Hydrogen in nominally anhydrous silicate minerals

Quantification methods, incorporation mechanisms and geological applications

FRANZ A. WEIS
Abstract


The aim of this thesis is to increase our knowledge and understanding of trace water concentrations in nominally anhydrous minerals (NAMs). Special focus is put on the de- and rehydration mechanisms of clinopyroxene crystals in volcanic systems, how these minerals can be used to investigate the volatile content of mantle rocks and melts on both Earth and other planetary bodies (e.g., Mars). Various analytical techniques for water concentration analysis were evaluated.

The first part of the thesis focusses on rehydration experiments in hydrogen gas at 1 atm and under hydrothermal pressures from 0.5 to 3 kbar on volcanic clinopyroxene crystals in order to test hydrogen incorporation and loss from crystals and how their initial water content at crystallization prior to dehydration may be restored. The results show that extensive dehydration may occur during magma ascent and degassing but may be hindered by fast ascent rates with limited volatile loss. De- and rehydration processes are governed by the redox-reaction \[ \text{OH}^- + \text{Fe}^{2+} \leftrightarrow \text{O}^2^- + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2. \] Performing rehydration experiments at different pressures can restore the water contents of clinopyroxene at various levels in the volcanic systems. Subsequently water contents of magmas and mantle sources can be deduced based on crystal/melt partition coefficients. This thesis provides examples from the Canary Islands, Merapi volcano in Indonesia and the famous Nakhla meteorite. Using NAMs as a proxy for magmatic and mantle water contents may provide a very good method especially for planetary science where sample material is limited.

The thesis’ second part focusses on analytical methods to measure the concentration of water in NAMs. Specifically the application of Raman spectroscopy and proton-proton scattering are tested. The hydrated mineral zoisite is thoroughly analyzed in order to be used as an external standard material. Polarized single crystal spectra helped to determine the orientation of the OH-dipole in zoisite. Further, Transmission Raman spectroscopy and a new method for the preparation of very thin samples for proton-proton scattering were developed and tested. The results provide new possibilities for the concentration analysis of water in NAMs such as three dimensional distribution and high spatial resolution.

Keywords: NAMs, clinopyroxene, hydrogen, hydrothermal pressure, magmatic water content, zoisite, OH-dipole, Raman spectroscopy, FTIR, luminescence, proton-proton scattering

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urn:nbn:se:uu:diva-306212 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-306212)
This thesis is dedicated to my mother Gabriele Maria Elisabeth Weis who passed away in August 2015.

Et si omnes, ego non! Semper fidelis!
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


III  **Weis, F.A.,** Stalder, R. and Skogby, H. (2016) Experimental hydration of natural volcanic clinopyroxene phenocrysts under hydrothermal pressures (0.5–3 kbar), *American Mineralogist*, 101(10): 2233-2247. (The article was selected as ‘Notable Paper’ in the issue)


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Personal Contributions

My individual contributions to each paper are listed below:

Paper I: My contribution to this paper was approximately 70 % of the total effort. I prepared all the samples and performed all the FTIR and EPMA measurements. I further performed all the rehydration experiments. Geochemical modelling was done with the assistance of Dahren. I led figure and manuscript preparation in collaboration with Skogby and Troll.

Paper II: My contribution to this paper was about 60 % of the total effort. I prepared the samples and performed the FTIR and Raman measurements with the assistance of Skogby, Lazor and Stalder. I wrote the manuscript and designed figures in cooperation with all the coauthors.

Paper III: My contribution to this paper was about 65 % of the total effort. I prepared all the samples and did most of the hydrothermal experiments with the assistance of Stalder. I further performed most of the FTIR measurements and the complete EPMA analysis. I led the manuscript and figure preparation in collaboration with Skogby and Stalder.

Paper IV: My contribution to this paper was about 60 % of the total effort. The rehydration experiments and FTIR analyses were conducted by me and Stalder. I carried out the EPMA analysis. I together with Bellucci led the manuscript and figure preparation in collaboration with Nemchin, Whitehouse and Skogby.

Paper V: My contribution to this manuscript was about 70 % of the total effort. I prepared all the crystals and conducted all FTIR and almost all Raman analyses. Most of the writing and figure editing was done by me in cooperation with all the other coauthors.

Paper VI: My contribution to this manuscript was about 60 % of the total effort. I performed all FTIR analyses and prepared all samples for the proton-proton scattering analysis. I wrote most of the manuscript and designed most of the figures in cooperation with the other coauthors.
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Abbreviations

Cpx  Clinopyroxene
EPMA  Electron probe micro analysis
FTIR  Fourier transformed infrared spectroscopy
NAM  Nominally anhydrous mineral
Ol  Olivine
OIB  Ocean island basalt
P-T  Pressure - Temperature
SIMS  Secondary ion mass spectrometry
SNC  Shergottite Nakhlite Chassignite
STIM  Scanning transmission ion microscopy
XRD  X-ray diffraction
Introduction

Hydrogen, just like in material science, plays an important role in geosciences due to its influence on physical and chemical properties of minerals, melts and rocks. The element often occurs together with oxygen anions in the form of hydroxyl ions that are more or less chemically equivalent to water (Sundvall & Stalder 2011). Hydroxyl ions are incorporated in hydrous minerals such as amphiboles or sheet silicates. However, during growth from a hydrous magma also nominally anhydrous minerals (NAMs), such as clinopyroxene (cpx) or olivine (ol), incorporate hydrogen in association with structural defects such as cation vacancies (e.g., \( \text{Mg}^{2+} \) vs. \( 2\text{H}^+ \)) and charge deficiencies (e.g., \( \text{Si}^{4+} \) vs. \( \text{Al}^{3+} + \text{H}^+ \)) where it is bonded to oxygen and, regarded as an oxide component, can be expressed as water concentration (Bell & Rossman 1992, Ingrin & Skogby 2000, Sundvall & Stalder 2011). The water concentration in NAMs is, compared to hydrous minerals, very low and usually does not exceed a few hundred wt. ppm (see review by Peslier 2010). Yet these small amounts are significant and quantification of the water content provides useful information.

By studying NAMs, which are also commonly the silicate minerals making up the Earth’s mantle (e.g., pyroxene, olivine) geologists gain knowledge about the amount of water that is stored within Earth’s interior. The Earth’s mantle as a reservoir for water most likely played a major role in the genesis of the hydrosphere and atmosphere as it is suggested that they formed from degassing of volatiles such as water from the young Earth’s interior (Rubey 1951). New studies led to the assumption that at present the upper mantle holds only a little less than the amount of water currently present in the hydrosphere (Hirschmann et al. 2005, Marty and Yokochi 2006, Pearson et al. 2014, Nestola and Smyth 2016). The interaction between the two systems, the hydrosphere and the mantle, is given as water is being stored in sediments and transported to the mantle at subduction zones and is later released again by volcanic eruptions (Lu and Keppler 1997).

This introduces an important point, since volatiles such as water are being held responsible for partial melting and magma generation due to the influence on physical properties like the melting temperature of minerals (Hirth and Kohlstedt 1996). Further the newly formed magma is greatly influenced by its water content, since a higher water content in a silicate melt will decrease its viscosity and density (e.g., Hess and Dingwell 1996, Ochs and Lange 1999). However, volcanoes bearing lavas enriched in water will often show a more explosive eruption behavior. During ascent and eruption mag-
mas lose their volatile contents and information about the initial magmatic water content may be difficult to retrieve. Thus measuring the water content in NAMs from erupted volcanic rocks will give an insight into the water content present in the magma chamber and the mantle. Such information, in turn, would aid to predict possible eruption behavior. However, the stability of hydrogen in NAMs under eruptive processes cannot be taken for granted. Hydrogen diffusion kinetics in pyroxenes in particular have been well studied regarding hydration, dehydration, self-diffusion and dependence on iron content (Hercule and Ingrin 1999, Ingrin and Skogby 2000, Woods et al. 2000, Ingrin and Blanchard 2006, Sundvall et al. 2009, Sundvall and Skogby 2011). Results from these studies demonstrate that hydrogen diffusion is strongly dependent on the Fe-content and subsequent equilibration for clinopyroxenes with \( x_{\text{Fe/(Fe+Mg)}} > 0.07 \) occurs within days to minutes at temperatures from 600 to 1000 °C, with kinetics similar to those of hydrogen self-diffusion (H-D exchange; see reviews by Ingrin and Blanchard 2006 and Farver 2010). Hydrogen diffusion in or out of pyroxene crystals follows the reversible redox reaction

\[
\text{(R1)} \quad \text{OH}^- + \text{Fe}^{2+} \leftrightarrow \text{O}^{2-} + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2
\]

where the exchange of hydrogen ions (protons) is counterbalanced by a flux of electron holes (e.g., Skogby and Rossman 1989, Skogby 1994, Bromiley et al. 2004, Koch-Müller et al. 2007, Sundvall and Skogby 2011). Depending on eruption style and fluid pressure, clinopyroxenes may rapidly lose parts of their hydrous content according to redox-reaction R1. Upon magma degassing, for example, clinopyroxenes are expected to dehydrate due to decreasing fluid pressures and while crystals in fast erupted and quenched pyroclastic materials may not, clinopyroxenes in slower cooling lavas may undergo extensive dehydration (e.g., Woods et al. 2000, Wade et al. 2008). The hydrogen-associated defects in the crystal structure, however, will remain after dehydration and cooling, because they are governed by cation and vacancy diffusion with kinetics many orders of magnitude slower than reaction R1 (e.g., Skogby and Ingrin 2000, Ingrin and Blanchard 2006, Cherniak and Dimanov 2010). Clinopyroxene is therefore expected to “keep a memory” of its initial hydrogen content during original crystallization, a feature that can be exploited as a proxy for parental magmatic water contents by performing rehydration experiments. The aim of this study is to provide more insights into the water content of NAMs, with particular focus on de- and rehydration processes and methods for quantification. I will show how the hydrogen associated defects in NAMs can be exploited as a tool for measuring magmatic volatile contents in the field of volcanology and petrology. Further this work investigates how various parameters such as pressure and temperature influence the water content in NAMs in a volcanic environment. In addition, I apply and test various analytical methods, each having its own advantages or disadvantages, for the quantification of water in NAMs.
2. Methodology

2.1 Whole rock major elements analysis

Whole rock compositional data for samples in Paper I was obtained for their precise petrological classification. Samples were first inspected for freshness, and potential weathered edges were cut off with a diamond-blade rock saw. Subsequently, the lava samples were crushed in a jaw crusher and ground to fine powder with an automated agate mortar at the Department of Earth Science at Uppsala University (UU). Whole-rock powders (n=10) were analyzed for major elements at Acme Analytical Labs Ltd in Vancouver, Canada. Major elements were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a Spectro Arcos system. Sample preparation included mixing of powdered rock material with a LiBO2/Li2B4O7 flux agent before sample fusion in a furnace. Prior to measurement, the sample bead was dissolved by applying dilute nitric acid digestion. Data quality during analysis was monitored using two certified, internal reference materials. Accuracy of the standard measurements is < 0.2 % for SiO2, Al2O3, Fe2O3, MgO, CaO, Na2O, K2O, TiO2, P2O5, MnO and Cr2O3. Duplicate analyses have a reproducibility of < 5 % (2 s. d.) for all oxides. The iron content is reported as Fe2O3. Loss on ignition (LOI) was determined by weight difference after heating of the samples to 1000 ºC.

