics of water in minerals (Winkler 1996) and for imaging of protons in geological solids (Nakashima et al. 1998).

Secondary ion mass spectrometry (SIMS)

SIMS, also commonly known as the ion microprobe, has held promise as an ideal method to analyze hydrogen in minerals. An ion beam sputters ions from the sample and the ions are directed to a mass spectrometer where they are counted. The analytical volume in a conventional

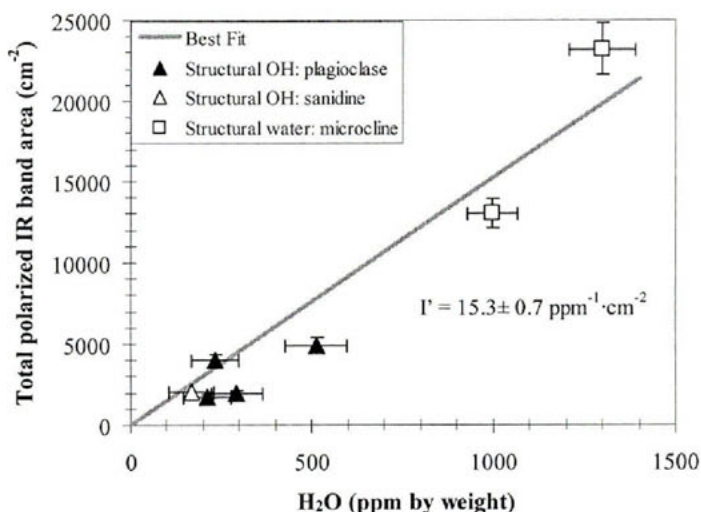


Figure 17. Total polarized integrated band area in the mid-IR per cm thickness versus the concentration of H (in ppm H₂O by weight) determined from NMR spectra for feldspars containing structural hydrogen. The slope of the best-fit line through the data is used to obtain the absorption coefficients (I and I'). From Fig. 5a of Johnson et al. (2003).

SIMS instrument is only a few tens of cubic micrometers, and the sensitivities are potentially in the few ppm range. NanoSIMS instruments have the potential to determine hydrogen in volumes on the order of tens of cubic nanometers. In practice, SIMS microanalysis for trace hydrogen in anhydrous minerals has proven challenging because of the high levels of background signals for hydrogen (Steele 1986; Yurimoto et al. 1989) and the matrix effects (Hervig et al. 1987). Most of the initial attempts to analyze hydrogen by SIMS reported detection limits of hundreds of ppm and few of these studies analyzed the samples by an independent analytical method to confirm the accuracy of low-hydrogen concentration measurements.

Early efforts were directed towards the analysis of H in quartz crystals. Yurimoto et al. (1989) used SIMS to analyze hydrogen in quartz crystals and fused silica glasses and found that the hydrogen secondary ion intensities were proportional to the hydrogen contents determined by infrared (IR) absorption over the range of 5 to 3000 ppm-atomic H/Si (down to about 6 ppm H₂O).

Kurosawa et al. (1992, 1993) reported the successful analysis trace hydrogen in mantle olivines by carefully considering the source of problems and instituting corrective measures. They used the Cameca IMS 3f ion microprobe at the University of Tsukuba with a primary high-purity, mass-filtered ¹⁶O⁻ ion beam that was accelerated to 14.5 keV with a beam current of about 100 nA and a spot size of 100 μm in diameter. As the methods were refined, Kurosawa et al. (1997) determined that the hydrogen content in mantle xenolithic olivines ranges from 10 to 60 ppm wt H₂O, a concentration range that is consistent with the previous range of hydrogen contents obtained by IR spectra (Miller et al. 1987). However, no single sample was ever run with the two analytical methods as a crosscheck for consistency.

A variety of precautions was necessary to obtain this level of sensitivity for hydrogen. Secondary ions, including ¹H⁺, were collected from the central 60 μm region of the sputtered area using a mechanical aperture while the pressure in the sample chamber was maintained at 0.2 μPa. In addition, a cold trap of liquid nitrogen was used to improve the vacuum near the sample. The samples for SIMS measurements were coated with a thin gold film to eliminate electrostatic charging.

Hydrogen amounts were determined from a calibration curve. For quantitative hydrogen analysis, the standards were H⁺-implanted San Carlos olivine. The method provided suitable standard materials for trace hydrogen while simultaneously resolving matrix effect problems. The calibration curve was obtained in the concentration ranges from about 2 to 1600 parts per million (ppm) H₂O by weight. Kurosawa et al. (1992a) report that the reproducibility was within 10% in repeat analyses.

SIMS determination of water in minerals has been practiced mostly when concentrations of water are in excess of 0.1% wt. A variety of synthetic phases such as silicate perovskite (Murakami et al. 2002) and majoritic garnet (Katayama et al. 2003) have analyzed by this method. The instrument has subsequently been used to study garnets, pyroxenes, and olivines from mantle xenoliths (Kurosawa et al. 1993, 1997).

One strategy to improve SIMS analyses for hydrogen is to use ²H (deuterium) rather than ¹H where possible. There are significant advantages with regard to background signals. For example, Pawley et al. (1993) report that background H counts are four orders of magnitude higher than the background D counts. This requires either synthesizing samples with deuterium or conducting deuterium exchange prior to analysis.

Koga et al. (2003) were the first to report analyses of hydrogen concentrations in both natural mantle minerals and experimentally annealed crystals where the calibration was established with olivine, pyroxene, garnet, amphibole and micas that were previously calibrated by other methods. They employed stringent cleaning and drying procedures to eliminate contamination from water and organic solvents and adhesives used in sample preparation.

They used a Cs^+ primary ion beam rather than an O^- beam that gave high hydrogen backgrounds. To minimize hydrogen backgrounds, they took extraordinary precautions. The entire Cameca 6f instrument was baked for at least 24 hours before an analytical session. The electron gun was kept on for 12 hours prior to the analysis at about 7 times the normal analytical current to desorb hydrogen. Organic adhesives were avoided and samples were mounted in indium metal. Through these precautions, they were able to reduce their background to 2 to 4 ppm wt of H on “zero”-hydrogen samples.

When they examined the SIMS calibrations for nominally anhydrous minerals, they considered the consistency of the calibration lines and placed a premium on reproducing samples for which OH measurements from nuclear reaction analysis (GRR1012, KLV-23 olivines) and manometry (KBH-1 orthopyroxene, PMR-53 clinopyroxene, MON-9 garnet, hydrous phases) are available. Their method resulted in SIMS calibrations that are less likely to inherit systematic errors from a particular corroborating method. Their results were excellent (Fig. 18). Their success points to the future where SIMS determinations of hydrogen in minerals will be more widely utilized. SIMS offers the advantages of analysis of a smaller volume, and the corresponding ability to obtain finer lateral and depth resolution. Furthermore, it appears not to require orientation of intrinsically anisotropic samples.

Further development of the SIMS method with additional calibrations and intercalibration with FTIR standards will be presented by Aubaud et al. (2006). They demonstrate that with careful attention to avoiding contamination and prolonged instrument bakeout, hydrogen background values equivalent to less than 5 ppm by weight H_2O in olivine can be obtained. They also observed phase-specific calibration trends for minerals such as olivine, pyroxenes and garnets that varied by up to a factor of four.

SIMS will probably always be a complimentary method to infrared spectroscopy because SIMS is, of course, unable to distinguish among hydrous species and cannot distinguish between intrinsic hydrogen and contaminating phases or inclusions. There is no doubt that this application of SIMS will be an area of significant growth in the future.

PREVIOUS REVIEWS OF METHODS

An earlier review that covered the use of IR spectroscopy to study hydrous components in minerals was presented by Rossman (1988). Subsequent reviews have focused on various aspects of OH in the nominally anhydrous minerals (Rossman 1996, 1998; Skogby 1999;

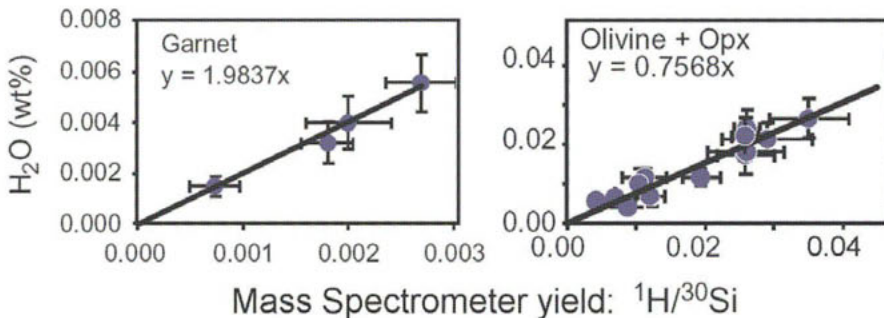


Figure 18. SIMS calibration for garnet and a combined olivine-orthopyroxene calibration from Figure 5 of Koga et al. (2003).

Ingrin and Skogby 2000; Beran and Libowitzky 2003). One review that deals with analytical methods for geological samples is Ihinger et al. (1994) that concentrates on glasses. Several reviews of nuclear reactions used to analyze hydrogen and other light elements have appeared. Among the ones that deal with hydrogen are Lanford (1978, 1992) and Cherniak and Lanford (2001). Reviews focused on mineral applications are few (Ryan 2004).

SURFACE WATER

Hydrous components can occur not only within a crystal, but will also occur on its surface. All of the nuclear analysis methods and SIMS show that the surfaces of minerals can contain considerably higher concentrations of hydrogen than is contained in the interior, even when under high-vacuum conditions. Bell et al. (2003) found about 20 times as much water on the surface of olivine KLV-23 as was present in the interior. The NPA analysis of Bell et al. (Fig. 19) shows that outermost 500 nm contains a highly elevated H concentration and that accurate analyses of the bulk hydrogen content should begin 1.5 to 2 μm below the surface. Similar surface concentrations were noted by Clark et al. (1978) and Dersch and Rauch (1999) on quartz samples. In their ERDA experiment with a garnet with 0.17 wt% H_2O , Sweeney et al. (1997) detected about 4.5 \times as much water in the outermost 50 nm of the sample (Fig. 20). Likewise, Katayama et al. (2003) found that a factor of 24 \times greater water was liberated from the surface of a pyrope when the SIMS experiment began than when a steady state was reached after rastering the surface (Fig. 21). This illustrates why it is common practice to clean the sample by ion-rastering before analyzing the water content of low-hydrogen-content minerals. Clark et al. (1978) obtained F-19 depth profiles of quartz and determined that it exhibited a region of high H concentration near surface region (down to a depth of about 200 nm), before the concentrations decreased to the bulk value of the sample.