2.2 Electron-probe micro analysis of major element oxides

Raw data for Papers I, III and IV, both in the form of compositional data and images obtained by backscatter electron imaging of mineral crystals were obtained using a JEOL JXA-8530F Hyperprobe electron-probe microanalyser (EPMA) at the Department of Earth Sciences at Uppsala University, Sweden.

The principle of EPMA analysis is based on the bombardment of a solid sample with an electron beam and the subsequent analysis of the X-ray spectra emitted by sample. In this way major elemental data are obtained, which can subsequently be recalculated as oxide weight percent (Reed 1995). In the case of anhydrous silicate minerals, the obtained totals of mineral compositional analyses should always be 100 ±1 wt. %. For EPMA analysis sample
preparation is a crucial step. The analysed crystals were prepared as pristine minerals after they had been handpicked under a binocular microscope. The crystals were mounted in epoxy resin in the individual wells of one-inch sample holders and polished. Several spots were analyzed on each crystal sample using a beam current of 10 nA with an acceleration voltage of 15 kV with 10 seconds on peak and 5 seconds on lower and upper background. For each crystal an average composition was calculated from all analyzed spots. The beam diameter was set to 1 μm for mineral analysis. A detailed description of the EPMA analysis and the analytical uncertainties and the standards used, is presented in Barker et al. (2015).

2.3 Thermobarometric modelling

Whole rock data, clinopyroxene compositional data and the derived magmatic water contents from clinopyroxenes were used to calculate crystallization pressures and temperatures for the investigated clinopyroxene crystals in Paper I. For this purpose thermobarometers that are based on the jadeite-diopside/hedenbergite exchange equilibria between clinopyroxene and coexisting melt (Putirka et al. 1996, 2003, Putirka 2008) were applied. Specifically, the equations 30 and 33 in Putirka (2008), which have been shown to be robust under disequilibrium conditions (Mollo et al. 2010) and have proven reliable in reconstruction of P-T conditions for magmas of a wide compositional range (e.g., Putirka and Condit 2003, Schwarz et al. 2004, Klügel et al. 2005, Galipp et al. 2006, Longpré et al. 2008, Barker et al. 2009, Dahrén et al. 2012) were used in Paper I. A two-stage equilibrium testing filters the data so that only mineral-melt pairs in equilibrium are taken for the subsequent thermobarometric calculations. First the $K_d$(Fe-Mg)$_{cpx-liq}$ values between clinopyroxene and various melts are tested. Crystals in equilibrium with their melt are required to satisfy $K_d$(Fe-Mg)$_{cpx-liq} = 0.28 \pm 0.08$ (see Putirka, 2008). Then the observed versus predicted diopside and hedenbergite components are compared. Once the crystallization pressure has been determined and a bedrock density is defined, estimates of the depths of potential magma storage regions underneath a particular volcano can be made.

2.4 Single crystal XRD

Single crystal x-ray diffraction data for paper II were recorded with an Oxford Diffraction Xcalibur-III diffractometer at the Department of Materials and Environmental Chemistry at Stockholm University. X-ray MoKα-radiation ($\lambda = 0.71073$ Å) came from a sealed tube source and the entire reciprocal space to $d = 0.8$ Å, was collected. The orientation matrix was determined from the diffraction data which enabled the indices of the different surfaces to be assigned.
The following information can be found in Massa (2004). Single crystal x-ray diffraction is based on the property of minerals to act as a kind of three-dimensional diffraction grating for x-ray wavelengths which are similar to the spacing between crystal lattice planes. Monochromatic X-rays directed onto a single crystal are diffracted by the crystal’s lattice planes and produce constructive interference if Bragg’s law \( n\lambda = 2d \sin \theta \) is fulfilled. In the Bragg equation \( n \) is an integer, \( d \) is the distance between the lattice planes, \( \theta \) is the incident and reflectance angle and \( \lambda \) is the wavelength of the X-ray. By changing the incident angle of the X-rays, the crystal orientation and the position of the detector a full spectrum of the diffracted rays can be obtained thus providing full information of all the lattice planes, i.e. the unit cell in the sample. If the X-rays, the sample and the detector are aligned horizontally, the rays diffracted by all lattice planes which fulfill the Bragg equation will appear as spots on the detector in a specific pattern, which is referred to as a Laue image. However, if several lattice planes, arising from different atoms, diffract the X-rays interference of the rays will be not always be fully constructive resulting in some of the spots appearing with weaker intensity. With the help of the Laue image and the intensities of the Laue spots the exact orientation of a crystal can thus be determined. Further, the phase difference between the scattered X-rays can be related to the electron density of atoms which in turn provides information on the crystal structure (i.e. position of individual atoms).

2.5 Crystal preparation for FTIR, Raman spectroscopy and proton-proton scattering

Rock samples were crushed to obtain loose clinopyroxene crystals of a size suitable for analysis (\( \geq 300 \mu m \)). These were hand-picked under a binocular microscope and individual clinopyroxene crystals were then mounted in thermoplastic resin for further processing. With the help of crystal morphology and optical microscopy (extinction angles), the crystals selected for FTIR were oriented along their crystallographic c-axis and their (100) and (010) crystal faces, on which the directions of the main refractive indices (\( \alpha \), \( \beta \) and \( \gamma \)) occur. A detailed procedure of the crystal alignment is described in Stalder and Ludwig (2007). Various particle size-grades of \( Al_2O_3 \)-grinding paper were used to thin and polish the oriented crystals to a thickness of a few hundred micrometers. For Raman analysis, both backscattered and transmission, crystals were polished to thicknesses of < 40 \( \mu m \) to make them more transparent and thus reduce the heating effect of the laser. For proton-proton scattering in Lund unoriented clinopyroxene crystals between 1 and 3 mm in diameter were polished to a flat plate of \( \sim 200 \mu m \) thickness. The polished crystals were embedded in thermoplastic resin and mounted on a glass plate. Subsequently holes with depth between 60 and 100
μm were drilled using a New Wave Research micro mill and solid-carbide micro end mills. The applied end mills were model 596 (diameter 200-250 μm) produced by the company Zecha Germany with center cut, two polished cutting edges and flutes. This particular model of end mill is designed to cut a cylindrical shaped well with a flat bottom. Since the shaft diameter of the end mills was 3 mm and thus too big for the drill holder of the micro mill (max. shaft diameter 2 mm) an adapter was built. For drilling the drill speed was set very low and holes were drilled in a stepwise manner by submerging the drill in intervals of 15 to 30 μm. A drop of water was placed onto the crystals for cooling and to remove chipping. After the wells were drilled, the bottom side of the crystals was polished until the remaining thickness of the crystal underneath the wells reached around 10 μm. The crystal thickness was monitored with an optical microscope and the mineral’s interference colors. For clinopyroxene, more precisely diopside, a thickness of ~10 μm corresponds to interference colors between first order grey and yellow, depending on the crystal’s orientation. The absolute thickness was finally measured using scanning transmission ion microscopy (STIM). A perfect cylindrical well was not always accomplished due to wobble during the drilling process. This error most likely resulted from a small miss-alignment due to the inserted adapter and fact that parts of the crystals broke off on occasion.

2.6 Fourier transformed infrared spectroscopy (FTIR)

IR measurements for all papers were done using either a Bruker Vertex 70 spectrometer at the Swedish Museum of Natural History or a Bruker Hyperion 3000 microscope at the Institute for Mineralogy and Petrography at Innsbruck University. Polarized FTIR spectra in the range 2000–5000 cm⁻¹ were acquired on oriented crystals along the directions of the main refractive indices (α, β and γ) to obtain the total absorbance: \( A_\alpha + A_\beta + A_\gamma = A_{\text{total}} \). \( A_\alpha \) and \( A_\gamma \) were measured on the (010) crystal face and \( A_\beta \) on (100). Cracks and inclusions in the crystals were avoided by applying small apertures (100 to 400 μm) for masking during analysis. For each individual spectrum, 128 scans were performed and then averaged.

FTIR spectroscopy is one of the best and most common tools used to analyze the composition and concentration of solids, liquids and gases. Thus it finds its application in many branches of chemistry, environmental science, remote sensing and geosciences. FTIR is known for its high sensitivity, the possibility to analyze multiple components simultaneously, its speed and the fact that it is easy to calibrate. FTIR can be used for quantitative as well as qualitative analysis. The information presented in the following paragraphs relies on Griffith and de Haseth (2007) if not stated otherwise.
Table 1. An overview of the spectra of light and various spectroscopic methods.