While there is certainly several thousand ppm-wt H_2O absorbed water on the surface of minerals while under high vacuum, there is some question of whether the ion beams drive hydrogen atoms below the surface during the analysis, or if a diffusion gradient naturally exists. Obviously, the depth of elevated hydrogen contents will strongly depend upon the quality of the surface and the amount of surface damage experienced by the sample during grinding and polishing.

An extreme example of water near the surface of a mineral was demonstrated during the heating experiments on sillimanite crystals (Beran et al. 1989). The experiment consisted of obtaining the infrared spectrum of OH bands after each step in a step-heating experiment. As Figure 22 shows, the weight loss proceeded at a proportionally faster rate than the decrease of

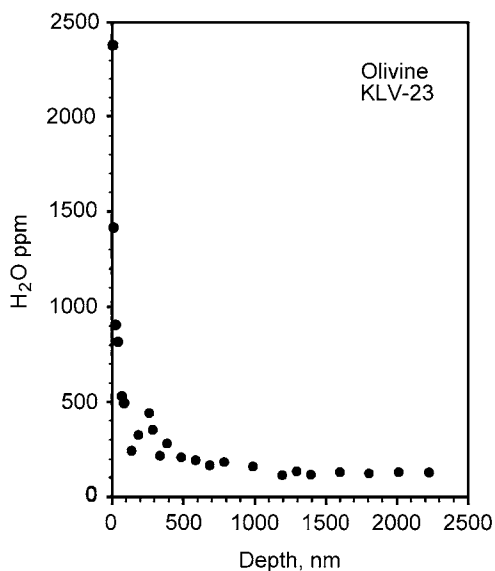


Figure 19. Nuclear reaction analysis depth profile of a mantle olivine that shows elevated water content at the surface of the sample even while held in an ultra-high vacuum chamber. From Bell et al. (2003).

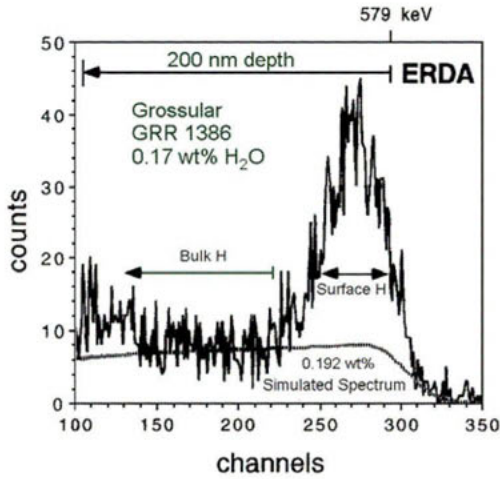


Figure 20. An ERDA profile of a grossular showing increased water at the surface. Modified after Figure 2b of Sweeney et al. (1997).

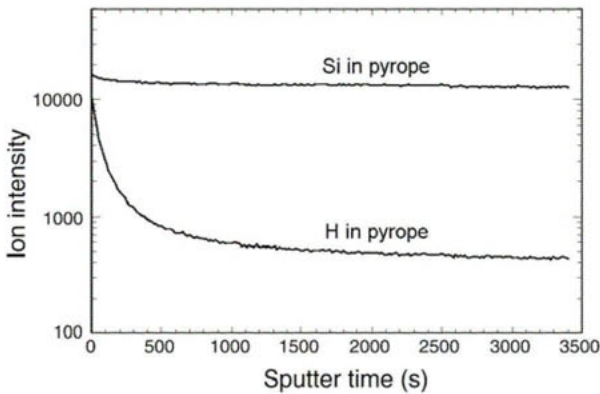


Figure 21. A SIMS analysis of pyrope that shows elevated water content at the surface of the sample. From Figure 2 of Katayama et al. (2003).

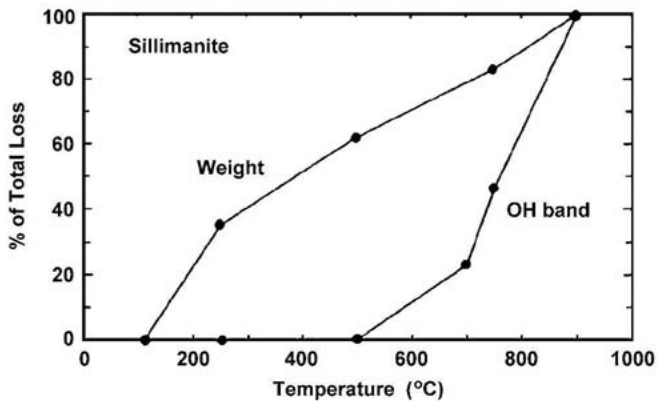


Figure 22. The results of a step-heating experiment where both the weight loss and the infrared spectrum are measured that shows much "impurity" water is lost from the sample before the intrinsic OH bands begin to decrease. From Figure 5 of Beran and Rossman (1989).

the OH bands. Beran et al. concluded that much of the water was held as molecular water at the edges of the crystal, probably associated with surface damage and incipient cleavages in a mineral with perfect cleavage perpendicular to the direction in which the infrared light was being transmitted through the crystal. In the infrared experiment, the OH bands were measured only in the center of the crystal, but the weight loss was occurring from both within the center (as OH groups) and from the damaged regions at the edge (mostly as molecular water). Quite likely, a similar problem contributed to the high values of OH in kyanite reported by Beran and Göttinger (1987).