<table>
<thead>
<tr>
<th>Effect of energy</th>
<th>Molecule rotation</th>
<th>Molecule vibration</th>
<th>Electron excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic method</td>
<td>Microwave absorption</td>
<td>FTIR</td>
<td>Raman</td>
</tr>
<tr>
<td>Spectrum</td>
<td>Radiowaves</td>
<td>Microwaves</td>
<td>Infrared (IR)</td>
</tr>
<tr>
<td>Wavelength (m)</td>
<td>10^{-3}</td>
<td>10^{-1}</td>
<td>10^{-2}</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>10^{7}</td>
<td>10^{9}</td>
<td>10^{11}</td>
</tr>
<tr>
<td>Wavenumber (cm^{-1})</td>
<td>10^{-3}</td>
<td>10^{-1}</td>
<td>10^{1}</td>
</tr>
</tbody>
</table>

The FTIR method is based on the interaction of electromagnetic radiation and atoms in molecules. The electromagnetic radiation used lies within the infrared spectrum of light (Table 1, wavelength $\lambda = 10^{-3}$ to $10^{-6}$ m), which can be divided into the near, middle and far IR-spectrum. In spectroscopy it is common to give the energy of the electromagnetic radiation in form of the wavenumber $\tilde{\nu}$ which is the number of waves per unit of distance (i.e. $1/\lambda$) and normally given in units of cm$^ {-1}$). Different spectra (i.e. radiation of different energy) of electromagnetic radiation cause different effects when they interact with molecules, such as electron excitation, molecule rotation and molecule vibration. When infrared radiation is shone through a substance or a mineral sample, it causes excitation in the forms of rotation and vibration of the atoms in the sample that it is interacting with. For this purpose the molecules absorb rotation and vibration energy which they obtain from the incoming IR radiation. Radiation from the far IR spectrum causes overall lattice vibrations in a crystal whereas the middle and near spectra cause characteristic vibrational modes of bonds between atoms within molecules. However, chemical bonds are only IR active if a change in the dipole moment $\mu$ occurs during their vibration resulting from the absorption of light. The dipole moment provides information about the charge separation in a molecule and can be expressed as

$$\text{Eq.1} \quad \mu = q \times r$$

where $q =$ charge of an atom
$r =$ distance expressed in coordinates x, y and z to the center of gravity of a molecule.

The intensity of the IR absorption is proportional to

$$\text{Eq.2} \quad I_{Abs} \propto \left(\frac{d\mu}{dQ}\right)^2$$

where $Q =$ the normal coordinates of a vibration. From the above expression it can be seen that with a bigger change in dipole moment due to a change in $r$ the IR activity of a bond increases. Most commonly polar bonds such as O-
H or N-H are highly IR active bonds while uniform bonds such as H-H, O-O or Cl-Cl are less suitable for detection with IR spectroscopy. Certain vibrations will show a characteristic IR absorption spectrum for a certain energy/wavenumber. The vibration activity of O-H bonds, for example, will absorb light with energies between 1600 and 3700 cm⁻¹ (Fig.1, Libowitzky and Beran 2004), which is fully within the energetic range of the middle infrared radiation (400-4000 cm⁻¹). The absorbed energy varies depending on other atoms and molecules that influence the O-H bond.

2.6.1 Absorption and measuring process

The absorption or alternatively the transmission of the infrared radiation through a sample is detected in a spectrometer and shown in a spectrogram (Fig.2). By determining the intensity of the absorbance of a certain wavenumber, it is possible to calculate the concentration of the absorber, i.e. the bond or molecule responsible. This is done with the Beer-Lambert law which is:

\[ A = \varepsilon \times c \times d \]

where
- \( A \) = absorption
- \( \varepsilon \) = absorption coefficient for a certain wavelength
- \( c \) = concentration
- \( d \) = thickness of the sample
The relation between the absorption and the measured intensity is given as follows:

\[
\text{Eq. 4} \quad \log \left( \frac{I_0}{I} \right) = A
\]

Here \(I_0\) depicts the intensity of the light before entering the analysed sample, while \(I\) is the intensity of the light wave measured by the detector after the exit of the light through the sample. Combining the two equations allows calculating the concentration of a certain component in a sample. When analyzing optically biaxial crystalline material the total absorbance, \(A_{\text{tot}}\), and thus total concentration of an absorber in a sample is the sum of the absorbance along the three refractive indices \(\alpha\), \(\beta\) and \(\gamma\) of the crystal (Libowitzky and Beran 2004):

\[
\text{Eq. 5} \quad A_{\text{tot}} = A_{\alpha} + A_{\beta} + A_{\gamma}
\]

The set-up of a typical FTIR spectrometer is shown in Fig. 3. A main part of the instrument is the so called Michelson interferometer. The Michelson interferometer is an apparatus which causes interference of the infrared radi-
ation before entering the sample and makes it possible to measure the absorption of all wavelengths at the same time. This is done by splitting the original light beam with a beam splitter into two separate beams (Fig. 3) since the beam splitter is partially transparent and partially reflecting. Ideally the new light beams each have 50% of the original radiation. The two generated beams are directed onto two mirrors. One of these mirrors is fixed while the other one is movable. The light beams are again reflected by these two mirrors and travel back to the beam splitter where they are recombined and further led onto the sample. Assuming that the two mirrors have the same distance $z_1$ to the beam splitter then the light beams travel a total path of $2z_1$ to and from the reflecting mirror. However, the distance to the moving mirror is changed by an amount $x$. Thus the distance the light travels to and from the moving mirror $z_2$ is $2(z_1 + x)$. The additionally travelled distance of $2x$ is referred to as path difference $\delta$.

The recombination of the two reflected light beams at the beam splitter causes interference of the light waves and the resulting phase difference influences the intensity of the recombined light beam. Considering a monochromatic light beam (i.e. only one wavelength) an overlap of two waves that are in phase with each other will cause an increased intensity (Fig. 4a). On the other side, overlap of two waves out of phase will cause a destructive interference and thus zero intensity of the light wave (Fig. 4b). These two cases
however, represent the two extremes, i.e. I_{max} and I_{min}. Changing the distance to the moving mirror in the interferometer will result in a phase difference. If the path difference δ = 0, the recombined light waves will be in phase thus enhancing the intensity. If the moving mirror is moved for example by a distance of λ/4 then the path difference δ is equal to λ/2 which will cause the two interfering waves to be out of phase resulting in the extinction of the light. The same will hold for polychromatic light, however, in this case interference will not only occur for light of the same but for all wavelengths (Fig.4c).

![Figure 4. The interference of light waves.](image)

The resulting intensity of a recombined light beam relative to the path difference is I'(δ) and can be expressed in terms of the original intensity of a light wave I(ṽ) emitted by the IR source as

$$\text{Eq.6} \quad I'(\delta) = \frac{1}{2} I(\bar{\nu})(1 + \cos(2\pi\bar{\nu}\delta))$$

The first part of Eq.4 is basically a constant. More important for gaining spectral information is the changing component $\frac{1}{2} I(\bar{\nu})\cos(2\pi\bar{\nu}\delta)$, which is referred to as the interferogram function I(δ),

$$\text{Eq.7} \quad I(\delta) = \frac{1}{2} I(\bar{\nu})\cos(2\pi\bar{\nu}\delta)$$

Eq.5 shows the change of light intensity as a function of path difference and depicts the case for only monochromatic light. For polychromatic light the interferogram function becomes the sum of all the wavelengths and thus wavenumbers included in the light beam and thus becomes

$$\text{Eq.8} \quad I(\delta) = \int_{0}^{\infty} \frac{1}{2} I(\bar{\nu})\cos(2\pi\bar{\nu}\delta) \, d\bar{\nu}$$
The combination of the intensities measured by the detector can be plotted in an interferogram (Fig. 8) to which Eq. 6 depicts the representative function.

As mentioned earlier Eq. 8 does show the intensity as a function of the path difference and thus as a unit of length such as cm. However, for a spectral analysis the intensity as a function of the wavenumber (cm⁻¹) is needed. Path difference and wavenumber are reciprocals and thus form a Fourier transform pair, meaning that from one part of the pair the other can be deduced by employing Fourier Transformation (FT). Applying Fourier Transformation to Eq. 8 produces

\[
I(\bar{\nu}) = \int_{-\infty}^{\infty} \frac{1}{2} I(\delta) \cos(2\pi\bar{\nu}\delta) \, d\delta
\]

With the help of Fourier Transformation and Eq. 9 the interferogram can thus be converted to an IR spectrum. The resulting IR spectrum after the analysis of a sample, however, does not immediately represent the absorptionspectrum. Considering Eq. 4, only the variable “I” has been determined. Even though I(\bar{\nu}) stands for the intensity originally emitted by the IR source, it has to be taken into account that the calculation of I(\bar{\nu}) has been done with data that already has undergone absorption and thus does not represent the true value. In order to obtain the original intensity I₀ of the light source, a standard reference which shows no absorption of the wavenumbers in focus of the analysis has to be analyzed and Fourier transformed. For example, if a sample is analyzed within KBr-plate, the reference simply would be a KBr-plate without the sample. Combining the two spectra of sample and reference gives the final absorption spectrum for a sample analysis.

*Figure 5.* The interferogram for a polychromatic IR light source. The intensities of the various wavelengths are shown as a function of the path difference δ.
Since the moving mirror is restricted in its ability to in- or decrease $\delta$, the interferogram is limited by truncation, meaning that only a certain interval is taken into account. This truncation leads to the side effect of having smaller peaks at the side which in reality do not exist. This can be corrected by changing the shape of the spectral line with multiplication of an apodization function (Fig.5).

2.6.2 Advantages and disadvantages of the FTIR method

One of the main advantages of the FTIR spectroscopy is that the application and the analytical procedure are very simple. Further the method is very suitable for detecting polar O-H bonds. The observed absorption bands for hydroxyl groups are distinct and do not overlap with peaks from the lattice they are incorporated in (e.g., SiO$_4$, 500–1000 cm$^{-1}$ vs. OH 3100–3800 cm$^{-1}$). Also different hydrogen bonds, their bond length, geometry and vibrational mode can be determined providing information about the location of these in the crystal lattice (e.g., Libowitzky 1999, Skogby 2006). In addition, samples of small sizes (~5 $\mu$m in diameter) can be analyzed with IR microscopy and synchrotron IR radiation which, in turn, allows FTIR spectroscopic imaging, i.e. the spatial distribution (2D) of an absorber in a sample (e.g., Meade et al. 1994, Libowitzky and Beran 2004, Sundvall and Stalder 2011).

Disadvantages are, however, that although spatial resolution can be very small, the actual limits are still larger than for example those of Raman spectroscopy (1–2 $\mu$m), which is caused by the much longer wavelength of IR radiation. Also the high sensitivity of hydrous components in a mineral can cause truncation of the spectra in the case of high concentrations since the absorbance becomes too strong. This however can sometimes be overcome by grinding down the sample to very small thickness (e.g., 10 $\mu$m; e.g., Libowitzky and Rossman 1996a, Treimer 2002), which on the contrary may cause problems depending on the sample material available. Well-polished samples can show interference fringes due to internal reflections of the light which will result in a sinusoidal pattern on the base line of the IR spectrum and inhibit accurate measuring (Griffith and de Haseth 2007). Measuring the total absorbance of water in crystalline material preferably requires the use of polarized light and optical orientation as well as clarity of the sample, which may be difficult to achieve. Using non-polarized light may work for semi-quantitative analyses, however is not ideal for concentration determination (Libowitzky and Rossman 1996b). This is the case especially for strongly anisotropic orientation of absorbers which partly leads to the non-polarized radiation simply passing through the sample without any absorbance occurring. Another disadvantage of the method is that it is not self-calibrating. Calibration against an independent hydrogen analysis method is necessary in order to find true values for the absorption coefficient $\varepsilon$. This requires other methods such as Karl-Fischer Titration (e.g., Behrens and
2.7 Raman spectroscopy

Raman spectra for paper II were taken with the self-built Raman spectrometer at the Department of Earth Sciences at Uppsala University as well as a Horiba Jobin Yvon LabRam-HR 800 confocal Raman spectrometer at the Institute for Mineralogy and Petrography at Innsbruck University. Raman spectroscopy is another method for quantitative and qualitative analysis in physics, chemistry and mineralogy. Different to the FTIR method, however, it relies not on the absorption of light but on the inelastic scattering of light waves also referred to as the Raman Effect. While FTIR spectroscopy uses mostly polychromatic light in the IR spectrum, Raman spectroscopy uses monochromatic lasers in the spectrum of visible light ($\lambda = 400–750$ nm) which are capable of exciting electrons in a molecule due to their higher energy. In addition, Raman spectroscopy can also be used to analyze symmetrical non-polar bonds with the help of an induced dipole. The information presented in the following paragraphs can be found in Colthup et al. (1990), Putnis (1992), Ball (2001), Nasdala et al. (2004), Rull (2012) if not cited otherwise.

2.7.1 The Raman effect

The visible light used in Raman spectroscopy oscillates at high frequencies ($\nu_0 = 4.0–7.5 \times 10^{14}$ s$^{-1}$). The electric field vector of this incoming radiation can interact with the electrons rotating around the nuclei in a molecule since the incoming radiation and the valence electrons in the molecule begin to establish coherence thus oscillating at the same frequency. This process causes a temporary displacement of the electron cloud of the molecule, and thus is capable of inducing a temporary dipole on usually non-polar bonds. The molecule is brought into a virtual excited state since the incoming photon energy is much bigger than the energy differences for the molecules’ vibrational states. The system, however, immediately recovers from the virtual state to the ground state and the vibrational energy of the newly formed dipole is usually immediately released again by the molecule. The intensity of this process is proportional to $\nu_0^4$. Since the released radiation is of the same frequency as the incoming radiation of the laser, no change in energy is observed when detecting it. Thus it is said that the incoming light from the laser is scattered elastically, which is also referred to as Rayleigh scattering (Fig.6). This makes up the biggest amount of the scattered light in Raman spectroscopy.
However, a small part of radiation (~10⁻⁶ %) can be scattered inelastically which is called Raman scattering (Fig. 6). This is due to the interaction of the incoming radiation (v₀) and the atomic vibrations or rotations of the molecule with their frequencies in the IR spectrum (v₁ = 10^{12}–10^{14} s⁻¹ << v₀). It can occur that during the relaxation process the molecule does not fall back to the ground state but remains at a higher vibrational state (v₁). Thus parts of the original energy are absorbed and the emitted radiation shows a lower frequency when detected (v = v₀ – v₁). This scenario, when the emitted radiation is of lower frequency than the original, is called the Stokes-type scattering and the reduction in energy is referred to as the Stokes shift when compared to the Rayleigh scattering. In addition a molecule can already be in an excited state when it is hit by the incoming laser beam. This may lead to an event where upon relaxation it falls down to the ground state, thus emitting more energy than during elastic scattering, i.e. the original energy of the incoming radiation is increased during emission (v = v₀ + v₁). The detected radiation is referred to as the Anti-Stokes type and the excess energy as the Anti-Stokes shift. The Anti-Stokes type scattering occurs, however, much less often than the Stokes type and has much lower peak intensities. However, the Anti-Stokes can be useful to calculate temperatures for measurements and to identify for example light contamination of the spectrum.

2.7.2 Selection rules for Raman active modes

The dipole induced by the incoming radiation from the laser beam in a Raman spectrometer can be expressed as
Eq.10  \[ \mu_{\text{in}} = \alpha E \]
where \[ \alpha = \text{the polarizability of the molecule} \]
\[ E = \text{electric field of the radiation} \]
\[ \mu_{\text{in}} = \text{the induced dipole moment} \]

The electric field \( E \) is expressed by the oscillating amplitude of the incoming radiation, \( E_0 \), as

Eq.11  \[ E = E_0 \cos 2\pi \nu_0 t \]
where \[ \nu_0 = \text{frequency of the incoming radiation} \]
\[ t = \text{time measured from a positive maximum in the field} \]

In its ground state a molecule has the equilibrium polarizability \( \alpha_0 \) which however changes in the excited state due to deformation of the electron cloud around the molecule caused by vibration. In the excited state the polarizability is expressed as

Eq.12  \[ \alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right) q \]
where \[ q = \text{the normal coordinates of the vibration} \]
\[ \left( \frac{\partial \alpha}{\partial q} \right) = \text{change in polarizability with change in position} \]

The normal coordinates of the molecule in the excited state (i.e. the change in position with respect to the equilibrium positions of the bond) can again be expressed in terms of a sinusoidal (sin or cosine based) function

Eq.13  \[ q = q_0 \cos 2\pi \nu_r t \]
where \[ q_0 = \text{maximum amplitude of the vibration (excited state)} \]
\[ \nu_r = \text{frequency of vibrational mode (excited state)} \]

Combination of equations Eq.10, Eq.11, Eq.12 and Eq.13 results in

Eq.14  \[ \mu_{\text{in}} = \left( \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right) q_0 \cos 2\pi \nu_r t \right) E_0 \cos 2\pi \nu_0 t \]

Eq.14 can be rewritten according to the trigonometric identity

\[ \cos A \times \cos B = \frac{1}{2} \left[ \cos (A + B) + \cos (A - B) \right] \]

and thus becomes

Eq.15  \[ \mu_{\text{in}} = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right) E_0 q_0 \cos (2\pi t (\nu_0 - \nu_r)) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right) E_0 q_0 \cos (2\pi t (\nu_0 + \nu_r)). \]

Rayleigh scattering  Stokes shift  Anti-Stokes shift
From Eq.15 the individual types of scattering, Rayleigh, Stokes and Anti-Stokes shift, can be observed. It also can be seen that when \( \frac{\partial a}{\partial q} = 0 \) then only the Rayleigh part of Eq.15 remains. This shows that there has to be a change in polarizability simultaneously with a vibrational mode of a bond or molecule for it to be Raman active. Such a change in polarizability preferably occurs in symmetrical bonds and symmetrical stretching modes. Asymmetrical stretching modes show no net effect on the polarizability (Fig.7) and are thus less Raman active. However, these modes more often show a change in dipole moment which makes them more IR active.

Water usually is a polar molecule which also undergoes asymmetrical stretching modes. However, from Fig.7 it can be seen that the water as well as the hydroxyl ion also have a symmetrical stretching mode. Thus water can be determined by Raman spectroscopy although the Raman signal will only be very weak. This makes it possible to use water as a solvent for other materials during Raman spectroscopy.

Raman spectroscopy can be used for both quantitative and qualitative analysis. The concentration of a certain compound giving a Raman signal in a sample is proportional to the intensity shown on the spectrum. Thus the concentration of a compound can be determined by using a formula similar to the Beer-Lambert law

\[
\text{Eq.16} \quad I = C \times I_0 \times \sigma \times X \times l
\]

(Sasic and Ozaki 2010)

where

- \( C \) = concentration of molecules in molecules/cm\(^3\)
- \( I_0 \) = laser intensity in photons/sec
- \( \sigma \) = absolute Raman cross section in cm\(^2\)/molecule
- \( X \) = experimental constant
- \( l \) = sample path length in cm

Unfortunately some of the variables in Eq.16 like the experimental constant or the Raman cross section are uncertain or unknown. In this case a quantitative analysis can be done using experimentally determined calibration curves and their corresponding equations (Sasic and Ozaki 2010). Calibration curves can be obtained by either internal or external calibration. External calibration establishes a calibration curve on the basis of well-defined standard samples (e.g., Behrens et al. 2006, Thomas et al. 2008). In the case of analyzing hydrogen or water contents these could be some hydroxyl-bearing glasses or minerals whose water content has been previously determined by Karl-Fischer titration or FTIR (e.g., Thomas et al. 2008). With the help of the known concentrations and Raman intensities of the standards the amount of water in other samples can be determined. Internal calibration uses the relation between concentration and area under Raman peaks (e.g., Chabiron et al. 2004, Le Losq et al. 2012). Le Losq et al. (2012) for example relate the
water concentration of glasses with the peak area ratio of water and silica bands. Again also internal calibration requires determination of water content by an independent method.

![Diagram of polarizability changes in water molecules](image)

Figure 7. The change in polarizability in a water molecule due to symmetrical and asymmetrical stretching.

### 2.7.3 Strengths and weaknesses of Raman spectroscopy

One major disadvantage of Raman spectroscopy is the lack of reliable reference data for minerals, which can make identification of unknown samples difficult and time consuming as other ways of identification than using a mineral database have to be applied. Standards and calibration curves can also only be used for analyses under similar conditions as the calibration was done. Further some materials might be difficult to analyze due to a lack of transparency, light absorption and thermal sensitivity (e.g., metals). The latter can cause the problem that with strong lasers the sample will heat up due to absorption of the laser light which can result in sample damage and hydrogen loss (Fig.8). Another disadvantage of Raman spectroscopy is the “Raman background”, a very broad Raman signal, which can result from fluorescence due to contaminants or possible defects within the sample (Splett et al. 1997). This background may overlap and hide the actual Raman spectrum. Some of these disadvantages, however, are easy to overcome. The lack of reference material is decreasing with each year since new analyses and databases are published. Heating and fluorescence can be reduced by
lowering the intensity of the laser, changing the laser wavelength or by thinning the sample.