CURRENT STATUS OF CALIBRATIONS

A number of minerals have been calibrated sufficiently well that their infrared spectra can be routinely used in determinations of the OH contents of important mantle phases and an assortment of crustal phases. Because the density of many of these phases is not highly variable as they are commonly encountered, a single calibration constant can provide a useful tool for many routine, practical applications. Those currently available are presented in Table 2. Several of these minerals have significant variation in the general appearance of their infrared spectra and require additional study to determine how the calibration varies with the different types of infrared spectra. It is certain that our work is far from over.

GLASSES

Also worth pointing out are the extensive efforts to calibrate the IR spectra of hydrous components in geological glasses (Stolper 1982; Newman et al. 1986; Silver and Stolper 1989). Methods used to analyze volatiles in glasses were reviewed by Ihinger et al. (1994). Since the original infrared calibrations appeared, a number of refinements have appeared involving a variety of calibration methods such as Karl-Fischer titration, nuclear reaction analysis, and SIMS (Ohlhorst et al. 2001; Hauri et al. 2002; Mandeville et al. 2002; Leschik et al. 2004; Okumura and Nakashima 2005). The glass calibrations have made it possible to examine melt inclusions in minerals and to study partitioning of water between crystal and melt.

Table 2. Representative calibration formulas for H₂O and OH in minerals*

Forsterite	H ₂ O (ppm wt) = 0.188 × Abs_{tot} (integrated per cm)	Bell et al. (2003)
Kyanite	H ₂ O (ppm wt) = 0.147 × Abs_{tot} (integrated per cm)	Bell et al. (2004)
Vesuvianite	H ₂ O (ppm wt) = 0.085 × Abs_{tot} (integrated per cm)	Bellatreccia et al. (2005)
Nepheline	H ₂ O (ppm wt) = 0.672 × Abs_{tot} (integrated per cm)	Beran and Rossman (1989)
Orthopyroxene	H ₂ O (ppm wt) = 0.067 × Abs_{tot} (integrated per cm)	Bell et al. (1995)
Clinopyroxene	H ₂ O (ppm wt) = 0.141 × Abs_{tot} (integrated per cm)	Bell et al. (1995)
Pyrope	H ₂ O (ppm wt) = 0.240 × Abs_{tot} (integrated per cm)	Bell et al. (1995)
Grossular	H ₂ O (ppm wt) = 0.140 × Abs_{tot} (integrated per cm)	Rossman and Aines (1991)
Hydrogrossular	H ₂ O (ppm wt) = 0.264 × Abs_{tot} (integrated per cm)	Rossman and Aines (1991)
Spessartine	H ₂ O (ppm wt) = 0.125 × Abs_{tot} (integrated per cm)	Rossman (1988)
Feldspars	H ₂ O (ppm wt) = 0.065 × Abs_{tot} (integrated per cm)	Johnson and Rossman (2003)
Rutile	H ₂ O (ppm wt) = 0.110 × Abs_{tot} (integrated per cm)	Maldener et al. (2001)
Cassiterite	H ₂ O (ppm wt) = 0.039 × Abs_{tot} (integrated per cm)	Maldener et al. (2001)

*These formula are representative only for minerals that have spectra close to those of the standard minerals used in the calibrations. In all cases, they represent the sum of the integrated absorption intensities in the OH region for three orientations.

ACKNOWLEDGMENTS

The results in this chapter from the author's laboratory have been supported for many years by the National Science Foundation (USA), most recently by grant EAR-0337816. The contributions of the author's students and postdocs, visitors and collaborators have been pivotal in the establishment of quantitative H determinations and are gratefully acknowledged. The collaboration of Prof. Friedel Rauch (Frankfurt, Germany) and his students with nuclear analyses has been invaluable and proved to be the key to quantitative determinations at low concentrations.