A big advantage of the Raman spectroscopy is the little effort which is needed for sample analysis since it requires more or less no preparation. However, just like for FTIR spectroscopy crystal orientation for water content determination and polishing for better beam quality may be required. Also Raman spectrometers are relatively affordable, easy to maintain and also available in portable versions. Raman spectroscopy has a very high spatial resolution of ~1 μm and high sensitivity. This makes the technique perfect for in situ analysis as well as analysis of amorphous materials (e.g., glasses, metamict minerals, melts). The analyses can also be done at different temperatures and pressures thus allowing investigation of different phases of a material (e.g., gas phase). In addition, the high spatial resolution can provide information about homo-/heterogeneity in a sample. This in turn makes it possible to generate Raman images of the distribution of various compounds.

2.8 Proton-proton scattering

Proton-proton scattering experiments were performed with the microprobe SNAKE (Superconducting Nanoscope for Applied Nuclear (Kern-) physics Experiments) at the Maier-Leibnitz Laboratory of the Technical University in Munich and the Lund Ion Beam Analysis Facility (LIBAF) at the Department of Nuclear Physics at Lund University. This method is particularly
helpful as it allows visualizing the three-dimensional distribution of hydrogen and thus water in a mineral sample. The method sometimes is also referred to as 3D-hydrogen microscopy (cf. Reichart et al. 2002).

2.8.1 Background on proton-proton scattering

The following information can be found in Cohen et al. (1971), Willemsen et al. (1986), Reichart et al. (2002), Dollinger et al. (2003), Reichart (2004) and Borysiuk et al. (2013) if not cited otherwise. In the proton-proton scattering technique a beam of protons (H\(^+\) ions) with energy \(E_0\) is pointed onto a hydrogenous sample. The incoming protons are fired onto the nuclei of the atoms within the samples. Upon collision of the incident protons with the protons within the nuclei scattering occurs. When an incoming proton hits the nucleus of a hydrogen atom a unique scattering event is triggered. Since the nucleus of hydrogen consists of precisely one proton the collision involves only particles of equal mass. The conservation of energy and momentum thus implies that upon impact the two particles are moving away in forward direction at an angle of 90° from each other (Fig. 9) and are deflected by an angle (e.g., 45° to 45° or 30° to 60°) to either side from the original beam direction.

These two protons can be detected in a time-coincidence of a few nanoseconds. Thus any two protons arriving within a certain time interval at the detector at 90° to each other can be referred to a hydrogen atom within the analyzed sample giving an indication of hydrogen concentration. The energy of the incoming proton is split upon the collision with a hydrogen nucleus in the sample. In an ideal case where the protons are scattered at 45° the two outgoing particles both hold the same amount of energy (\(E_1\) and \(E_2\)) where

\[
E_1 = E_2 = \frac{1}{2} E_0.
\]

If the particles separate at different angles they will hold different energies but the sum of their energies is also equal to \(E_0\). However, upon traveling through the sample some of the energy is lost from \(E_0\) which leads to

\[
E_1 + E_2 = E_0 - \Delta E
\]

where \(\Delta E\) = amount of energy lost during sample transmission.

The energy loss, i.e. the change in energy, which is determined at the detector, is dependent on the distance travelled by the particles through the sample and the energy of the incoming protons. \(\Delta E\) is thus also dependent on the position of the particle collision in the sample, which will allow determining a spatial distribution of hydrogen in three dimensions (cf. Reichart et al. 2004a, Wegdén et al. 2005). If a sample with thickness \(t\) is considered
(Fig.10), and scattering events at points A and B, the change in energy will be as follows:

\[
\text{Eq.19} \quad \Delta E_A = \left( \frac{dE}{dx} \right)_{E_0} t
\]

\[
\text{Eq.20} \quad \Delta E_B = 2 \left( \frac{dE}{dx} \right)_{E_0/2} \frac{t}{\cos \theta}
\]

where \( \left( \frac{dE}{dx} \right)_{E_{xy}} \) = rate of energy loss per unit of distance at a certain energy and is proportional to \( 1/E \) and \( \theta \) is the angle at which the particle is scattered relative to the incident beam direction.

\[
\text{Eq.21} \quad \Delta E_X = \left( \frac{dE}{dx} \right)_{E_0} (t - d) + 2 \left( \frac{dE}{dx} \right)_{E_0/2} \frac{d}{\cos \theta}
\]

Figure 9. The principle of the proton-proton scattering technique. A beam of protons (\( H^+ \)-ions) is placed onto a hydrogen bearing sample. Upon collision of two hydrogen nuclei, the particles are scattered 90° to each other.
Since $\frac{dE}{dx} \propto 1/E$, the change in energy will be very small if $E_0$ is rather high thus leaving $E_0 \approx E_0'$. It also follows that $\left(\frac{dE}{dx}\right)_{E_0/2} \approx 2\left(\frac{dE}{dx}\right)_{E_0}$. Thus Eq.21 can be simplified to

$$\text{Eq.22} \quad \Delta E_x \approx \left(\frac{dE}{dx}\right)_{E_0} (t - d) + 4\left(\frac{dE}{dx}\right)_{E_0/2} \frac{d}{\cos\theta}$$

$$\approx \left(\frac{dE}{dx}\right)_{E_0} (t + 4.6d).$$

Above the basic principle of the proton-proton scattering method has been outlined. For a full analysis however, several other factors have to be taken into account. During analysis there is of course also the possibility that the protons do not solemnly hit hydrogen atoms but also collide with other nuclei. This leads to the multiple scattering of the incoming as well as outgoing protons.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Different positions of proton-proton collisions within a hydrogen bearing sample of thickness $t$.}
\end{figure}
If an incoming proton has been deflected from the original beam direction by an angle $\alpha$ due to a collision before the actual proton-proton collision (Fig.11), the consequences are less severe, since the emerging two protons will propagate at different angles other than 45° relative to beam direction, which would represent an ideal case. However, the overall angle sum ($\theta_1 + \theta_2$) will remain 90° and an adequate time coincidence interval can still determine the scattering event. The steepest deflection of the scattering angles together with the path dependent change in energy also determines the maximum sample thickness. More difficult is, however, multiple scattering of the emerging protons since they may escape detection. These multiple collisions can however be corrected in the analysis. The deflection angle of a proton depends on the atomic number $Z$ of the atom involved in the collision and is roughly given by

$$\alpha \approx (1.8Z \Delta E/E)^{1/2}.$$ 

So knowledge about the chemistry of the sample will help in the correction. Additionally, an exponential loss of detections can be assumed from the entering side of the sample to the exit side. By determining the exponent, the analysis can be corrected (Fig.12). Another good way to reduce analytical error by multiple collision events is to apply a big detector area during analysis in order to capture all different scattering angles and avoid escape.

*Figure 11. The deflection of a proton due to collision with another element other than hydrogen. If a proton deflected by the angle $\theta$ collides with another proton in the sample, the scattering angle of each proton will no longer be 45° relative to the beam direction but still 90° with respect to each other.*
2.8.2 Advantages and disadvantages of the proton-proton scattering

One of the best advantages of the proton-proton scattering method is its 3D spatial resolution. It allows the identification of the depth of the incorporated hydrogen within a sample and thus provides the possibility to distinguish between actual hydrogen within and water being adsorbed to the surface of the sample. It is thus good for the determination of trace concentrations of hydrogen (e.g., < 1 at-ppm) on a micrometer depth resolution (0.6–0.8 μm) (e.g., Reichart et al. 2004b, Borysiuk et al. 2013). Also in this way the investigation of melt inclusions are possible. Melt inclusions are also often used to quantify the water content of a magma, however, they are usually difficult to analyze and the proton-proton scattering method may provide a convenient way to overcome this problem. Further proton-proton scattering for hydrogen analysis unlike other analytical techniques (e.g., FTIR) does not require another independent analytical technique (e.g., NRA) for calibration (Wegdén et al. 2005). While some analytical techniques can lead to radiation damage in the sample (e.g., heating in Raman spectroscopy), the effect is very small in the case of proton-proton scattering.

Figure 12. The measured and exponentially corrected curve of a proton-proton scattering analysis. The diagram shows how the depth profiling of hydrogen concentrations is possible with this method. The two peaks at points A and B indicate the surface water stuck to the sample. (Diagram after Cohen et al. 1971)
A negative aspect of the method is the strong dependence on sample thickness. It was mentioned that the stopping power in the sample determines the maximum thickness allowed for the sample. If the energy of the proton beam is rather low, the samples have to be very thin (~10 μm) and self-supported which exposes them to the risk of breaking (cf. Wegdén et al. 2005, Borysiuk et al. 2013, Kristiansson et al. 2013). This may however be overcome by simply using a proton beam of higher energy.

2.9 Mössbauer spectroscopy

Mössbauer spectroscopy is a very good technique to identify the oxidation state of iron in a sample. This is of great help when the redox-processes associated with hydrogen incorporation in NAMs are investigated. The method is built on the Mössbauer effect, which is the recoilless emission and resonant absorption of γ-rays in nuclei of the same element in solids (Fultz 2011). The following information can be found in Gütlich (1975), Marfunin (1979) and Fultz (2011) if not stated otherwise. Mössbauer analyses in this thesis have been performed using the Mössbauer spectrometer at the Swedish Museum of Natural History.

A quantum of energy in form of a γ-ray is emitted when the nuclei of one atom returns from an excited state (i.e. energy surplus) to its ground state. The generated and emitted γ-ray can again be absorbed by an atom of the same element which will then turn into an excited state. The process of emission and absorption forms a continuum. The emission of a γ-ray, however, usually occurs under the loss of a certain amount of energy, the so called re-coil:

\[
\text{Eq.24} \quad E_{\gamma,e} = E_0 - E_R
\]

where \( E_{\gamma,e} \) = Energy of the emitted γ-ray

\( E_0 \) = Energy difference between ground state and excited state

\( E_R \) = Energy lost during the recoil.

\( E_R \) itself is defined as:

\[
\text{Eq.25} \quad E_R = \frac{E_0^2}{2 \times m \times c^2}
\]

where

\( m \) = mass of nucleus

\( c \) = speed of light.