REFERENCES

- Aines RD, Rossman GR (1984) Water content of mantle garnets. *Geology* 12:720-723
- Asimow PD, Stein LC, Mosenfelder JL, Rossman GR (2006) Quantitative polarized infrared analysis of trace OH in populations of randomly oriented mineral grains. *Am Mineral* 91:278-284
- Aubaud C, Withers AC, Hirschmann MM, Guan Y, Leshin LA, Mackwell SJ, Bell DR (2006) Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals. *Am Mineral*. submitted.
- Barbour JC, Doyle BL (1995) Elastic Recoil Detection: ERD (or Forward Recoil Spectrometry: FRES). *In: Handbook of Modern Ion Beam Analysis*. Tesmer JR et al. (eds) Materials Research Society, p 83-138
- Bell DR, Ihinger PD, Rossman GR (1995) Quantitative analysis of trace OH in garnet and pyroxenes. *Am Mineral* 80:463-474
- Bell DR, Rossman GR, Maldener J, Endish D, Rauch F (2003) Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum. *J Geophys Resch* 108:ECV 8-1 - 8-9. doi:10.1029/2001JB000679, 2003
- Bell DR, Rossman GR, Maldener J, Endish D, Rauch F (2004) Hydroxide in kyanite: A quantitative determination of the absolute amount and calibration of the IR spectrum. *Am Mineral* 89:998-1003
- Bellamy LJ, Owen AJ (1969). A simple relationship between the infrared stretching frequencies and the hydrogen bond distances in crystals. *Spectrochim Acta* A25:329-333.
- Beran A, Zemann J (1969a) Messung des Ultrarot-Pleochroismus von Mineralen. XI. Der Pleochroismus der OH Streckfrequenz in Andalusite. *Tschermaks Miner Petr Mitt* 13:285-292
- Beran A, Zemann J (1969b) Ultrarotspektroskopische Untersuchung über den OH-Gehalt von Rutile, Anatas, Brookite, Cassiterite. *Österreich Akad Wiss, Sitzung Juni, 27:165-167*
- Beran A (1970a) Messung des Ultrarot-Pleochroismus von Mineralen. IX. Der Pleochroismus der OH-Streckfrequenz in Titanit. *Tschermaks Miner Petr Mitt* 14:1-5
- Beran A (1970b) Ultrarotspektroskopischer Nachweis von OH-Gruppen in den Mineralen der Al_2SiO_5 -Modifikationen. *Österr Akad Wiss, Math-naturwiss K2, Anzeiger Jg 1970:184-185*
- Beran A (1970c) Messung des Ultrarot-Pleochroismus von Mineralen. XII. Der Pleochroismus der OH-Streckfrequenz in Disthen. *Tschermaks Miner Petr Mitt:16:129-135*
- Beran A (1970d) Messung des Ultrarot-Pleochroismus von Mineralen. XIII. Der Pleochroismus der OH-Streckfrequenz in Axinit. *Tschermaks Miner Petr Mitt* 15:71-80
- Beran A, Zemann, J. (1971) Messung des Ultrarot-Pleochroismus von Mineralen. XI. Der Pleochroismus der OH-Streckfrequenz in Rutil, Anatas, Brookit und Cassiterit. *Tschermaks Miner Petr Mitt* 15:71-80
- Beran A, Göttinger MA (1987) The quantitative IR spectroscopic determination of structural OH groups in kyanites. *Mineralogy Petrology* 36:41-49
- Beran A, Rossman GR, Grew ES (1989) The hydrous component of sillimanite. *Am Mineral* 74:812-817
- Beran A, Rossman GR (1989) The water content of nepheline. *Mineral Petrology* 40:235-240
- Beran A and Libowitzky E (2003) IR spectroscopic characterization of OH defects in mineral phases. *Phase Transitions* 76:1-15
- Brunner GO, Wondratschek H, Laves F (1961) Infrared studies on the incorporation of H in natural quartz. *Z Elektrochem Angewandte Physik Chemie* 65:735-50
- Carson DG, Rossman GR, Vaughan RW (1982) Orientation and motion of water molecules in cordierite: A proton nuclear magnetic resonance study. *Phys Chem Mineral* 8:14-19
- Charoy B, de Donato P, Barres O, Pinto-Coelho C (1996) Channel occupancy in an alkali-poor beryl from Serra Branca (Goias, Brazil): spectroscopic characterization. *Am Mineral* 81:395-403
- Cherniak DJ, Lanford WA (2001) Nuclear reaction analysis. *In: Non-Destructive Elemental Analysis*. Alfassi ZB (ed) Blackwell Science Ltd., p 308-338
- Cho H, Rossman GR (1993) Single-crystal NMR studies of low-concentration hydrous species in minerals: Grossular garnet. *Am Mineral* 78:1149-1164