In order for the γ-quantum to be absorbed again and the nucleus to turn into an excited state the energy of the absorbed quantum \( (E_{\gamma,a}) \) has to be
\[
E_{\gamma,a} = E_0 + E_R
\]

Any difference in energy between \( E_{\gamma,e} \) and \( E_{\gamma,a} \) is thus

\[
\Delta E = E_{\gamma,a} - E_{\gamma,e} = 2E_R = \frac{E_0^2}{m \times e^2}
\]

If the two nuclei, the emitting and absorbing one, are chemically bound in a solid crystal structure, it is likely that parts of the recoil energy is absorbed by the whole crystal lattice as lattice vibrations. In this case the variable \( m \) in Eq.25 can be seen as the mass of the whole crystal lattice and thus increasing massively and simultaneously pushing \( E_R \) towards zero. Thus the emission process appears recoilless and thus without any energy loss which makes the absorption a resonant process and makes it possible to measure \( E_0 \).

The Mössbauer effect, in addition, is affected by the interaction of the two “Mössbauer nuclei” (i.e. source and absorber of \( \gamma \)-ray) with the electrons in their proximity and the differences in their environment. This is referred to as the magnetic and electric hyperfine interactions, which are

i) Isomer shift, which is a shift in energy relative to \( E_0 / a \) standard absorber due to differences in the chemical environment, i.e. the local electronic environment, between the source and the absorber as well as differences in nuclear radius of excited and ground state (Fig.13).

ii) Electrical quadrupole interaction or also called quadrupole splitting, which results from the interaction of a nuclear quadrupole moment (a non-spherically symmetric nuclear charge) with the electric field gradient. This will result in a splitting of the various energy levels of a nucleus and cause a splitting of the \( E_0 \)-line in a Mössbauer spectrum due to the absorbance of \( \gamma \)-rays of different energies. The electrical quadrupole interaction depends on the spin (\( I \)) of the nucleus since a quadrupole moment is only given for a nuclear spin \( I \geq 1/2 \). For iron the ground state has \( I_g = \pm 1/2 \) and the excited state has \( I_e = \pm 3/2 \). Since for the excited state two constellations are possible for the total electron angular momentum \( m_I \) (\( m_I = \pm 1/2 \) and \( m_I = \pm 3/2 \) the
energy level gets split resulting in two peaks, i.e. a doublet (Fig.13A, B, Fig.14).

iii) Magnetic hyperfine splitting, which is an additional splitting of the nuclear energy levels and $E_0$-line due to the presence of a magnetic dipole moment and an effective magnetic field at the nucleus. The hyperfine interactions provide various pieces of information (see Table 2) about the investigated nuclei and the crystal structures in which they are situated.

![Figure 13. A) Sketch of the ground and excited state of a nucleus showing the nuclear spin, the isomer shift and the resulting electrical quadrupole interaction/splitting. The two different energies resulting for the $\gamma$-rays are responsible for a doublet on the Mössbauer spectrum. B) Sketch of a doublet on a Mössbauer spectrum showing the various energies of $\gamma$-rays and the isomer shift.](image-url)
Not every element is suitable for Mössbauer spectroscopy and for iron it is the isotope $^{57}$Fe which can be practically applied. In order to perform a Mössbauer experiment in which iron is investigated a source is applied which contains $^{57}$Fe nuclei in an excited state. For this a $^{57}$Co source is applied. The $^{57}$Co decays to $^{57}$Fe which is in an excited state and releases a $\gamma$-quantum upon relaxation. The source is usually $^{57}$Co in a matrix of rhodium and has cubic symmetry in order to avoid the electrical quadrupole interaction. In addition it is normally covered by aluminum for protection. The emitted $\gamma$-rays are then directed onto the crystalline absorber. Although $^{57}$Fe

\begin{figure}
\centering
\includegraphics[width=\textwidth]{mossbauer_spectrum.png}
\caption{Representative Mössbauer spectrum of clinopyroxene and olivine from the Nakhla meteorite showing the transmission of $\gamma$-rays through an absorber. The x-scale shows the velocity with which the source is moved relative to the absorber. The y-scale shows the transmission of the $\gamma$-rays. The red and green lines show the fitting of the isomer shift and the splitting due to the electrical quadrupole interaction and are representative for various iron oxidation states.}
\end{figure}
only makes up 2.2 % of natural iron it still provides good Mössbauer measurements due to its ideal properties and a natural distribution of the various iron species (i.e. Fe$^{2+}$/Fe$^{3+}$) among the isotopes is assumed for the absorbing sample. In order to scan the various energy shifts of the hyperfine interactions and to generate a Mössbauer spectrum the source is moved relative to the absorber with changing velocities (v). As a consequence of the Doppler Effect this will cause a change in energy of the emitted $\gamma$-rays according to

$$\delta E = E_{\gamma} \times \frac{v}{c}.$$  

Thus a whole spectrum can be scanned. Behind the absorber a detector synchronized with the source velocity will measure the $\gamma$-rays that pass through the investigated sample and with this data an absorption/transmission spectrum can be generated (Fig.14). Additional detectors can be used in front of the absorber which will measure re-emitted $\gamma$-rays, conversion electrons or X-rays (Fig.15).

The obtained spectrum can then be investigated by using fitting programs such as the spectral analysis software MossA (Prescher et al. 2012). Programs like this assign doublets to the obtained curve and using the isomer shift and the electrical quadrupole interaction the number of 3d electrons and local atomic arrangements can be identified and by this the various valence states of iron (Fe$^{2+}$, Fe$^{3+}$) and their position within the crystal structure. The electrical quadrupole interaction/splitting on the spectrum is determined from the separation of the maxima of the doublet while the isomer shift corresponds to the middle point of the doublet (Fig.13, 14). The ratio of Fe$^{2+}$/Fe$^{3+}$ is analogue to the ratio of the area under the doublets. Here, however, lies a source of error. Factors causing analytical error may be the result of varying distribution of the recoil-free fraction in a crystal lattice and disturbances from the electric field gradient.

The recoil-free fraction consists of those $\gamma$-rays emitted without energy loss. Within a crystal lattice this process is not everywhere the same due to differences in for example chemical environment (e.g., coordination) and bonding strength (e.g., oxidation state) which, in turn, can lead to the wrong estimation of $\gamma$-ray absorption and thus the wrong concentration for a certain oxidation state. However, usually this error is assumed to be small and can be neglected. Another problem which affects especially the fitting process is an asymmetry of the doublets. It is most common in single crystals and is a result of changes in electric field gradient due to crystal orientation. The area under the doublet theoretically remains the same, however, since several doublets may overlap, the asymmetry may cause problems in the fitting process. One way to avoid this source of error is to analyze powdered polycrystalline samples in order to get a distribution of random orientations. However, also this can be affected especially when also the powdered sample con-
tains one preferred crystal orientation, which may for example be the case for mica crystals. A possibility to account for the asymmetry is to use a so-called asymmetry parameter in the fitting process, which has been determined experimentally for various crystalline samples.

Figure 15. The setup of a Mössbauer spectrometer.
3. Summary of papers

3.1 Paper I

Magmatic water contents determined through clinopyroxene: examples from the Western Canary Islands, Spain

In this paper we try to provide an alternative method for the determination of magmatic water contents. The H₂O component in magmas plays an important role during magma evolution and for the eruption style of a volcano which may evolve into a major natural hazard. Thus it is useful for volcanologists to examine the volatile content of magmas. Several options do exist for this purpose such as analysis of phase assemblages or feldspar-liquid hygrometry. Yet probably the most common method to measure magmatic volatiles is the application of quenched volcanic glasses or melt inclusions in minerals, which provide a direct estimate for volatile content of the rock in question (e.g., Dixon et al. 1997, Dixon and Clague 2001, Vigouroux et al. 2012). However, glasses and melt inclusions may be difficult to analyze or absent or they could have undergone degrees of post-entrapment H₂O loss or gain (e.g., Massare et al. 2002, Portnyagin et al. 2008, Baker 2008, Esposito et al. 2014, Gaetani et al. 2014, Le Voyer et al. 2014). In this paper we try to provide an alternative approach for determining the magmatic water content using the water content in clinopyroxene crystals. Clinopyroxene takes up low concentrations of hydrogen in structural defects (e.g., charge deficiencies) as a function of the magma’s water content. This approach has been tested before (e.g., Nazzareni et al. 2011); however, one limitation to this method is that clinopyroxene crystals may lose parts of their water component during magma degassing and during the eruption, especially in slowly cooling effusive lavas. At magmatic temperatures hydrogen diffusion profiles in clinopyroxene can occur over distances of several mm during minutes. Thus in this article we tested the rehydration of potentially dehydrated clinopyroxene phenocrysts from the Western Canary Islands (La Palma, El Hierro and Tenerife) in hydrogen gas at 700 °C. The potential for a rehydration of the crystals is provided by the difference in kinetics for cation and vacancy diffusion (logD ≤ –16 m²/s) and the reversible redox reaction OH⁻ + Fe²⁺ ↔ O²⁻ + Fe³⁺ + ½ H₂ (logD = –11.5 m²/s) which governs the dehydration (e.g., Ingrin and Skogby 2000, Ingrin and Blanchard 2006, Cherniak and Dimanov 2010). Subsequently the annealed crystals’ water contents together with available crystal/melt partition data were used to cal-
culate magmatic water contents. To test the validity of the method the data was compared to previously published data and specifically to calculated values from a feldspar-liquid hygrometer. Upon rehydration experiments the water content in all clinopyroxene crystals increased and the accompanied reduction of Fe$^{3+}$ was observed with Mössbauer spectroscopy. With rehydrated clinopyroxenes parental magmatic water contents of 0.71 ±0.07 to 1.49 ±0.15 wt. % were calculated. This range overlaps with the already available data for the Canary Islands and ocean island basalts (OIB) globally (0.63 ±0.13 to 1.08 ±0.11 wt. % H$_2$O) (Moore 1970, Dixon et al. 1997, Wallace 1998, Gurenko and Schmincke 2000, Dixon and Clague 2001, Kovalenko et al. 2007, Deegan et al. 2012). Further, the results obtained with clinopyroxene are reproduced by the feldspar-liquid hygrometer (cf. Waters and Lange 2015). Thus a major conclusion of this paper were that the water content of clinopyroxene phenocrysts cannot be taken for granted to be representative for magmatic water contents. However, rehydration experiments can help to restore their initial water component at crystallization and thus has great potential as a useful method for magmatic volatile quantification. In addition to these results, the paper provides new thermobarometric data and thus insights into the volcanic plumbing system underneath the Western Canary Islands.

3.2 Paper II

**Polarized IR and Raman spectra of zoisite: insights into OH-dipole orientation and the luminescence**

Several analytical methods such as for example Raman spectroscopy do rely on calibration using well described standards in order to be able to quantify water in NAMs (e.g., Bolfan-Casanova et al. 2014). Potential standards can be glasses or hydrated minerals such as zoisite. While the mineral zoisite has been described in great detail regarding its crystal chemistry, structure and optical properties, yet no polarized FTIR or Raman measurements had been published. These are of significance since the orientation and vibrational modes of the OH-dipole within the mineral have been under discussion. If the mineral would be anticipated as a standard, the orientation of the dipole is important for Raman experiments. Previous studies proposed the orientation of the OH-dipole to be along the crystallographic c axis forming a hydrogen bridge O(10)-H…O(4) represented by two main vibrational bands at 3150 cm$^{-1}$ and 2170 cm$^{-1}$ in FTIR (Dollase 1968, Linke 1970, Winkler et al. 1989, 2008). However, another hydrogen bridge O(10)-H…O(2) has been proposed and discussed (Langer and Lattard 1980, Smith et al. 1987, Liebscher et al. 2002, Winkler et al. 2008). In this paper we present polarized single crystal Raman and FTIR analysis on a near end-member zoisite sample whose precise orientation was confirmed by single crystals X-ray diffrac-
tion. The measured spectra confirm the orientation of the OH-dipole along the crystallographic c-axis, however, with a slight deviation towards the crystallographic a-axis which was detected in the FTIR measurements. Further the polarized measurements in this study exclude a potential second hydrogen bridge O(10)-H⁻O(2). With the polarized Raman measurements new insights were gained in the fluorescence caused by V²⁺ and Cr³⁺ in the mineral (cf. Koziarska et al. 1994, Gaft et al. 2005, O’Leary et al. 2007). The results show fluorescence to be strongest for measurements along the crystallographic a-axis and fluorescence bands can for certain laser wavelengths interfere in the OH-region of the spectrum. The article overall thus contributed in completing the full characterization of the mineral zoisite and makes it a potential standard sample for the quantification of water using Raman spectroscopy and Proton-scattering.

3.3 Paper III

Experimental hydration of natural volcanic clinopyroxene phenocrysts under hydrothermal pressures (0.5–3 kbar)

The paper builds on the experiments and results obtained in Paper I. Upon performing rehydration experiments in hydrogen gas on dehydrated clinopyroxene crystals from Tanganasoga volcano on El Hierro, a location where clinopyroxene crystals exhibit high water contents, several observations were made. It was not possible to rehydrate dehydrated crystals to the higher values observed in other crystals. In addition, crystals exhibiting high water contents lost parts of their hydrous component upon annealing in hydrogen gas. Since the lava samples from Tanganasoga have been interpreted to have undergone rapid ascent from greater depth with little to no magma degassing (cf. Pinel and Jaupart 2000, Manconi et al. 2009, Stroncik et al. 2009, Pedrazzi et al. 2014) a potential effect of pressure on the water content and dehydration in crystals was indicated. In this paper we test the rehydration of clinopyroxene crystals at 1 atm in hydrogen gas and under hydrothermal pressures between 0.5 and 3 kbar. Besides the samples from Tanganasoga volcano, different crystals from a variety of volcanic settings (e.g., Merapi volcano, Indonesia) and the Nakhla meteorite have been included to get a broad comparison. In addition to the effect of hydrothermal pressure on water content, the effect on redox-processes and diffusion was tested. Subsequently, after rehydration experiments magmatic water contents were determined and compared to available melt inclusion data and data from amphibole thermobarometry (Gertisser 2001, Nadeau et al. 2013, Preece et al. 2014, Barker et al. 2015). The results showed that a hydrothermal pressure was required to reach higher water contents in dehydrated crystals. Thus a dependence of the water content in the clinopyroxene crystals with pressure is indicated as the phenocrysts begin to dehydrate upon lower water fugaci-
ties in the experiments. Further water loss or gain in a crystal occurs according to the relatively fast redox-reaction $\text{OH}^- + \text{Fe}^{2+} \leftrightarrow \text{O}^{2-} + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2$ which was confirmed by an almost perfect 1:1 relation detected with Mössbauer spectroscopy. Also the kinetics of the hydrogen diffusion is independent of pressure. The results revealed further connections between rehydration experiments and magmatic water contents. Rehydration experiments under pressure on clinopyroxenes were able to reconstruct magmatic water contents in the deeper parts of volcanic systems while rehydration experiments at 1 atm in hydrogen gas resembled more the volatile contents in the upper and near surface parts of a volcanic system. Despite the new Mössbauer and diffusion data the key conclusion of the manuscript is that there is a simultaneous dehydration of clinopyroxene crystals with magma ascent and degassing. Thus water contents in clinopyroxene crystals may, beside the problem of dehydration during eruption, be evaluated with great care as to which level in the volcanic system they represent.

3.4 Paper IV

Water content in the Martian mantle from the perspective of Nakhla

The ability to exploit the water or rehydration of hydrogen associated defects in clinopyroxene as a proxy for magmatic or mantle water contents provides also great potential for the study of planetary bodies other than Earth. For example a key question of interest to planetary geologists is the water content of the Martian mantle and its role in plate tectonics which nowadays is absent on Mars. Most of our knowledge of the interior geology of Mars is based on Martian meteorites which are collectively known as the SNCs with the name derived from the three main groups Shergottites (basalts), Nakhlites (cpx cumulates) and Chassignites (dunites). A simple approach to quantify the water content of the Martian mantle is to estimate the magmatic water contents of parental melts of the available Martian rocks and estimating the mantle/melt partitioning of water (e.g., McCubbin et al. 2010a, 2012). Several methods have been applied to determine pre-eruptive magmatic water contents in the parental melts and subsequently mantle water contents for Shergottites and Chassigny, such as the analysis of phase assemblages and melt compositions (e.g., Dann et al. 2001), water contents of apatite crystals, (e.g., McCubbin et al. 2012), or the measurement of volatile contents directly from quenched volcanic glass or melt inclusions (e.g., Bector et al. 2003, McCubbin et al. 2010a, Usui et al. 2012). However, no detailed studies had yet been conducted on the Nakhla meteorite regarding magmatic or mantle water content. On the basis of Paper III we performed rehydration experiments at 700 °C and 2 kbar on dry Nakhla clinopyroxene to determine magmatic water contents at Martian upper mantle depth. From these values for the water content of the Nakhla mantle source are deduced.
Further the study provides new Mössbauer data on Nakhla clinopyroxene and olivine and tests the validity of a previous attempt to estimate water content in Martian NAMs by measuring the Fe$^{3+}$ content. After annealing clinopyroxene crystals exhibit water contents $\sim 130 \pm 26$ ppm and thus similar to values observed in phenocrysts from terrestrial basalts. These water contents imply that the basaltic magma crystallizing Nakhla may have had $\sim 1.42 \pm 0.28$ wt. % H$_2$O, despite previous assumptions of a relatively dry melt. Assuming a low degree of partial melting this implies a water content of $72 \pm 16$ ppm for Nakhla’s mantle source region and combining this value with data from other SNC meteorites an average mantle value of $102 \pm 9$ ppm H$_2$O for the Martian upper mantle throughout geologic time is determined. Thus the Martian upper mantle overall appears much drier than Earth’s upper mantle ($\sim 250$ ppm H$_2$O) but similar to the terrestrial MORB mantle source ($142 \pm 82$ ppm H$_2$O). The results of this study could point towards a profound volatile loss in the early history of the planet most likely enabled by an early outgassing of Martian mantle either as a result of magma ocean crystallization or extensive magmatic activity during the first few hundreds of millions of years. In addition, Mössbauer results and compositional data of clinopyroxene and olivine show that the total Fe$^{3+}$ content in the minerals is unlikely to be representative of the initial water component and thus this approximation should not be used.

3.5 Paper V

**Hydrogen analysis in nominally anhydrous minerals by Transmission Raman spectroscopy**

A number of different analytical methods such as for example FTIR spectroscopy and SIMS analysis have been well established to quantify the water content in NAMs. Each single one may have certain advantages such as a very low detection limit (e.g., FTIR) or that no crystal orientation is needed for the analysis (e.g., SIMS). Yet, disadvantages such as spatial resolution and sample preparation do exist. Recently the use of Raman spectroscopy has been tested as an alternative method for the OH quantification in glasses and NAMs (e.g., Thomas et al. 2008, Bolfan-Casanova et al. 2014). One particular advantage of this method is the good spatial resolution which allows the analysis of small samples in a non-destructive manner. One problem which yet might arise is that crystals may still require orientation and that sample induced background from sample heating in dark crystals or fluorescence can affect the quality of spectra and thus the detection limit. In this study we test the application of transmission Raman spectroscopy in contrast to the more common backscattered Raman configuration. The application of transmission Raman spectroscopy has so far been limited to pharmacy (e.g., Matousek and Parker 2007, Griffen et al. 2015) where it was
shown to reduce sample induced background drastically, improve the quality of the spectra and to be more representative of the whole sample material rather than just a single spot within the sample. Crystals of clinopyroxene and garnet as well as pieces of a synthetic rhyolite glass were polished to very thin thickness and near transparency and analyzed by transmission Raman spectroscopy using a blue laser (488 nm). The transmission configuration provided very good quality spectra of the OH region of the analyzed mediums. Further, specifically for clinopyroxene, a reference spectrum of a dehydrated crystal was taken and subtracted from the other obtained spectra and by such the sample induced background was reduced to a very low level, making the detection of even low water contents possible applying low laser power (28 mW). The results show the best orientation for Raman measurements on clinopyroxene and demonstrate the effect of sample thickness on integrated peak intensities when measuring in transmission configuration. A main conclusion of the manuscript is that with increasing crystal thickness the integrated intensity increases first in a near linear fashion and then more logarithmic thus showing that thickness has a big effect on the detection limit but implies also the need for a thickness normalization of the results. Further, to obtain best results, specifically for a subsequent quantification, all mediums should be analyzed at the same or similar thickness. The quantification of OH in garnet and clinopyroxene was tested by applying the comparator technique and the rhyolite glass. For clinopyroxene the results correspond well with data obtained through FTIR spectroscopy in combination with wavenumber-dependent absorption coefficients (e.g., Libowitzky and Rossman 1997) and proton-proton scattering in conjunction with a zoisite standard (see Paper II) which was employed on two crystals to get a third independent comparison. For garnet crystals the match between analytical methods was less good and revealed significant differences for different IR absorption coefficients, thus pointing out the necessity for further research in this area. Overall the study demonstrated the application and showed the advantages of transmission Raman spectroscopy for OH quantification in NAMs. In addition, a set of clinopyroxene crystals was presented which can serve as a standard for an internal, mineral specific calibration when using Raman spectroscopy to analyze water in NAMs.