- Clark GJ, White CW, Allred DD, Appleton BR, Tsong IST (1978) Hydrogen concentration profiles in quartz determined by a nuclear reaction technique. *Phys Chem Mineral* 3:199-211
- Cohen BL, Fink, CL, Degnan JH (1972) Nondestructive analysis for trace amounts of hydrogen. *J Appl Phys* 43:19-25
- Dersch O, Rauch F (1999) Water uptake of quartz investigated by means of ion-beam analysis. *Fresenius J Anal Chem* 365:114-116
- Dodd DM, Fraser DB (1965) The 3000-3900 cm^{-1} absorption bands and anelasticity in crystalline α -quartz. *Phys Chem Solids* 26:673-86
- Dodd DM, Fraser DB (1967) Infrared studies of the variation of H-bonded OH in synthetic alpha-quartz. *Am Mineral* 52:149-160
- Dyar MD, Martin SV, Mackwell LSJ, Carpenter S, Grant CA, McGuire AV (1996) Crystal chemistry of Fe^{3+} , H^+ , and D/H in mantle-derived augite from Dish Hill: Implications for alteration during transport. *Mineral Spectroscopy: A Tribute to Roger G. Burns*. The Geochemical Society, Special Publication No. 5:289-303.
- Dyar MD, McCammon C, Schaefer MW (eds)
- Eiler JM, Kitchen N (2001) Hydrogen-isotope analysis of nanomole (picoliter) quantities of H_2O . *Geochim Cosmochim Acta* 65:4467-4470
- Endisch D, Sturm H, Rauch F (1993) Development of a measuring set-up for high-sensitivity analysis for hydrogen by the nitrogen-15 nuclear reaction technique. *Fresenius J Anal Chem* 346:205-207
- Endisch D, Sturm H, Rauch F (1994) Nuclear reaction analysis of hydrogen at levels below 10 at.ppm, *Nucl Instrum Methods Phys Res Sect B* 84:380-392
- Farrell EF, Newnham RE (1967) Electronic and vibrational absorption spectra in cordierite. *Am Mineral* 52:380-388
- Flörke DW, Köhler-Herbertz B, Langer K, Törges I (1982) Water in microcrystalline quartz of volcanic origin: Agates. *Contrib Mineral Petrog* 80:329-333
- Fujimoto K, Fukutani K, Tsunoda M, Yamashita H, Kobayashi K (1993) Hydrogen depth profiling using $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonant nuclear reaction on water-treated olivine surfaces and characterization of hydrogen species. *Geochem J* 27:155-162
- Furuno K, Komatsubara T, Sasa K, Oshima H, Yamato Y, Ishii S, Kimura H, and Kurosawa M (2003) Measurement of hydrogen concentration in thick mineral or rock samples. *Nucl Instr Meth Phys Research Sect B* 210:459-463
- Griggs DT, Blacic JD (1965) Quartz: anomalous weakness of synthetic crystals. *Science* 147:292-295.
- Hammer VMF, Beran A, Endisch D, Rauch F (1996) OH concentrations in natural titanites determined by FTIR spectroscopy and nuclear reaction analysis. *Eur J Mineral* 8:281-288
- Hauri E, Wang JH, Dixon JE, King PL, Mandeville C, Newman S (2002) SIMS analysis of volatiles in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chem Geol* 183:99-114
- Hervig RL, Stanton TR, Williams P (1987) Ion probe microanalyses of hydrogen in glasses and minerals (abstr). *EOS* 68:441
- Hofmeister AM, Rossman GR (1985a) A model for the irradiative coloration of smoky feldspar and the inhibiting influence of water. *Phys Chem Mineral* 12:324-332
- Hofmeister AM, Rossman GR (1985b) A spectroscopic study of irradiation coloring of amazonite: structurally hydrous, Pb-bearing feldspar. *Am Mineral* 70:794-804
- Holdaway MJ, Dutrow BL, Borthwick J, Shore P, Harmon RS, Hinton RW (1986) H content of staurolite as determined by H extraction line and ion microprobe. *Am Mineral* 71:1135-1141
- Ilchenko EA, Korzhinskaya VS (1993) Hydroxyl groups in synthetic and natural zircons. *Mineralogicheskii Zhurnal* 15:26-39
- Ihinger PD, Hervig RL, McMillan PF (1994) Analytical methods for volatiles in glasses. *Rev Mineral* 30:67-121
- Ingrin J, Skogby H (2000). Hydrogen in nominally anhydrous upper-mantle minerals: concentration levels and implications. *Eur J Mineral* 12:543-570
- Johnson EA, Rossman GR (2003) The concentration and speciation of hydrogen in feldspars using FTIR and ^1H MAS NMR spectroscopy. *Am Mineral* 88:901-911
- Kalinichenko AM, Katalenets AI, Proshko VY, Pasal'skaya LF (1989) Water in minerals of Al_2SiO_5 composition (based on the hydrogen-1 and silicon-29 NMR spectra). *Geokhimiya* 1989:1024-8 (in Russian)
- Katayama I, Hirose K, Yurimoto H, Nakashima S (2003) Water solubility in majoritic garnet in subducting oceanic crust. *Geophys Resch Letts* 30:2155: doi:10.1029/2003GL018127, 2003
- Kats A, Haven Y (1960) Infrared absorption bands in α -quartz in the 3- μ region. *Phys Chem Glasses* 1:99-102
- Kats A (1962) Hydrogen in α -quartz. *Philips Research Reports* 17:133-195, 201-279
- Keppler H, Rauch M (2000) Water solubility in nominally anhydrous minerals measured by FTIR and ^1H MAS NMR: the effect of sample preparation. *Phys Chem Mineral* 27:371-376
- King JC, Wood DL, Dodd DM (1960) Infrared and low-temperature acoustic absorption in synthetic quartz. *Phys Rev Lett* 4:500-501

- King PL, Vennemann TW, Holloway JR, Hervig RL, Lowenstern JB, Forneris JF (2002) Analytical techniques for volatiles: A case study using intermediate (andesitic) glasses. *Am Mineral* 87:1077-1089
- Kirby SH, McCormick JW (1979) Creep of hydrolytically weakened synthetic quartz crystals oriented to promote {2-1-10}<0001> slip: a brief summary of work to date. *Bull Minéral* 102:124-137
- Koga K, Hauri E, Hirschmann M, Bell D (2003) Hydrogen concentration analyses using SIMS and FTIR: Comparison and calibration for nominally anhydrous minerals. *Geochem Geophys Geosyst* 4: doi: 10.1029/2002GC000378
- Kohn SC (1996) Solubility of H₂O in nominally anhydrous mantle minerals using ¹H MAS NMR. *Am Mineral* 81:1523-1526
- Kohn SC (1998) ¹H MAS NMR studies of water solubilities and dissolution mechanisms in olivine, clinopyroxene and orthopyroxene. *Mineral Mag* 62A:799-800
- Kuhn D, Rauch F, Baumann H (1990) A Low-background detection system using a BGO detector for sensitive hydrogen analysis with the ¹H (¹⁵N, alpha-gamma)¹²C reaction. *Inst Methods Phys Res B* 45:252-255
- Kurosawa M, Yurimoto H, Matsumoto K, Sueno S (1992) Hydrogen analysis of mantle olivine by secondary ion mass spectrometry. *In: High-Pressure Research in Mineral Phys: Application to Earth and Planetary Sciences*. Syono S, Manghnani MH (eds) Terra Pub-Am Geophys Union, p 283-287
- Kurosawa M, Yurimoto H, Matsumoto K, Sueno S (1993) Water in Earth's mantle: hydrogen analysis of mantle olivine, pyroxenes and garnet using the SIMS. *Proc Lunar Planet Sci Conf* 24th, 839-840
- Kurosawa M, Yurimoto H, Sueno S (1997) Patterns in the hydrogen and trace element compositions of mantle olivines. *Phys Chem Mineral* 24:385-395
- Lanford WA (1978) ¹⁵N Hydrogen profiling: Scientific applications, *Nucl Instr Meth Phys Res B* 149:1-8
- Lanford WA (1992) Analysis for hydrogen by nuclear reaction and energy recoil detection. *Nucl Instrum Methods in Phys Res Sect B* 66:65-82
- Langer K, Flörke OW (1974) Near infrared absorption spectra (4000-9000 cm⁻¹) of opals and the role of "water" in these SiO₂·nH₂O minerals. *Fortschr Minereral* 52:17-51
- Lee RR, Leich, DA, Tombrello TA, Ericson JE, Friedman I (1974) Obsidian hydration profile measurements using a nuclear reaction technique. *Nature* 250:44-7
- Leschik M, Heide G, Frischat GH, Behrens H, Wiedenbeck M, Wagner N, Heide K, Geissler H, Reinholz U (2004) Determination of H₂O and D₂O contents in rhyolitic glasses. *Phys Chem Glasses* 45:238-251
- Libowitzky E, Rossman GR (1996) Principles of quantitative absorbance measurements in anisotropic crystals. *Phys Chem Mineral* 23:319-327
- Libowitzky E, Rossman GR (1997) An IR absorption calibration for water in minerals. *Am Mineral* 82:1111-1115
- Libowitzky E (1999) Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie* 130:1047-1059
- Lodzinski M, Sitarz M, Stec K, Kozanecki M, Fojud Z, Jurga, S (2005) ICP, IR, Raman, NMR investigations of beryls from pegmatites of the Sudety Mts. *J Mol Struct* (2005) 744-747:1005-1015
- Lutz HD (1995) Hydroxide ions in condensed materials - correlation of spectroscopic and structural data. *Struct Bonding* 82:85-103
- Mackwell SJ, Kohlstedt DL, Paterson MS (1985) The role of water in the deformation of olivine single crystals. *J Geophys Res* 90:1319-1333
- Maldener J, Rauch F (1997) High energy ion-beam analysis in combination with keV sputtering, in *Application of Accelerators in Research and Industry*. Duggan JL, Morgan IL (eds) AIP Press, p. 689-692
- Maldener J, Rauch F, Gavranic M, Beran A (2001) OH absorption coefficients of rutile and cassiterite deduced from nuclear reaction analysis and FTIR spectroscopy. *Mineral Petrol* 71:21-2
- Maldener J, Hösch A, Langer K, Rauch F (2003) Hydrogen in some natural garnets studied by nuclear reaction analysis and vibrational spectroscopy. *Phys Chem Mineral* 30:337-344
- Mandeville CW, Webster JD, Rutherford MJ, Taylor BE, Timbal A, Faure K (2002) Determination of molar absorptivities for infrared absorption bands of H₂O in andesitic glasses. *Am Mineral* 87:813-821
- Martin RF, Donnay G (1972) Hydroxyl in the mantle. *Am Mineral* 57:554-570
- Miller GH, Rossman GR, Harlow GE (1987) The natural occurrence of hydroxide in olivine. *Phys Chem Mineral* 14: 461-47
- Murakami M, Hirose K, Yurimoto H, Nakashima S, Takafuji N (2002) Water in earth's lower mantle. *Science* 295:1185-1187
- Nakamoto K, Margoshes M, Rundle RE (1955) Stretching frequencies as a function of distances in hydrogen bonds. *J Am Chem Soc* 77:6480-6486
- Nakashima Y, Nakashima S, Gross D, Weiss K, Yamauchi K (1998) NMR imaging of ¹H in hydrous minerals. *Geothermics* 27:43-53
- Newman S, Stolper EM, Epstein SR (1986) Measurement of water in rhyolitic glasses: calibration of an infrared spectroscopic technique. *Am Mineral* 71:1527-1541
- Novak A (1974) Hydrogen bonding in solids. Correlation of spectroscopic and crystallographic data. *Structure and Bonding* 18:177-216