3.6 Paper VI

Common analytical methods to quantify water in NAMs are FTIR spectroscopy (e.g., Skogby 2006), SIMS (e.g., Wade et al. 2008) or even Raman spectroscopy (e.g., Thomas et al. 2008). These methods provide many advantages such as good spatial resolution and low detection limits but may also include disadvantages. One disadvantage for example is the need of crystal orientation (e.g., FTIR, Raman spectroscopy) for more precise measurements. Yet another drawback is that a three-dimensional analysis of the
hydrogen and thus water distribution in NAMs is difficult or impossible with these techniques. In this paper an alternative method, the proton-proton scattering technique (e.g., Reichart et al. 2002, 2004, Borysiuk et al. 2013), is applied for the analysis of hydrogen in clinopyroxene. The technique is independent of crystal orientation, does not rely on absorption coefficients and offers a high spatial resolution together with the ability to provide a visualization of hydrogen distribution at depth within the sample. In this way potential inclusions or concentration differences due to crystal chemistry or even diffusion profiles can easily be investigated. Further, the method measures the total concentration of hydrogen within the sample which can thus be used to test the validity various IR absorption coefficients. In this study, two proton-proton scattering systems together with crystals of the hydrated minerals zoisite (see Paper II) and muscovite as standard material were applied to measure the water content in clinopyroxene crystals from Tanganasoga volcano on the Canary island El Hierro as well as a mantle xenolith from Kilbourne Hole in New Mexico (see Paper III). Four crystals from Tanganasoga volcano were analyzed by FTIR spectroscopy in order to get a comparison to water contents determined with the proton-proton scattering and to test wavenumber-dependent (Libowitzky and Rossman 1997) and mineral-specific (Bell et al. 1995) absorption coefficients. One disadvantage of the proton-proton scattering technique is its dependency of sample thickness on the beam energy of the available system. By such samples for low energy beams must be very thin (~10 μm) which imposes difficulties for sample preparation. This work tests a new method involving a micro mill to drill wells into crystals and subsequent polishing which leaves the bottom of the well with the appropriate thickness for analysis while the rest of the crystal remains at a size and thickness which allows for easy handling. The proton-proton scattering analyses of selected single crystals reveal water contents similar to those obtained by FTIR spectroscopy and the application wavenumber-dependent absorption coefficients thus proposing them to be more applicable than their mineral-specific counterparts. Further, the analysis and identification of depth variations in hydrogen and inclusions within a crystal were shown. In addition, measurements on thin clinopyroxene crystals from both Tanganasoga volcano and Kilbourne Hole revealed similar water contents as previously determined for other crystals by FTIR (see Paper III) thus showing the usefulness of the new sample preparation. One disadvantage of such thin samples, however, is yet that potential depth variation of hydrogen content in crystals is difficult or impossible to observe.
4. Conclusions

The outcomes of the research presented in this thesis can be evaluated by looking at the three individual aspects on which the research focused, namely quantification methods, incorporation mechanisms and geological applications of water in nominally anhydrous minerals.

Conclusions regarding incorporation of hydrogen into NAMs can mostly be drawn from Papers I and III and focus on the following: The water content in NAMs, especially clinopyroxene in volcanic rocks, cannot be taken for granted as to represent initial mantle or magma chamber conditions. Upon a change, more precisely a drop in water fugacity during magma ascent and degassing as well as during the eruption process, phenocrysts gradually lose their hydrous component as they equilibrate to the new conditions. Water contents in clinopyroxene phenocrysts may thus represent different stages in a volcanic system. In extreme cases they completely dehydrate during volcanic eruptions. A further conclusion is that the rate of diffusion of hydrogen into and out of structural defects in clinopyroxene is independent of pressure as compared to its dependence on temperature. Especially the Mössbauer results of this study show the hydrogen diffusion in and out of clinopyroxene crystals to function via the redox-reaction $\text{OH}^- + \text{Fe}^{2+} \leftrightarrow \text{O}^{2-} + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2$ in a 1:1 relation. A potential dehydration of a crystal can be reversed by applying rehydration experiments in hydrogen gas or hydrothermal pressure.

In the field of geological applications, the studies conducted for this thesis has shown that the water content as well as the structural defects within NAMs in conjunction with rehydration experiments can be exploited as a proxy for magmatic and subsequently mantle water contents. Several examples for this were outlined. Despite the advantage for volcanologists this method provides new opportunities for planetary geologists studying extra-terrestrial sample material and to draw conclusions for mantle water contents of other planetary bodies (see Paper IV).

Regarding analytical methods this thesis showed new approaches on how to quantify water in NAMs by using Raman spectroscopy and proton-proton scattering. New polarized FTIR and Raman spectra of the hydrated mineral zoisite were shown in Paper III which helped to identify the position of the OH-dipole in this mineral. The precise orientation of the dipole is essential when the mineral is applied as an external standard for spectroscopic meth-
ods such as Raman spectroscopy when quantifying water in NAMs. In Paper V transmission Raman spectroscopy, which previously has been used mostly in pharmaceutical studies, was successfully applied to quantify water contents in clinopyroxene crystals by applying a low laser power. One major conclusion of this work is that for the transmission configuration sample thickness has a big impact on spectrum-quality and consequently on the detection limit. Samples should ideally be near transparent and have the same thickness when being analyzed in the transmission configuration to achieve best results. Transmission Raman spectroscopy offers new potential for using the high spectral resolution that Raman spectroscopy offers and yet to be able to identify low concentrations of water. With proton-proton scattering in Paper VI it was shown that when using FTIR for water quantification in clinopyroxene wavenumber-dependent absorption coefficients seem more generally applicable than their mineral-specific counterparts. Further, the investigation of three dimensional distribution of water in clinopyroxene crystals was shown. By such an efficient way to analyze hydrogen variation in connection with composition as well as inclusions was shown. The new method for sample preparation for the analysis by proton-proton scattering allows further the analysis of the same sample by other analytical methods such as transmission Raman spectroscopy where transparency and thin samples provide good results.
Grundämnet vätes betydelse inom geologi är stort, eftersom väte har stor påverkan på de fysikaliska och kemiska egenskaperna hos mineral, bergarter och småltor. Den vanligaste förekomsten av väte i mineral är i form av hydroxidjoner (OH⁻), bundna i strukturella positioner i hydramerade mineral, såsom glimrar och amfiboler. Under senare år har det dock visats att väte även förekommer i nominellt ohydramerade mineral (NAMs), d.v.s. mineral som inte har OH⁻ eller H₂O som en komponent i sin grundformel, som exempelvis pyroxen eller olivin. Väte inkluderas i nominellt ohydramerade mineralen när de växer i en magma eller hydrotermal miljö, och kopplas till strukturella defekter som katjonvakanser (t.ex. 2H⁺ vs. Mg²⁺) eller fungerar som laddningsbalans (t.ex. Al³⁺ + H⁺ vs. Si⁴⁺). Jämfört med hydramerade mineral är koncentrationen av väte i NAMs oftast väldigt låg, men kan ställa viktig information till förfogande. Så kan nominellt ohydramerade mineral till exempel ge upplysningar om vattenhalter i en vulkans magma eller en planets mantel. En komplicerande faktor är dock att mineralen kan föröra väte genom diffusion under uppstigning i en vulkan eller under ett vulkanutbrott. Diffusionen har visats förriggja genom den reversibla redox-reaktionen OH⁻ + Fe²⁺ ↔ O²⁻ + Fe³⁺ + ½ H₂.

Syftet med denna studie fokuseras på hur väte i detalj kan inkluderas i och lämna en kristall, vilka olika metoder som finns för att analysera vätekoncentrationen och hur man kan använda nominellt ohydramerade mineral, speciellt klinopyroxen, för att få information om volatiler i magma och manteln i jordens inre och på andra planeter. Avhandlingen är uppdelad i två delar. Första delen handlar om den praktiska tillämpningen av nominellt ohydramerade mineral inom geologi, och fokuserar på möjligheten att bestämma magmatiska vattenhalter och problemet med dehydreringen av kristaller i vulkaniska system. När en kristall dehydreras genom redox-processer, så bevaras de strukturella defekterna eftersom kinetiken för vakansdiffusionen är betydligt långsammare än redox-reaktionen under magmatiska temperaturer. Detta tillsammans med möjligheten att reversera redox-reaktionen kan utnyttjas för att rehydrera dehydrerade kristaller. Rehydrering och redoxprocesser testades på klinopyroxen från olika geologiska områden genom att upphetta kristallerna i vätgas vid 1 atm, och även under hydrotermalt tryck mellan 0.5 och 3 kbar för att återställa deras ursprungliga vattenhalter. Där-efter användes vattenhalterna för att bestämma motsvarande magmatiska vattenhalter som jämfördes med data från småltinklusioner, bergartsanalyser,

prover (~10 µm), utvecklades och testades en ny metod för prepareringen av tunna kristaller. Mätningar med protonspridningen i denna studie visade den stora potentialen för tredimensionell kvantifiering av väte i kristaller. Ytterligare framgick att vågaltätsberoende absorptionskoefficienter för IR spektroskopiska data generellt verkar lämpligare för kvantifiering av OH i klinopyroxenkristaller än mineralspecifiska absorptionskoefficienter.
\[
\text{OH}^- + \text{Fe}^{2+} \leftrightarrow \text{O}^{2-} + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2
\]

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