- Ohlhorst S, Behrens H, Holtz F (2001) Compositional dependence of molar absorptivities of near-infrared OH- and H₂O bands in rhyolitic to basaltic glasses. *Chem Geol* 174:5-20
- Okumura S, Nakashima S (2005) Molar absorptivities of OH and H₂O in rhyolitic glass at room temperature and at 400-600 °C. *Am Mineral* 90:441-447
- O'Leary JA, Rossman GR, Eiler J (2006) Hydrogen analysis in minerals by continuous-flow mass spectrometry. *Am Mineral*. in prep.
- Pare X, Ducros P (1964) Nuclear magnetic resonance study of beryl water. *Bull Soc Franc Mineral Crist* 87: 429-33 (in French)
- Paterson MS (1982). The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. *Bull Min ral* 105:20-29
- Pawley AR, McMillan PF, Holloway JR (1993) Hydrogen in stishovite, with implications for mantle water-content. *Science* 261:1024-1026
- Rauch F, Ericson JE, Wagner W, Grimm-Leimsner C, Livi RP, Shi Chengru, Tombrello TA (1992) Hydration of tektite glass. *J Non-Cryst Solids* 144:224-30
- Reichart P, Datzmann G, Hauptner A, Hertenberger R, Wild C, Dollinger G (2004) Three-dimensional hydrogen microscopy in diamond. *Science* 306:1537-1540
- Rossman GR (1975) Joaquinite: the nature of its water content and the question of four-coordinated ferrous iron. *Am Mineral* 60:435-440
- Rossman GR, Rauch F, Livi R, Tombrello TA, Shi CR, Zhou ZY. (1988) Nuclear reaction analysis of hydrogen in almandine, pyrope and spessartite garnets. *N Jb Miner Mh* 1988:172-178
- Rossman GR (1988) Vibrational Spectroscopy of Hydrated Components. *Rev Mineral* 18:193-206
- Rossman GR (1990) Hydrogen in "anhydrous" minerals. *Nucl Instr Meth Phys Res Sect B* 45:41-44
- Rossman GR, Aines RG (1991) The hydrous components in garnets: grossular-hydrogrossular. *Am Mineral* 76: 1153-1164
- Rossman GR (1996) Studies of OH in nominally anhydrous minerals. *Phys Chem Mineral* 23:299-30
- Ryan CG (2004) Ion beam microanalysis in geoscience research. *Nucl Instr Meth Phys Res Sect B* 219-220: 534-549
- Schreyer W, Yoder HS (1964) The system Mg cordierite-H₂O and related rocks. *N Jb Mineralogie Abh* 101: 271-342
- Sie SH, Suter G, Chekmir A, Green TH (1995) Microbeam recoil detection for the study of hydration of minerals. *Nucl Instr Methods Phys Res Sect B* 104:261-26
- Silver L, Stolper E (1989) Water in albitic glasses. *J Petrol* 30:667-709
- Skogby H, Bell DR, Rossman GR (1990) Hydroxide in pyroxene: Variations in the natural environment. *Am Mineral* 75:764-774
- Skogby H (1999) Water in nominally anhydrous minerals. In: *Microscopic Properties and Processes in Minerals*. NATO Science Series. Wright K, Catlow R (eds), Kluwer Acad. Publishers, p 509-522
- Steele LM (1986) Ion probe determination of hydrogen in geologic samples. *N Jb Mineral Mh* 1986:193-202
- Stolper EM (1982) Water in silicate glasses: an infrared spectroscopic study. *Contrib Mineral Petrol* 81:1-17
- Sugitani Y, Nagashima K, Fujiwara S (1966) NMR (nuclear magnetic resonance) analysis of the water of crystallization in beryl. *Bull Chem Soc Japan* 39:672-4
- Sweeney RJ, Prozesky VM, Springhorn KA (1997) Use of the elastic recoil detection analysis (ERDA) microbeam technique for the quantitative determination of hydrogen in materials and hydrogen partitioning between olivine and melt at high pressures. *Geochim Cosmochim Acta* 61:101-113
- Wegdén M, Kristiansson P, Pastovic Z, H. Skogby, Skogby H, Auzelyte V, Elfman M, Malmqvist KG, Nilsson C, Pallon J, Shariff A (2004) Hydrogen analysis by p-p scattering in geological material *Nucl Instr Meth Phys Res Sect B* 219-220:550-554
- Wegdén M, Kristiansson P, Skogby H, Auzelyte V, Elfman M, Malmqvist KG, Nilsson C, Pallon J, Shariff A (2005) Hydrogen depth profiling by p-p scattering in nominally anhydrous minerals. *Nucl Instr Meth Phys Res Sect B* 231:524-529
- Wilkins RWT, Sabine W (1973) Water content of some nominally anhydrous silicates. *Am Mineral* 58: 508-516
- Winkler B (1996) The dynamics of H₂O in minerals. *Phys Chem Mineral* 23:310-318
- Wirth R (1997) Water in minerals detectable by electron energy-loss spectroscopy EELS. *Phys Chem Minerals* 24:561-568
- Wood DL, Nassau K (1967) Infrared spectra of foreign molecules in beryl. *J Chem Phys* 47:2220-8.
- Woodhead JA, Rossman GR, Thomas AP (1991) Hydrous species in zircon. *Am Mineral* 76:1533-1546
- Xia Q, Pan Y, Chen D, Kohn S, Zhi X, Guo L, Cheng H, Wu Y. (2000) Structural water in anorthoclase megacrysts from alkalic basalts: FTIR and NMR study. *Acta Petrologica Sinica* 16:485-491 (in Chinese)
- Xiong F, Rauch F, Shi C; Zhou Z, Livi RP, Tombrello TA (1987) Hydrogen depth profiling in solids: a comparison of several resonant nuclear reaction techniques. *Nucl Instr Meth Phys Res Sect B* 27:432-41

- Yesinowski JP, Eckert H, Rossman GR (1988) Characterization of hydrous species in minerals by high-speed ^1H MAS-NMR. *J Am Chem Soc* 110:1367-1375
- Yurimoto H, Kurosawa M, Sueno S (1989) Hydrogen analysis in quartz crystals and quartz glasses by secondary ion mass spectrometry. *Geochim Cosmochim Acta* 53:751-755
- Zavarzina NI, Gabuda SP, Bakakin VV, Rylov GM (1969) N.M.R. analysis of water in beryls. *Zh Struktur Khimii* 10:804-810 (in Russian)