Method Development for the Measurement of Water in Plagioclase by Fourier Transform Infrared Spectroscopy

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ABSTRACTS

Abstract 1: Scientific

Water concentrations in volcanic phenocrysts and glasses can be used to reconstruct the eruptive histories of volcanoes and their magmatic systems. With current analytical methods, it is difficult to determine water concentrations of small samples (less than a few hundred micrometers in diameter) like some volcanic phenocrysts. A new method proposed by Nils B. Gies at the University of Bern uses Fourier Transform Infrared (FTIR) spectroscopy and requires less preparation time than traditional methods. The goal of this study is to test this new method on the mineral plagioclase.

The traditional method for obtaining a water concentration of an anisotropic mineral by FTIR involves polishing four sides of a block and taking spectra in three perpendicular directions. With the Gies Tetrahedron Holder (GTH) method, water concentrations can be obtained from a mineral slab polished on only two sides. Before this work, the GTH method had never been tested on plagioclase. Through this research, the hypothesis that the total water content determined from measuring water absorbance in three perpendicular directions by FTIR within a slab of plagioclase on a pyramid holder is the same within uncertainty as the water content found from measuring water absorbance in three perpendicular directions on a polished plagioclase block (the traditional method) was tested.

Five different samples of plagioclase were tested: (1) albite; (2) oligoclase; (3) labradorite; (4) bytownite; and (5) anorthite. These gem quality samples were obtained from the Smithsonian National Museum of Natural History. Based on the testing of these various compositions, the GTH method shows mixed results when compared to the block method. The GTH method produces values higher and lower than the water content determined using the block method.

Improvements can be made to this method and new ideas can be explored. Overall the results for this new method are promising for a cheaper and quicker alternative to current methods. With additional time and samples, I clearer conclusion can be made regarding the method.

Abstract 2: Plain Language

Measuring water in minerals is important and useful. Determining the water content of minerals in volcanic rocks and meteorites provides information about the eruptive history of volcanoes and helps us to better understand the origin of Earth’s water.

With current methods, it is difficult to calculate the water content of small samples like volcanic minerals that crystallize out of melt. Current analytical methods involve a lot of sample preparation time. One of those methods uses a block of a mineral that is polished on four sides. Infrared light (IR) is sent through the sample in three perpendicular directions. The amount of IR light that is absorbed by the mineral can be measured and used to determine water content. A new method has been developed by Nils B. Gies from the University of Bern. It uses a 3D printed holder that keeps a crystal oriented 55° up from the surface. The crystal is called a slab and is only polished on two sides; this requires less preparation time. IR light is sent through the sample in three perpendicular directions by rotating the holder.

Based on the testing of various compositions of plagioclase, the GTH method shows mixed results when compared to the block method. The GTH method produces values higher and lower than the water content determined by using the block method.

New spectra and samples are needed to investigate this further. Improvements can be made to this method and new ideas can be explored. Overall the results for this new method are promising for a cheaper, quicker alternative to current methods.

INTRODUCTION AND BACKGROUND

The measurement of water in volcanic minerals can be used to constrain the eruptive history of volcanoes and their magmatic systems, including their degassing rates and magma storage depths. Water also "has profound effects on melting temperatures, crystallization pathways, and explosivity" (Hamada et al. 2011). Measuring water in minerals can also be used to understand the water budget of meteorites, representing the building blocks of the Earth.

One widely used method for measuring the water content of minerals is Fourier Transform Infrared (FTIR) spectroscopy. This is a widely available and relatively cheap method that can be found in many laboratories. It is "ideally suited to investigate even very low concentrations of hydrogen in geologic samples because it is highly sensitive to polar O-H bonds in the structure" (Libowitzky and Beran, 2006). It works by emitting infrared (IR) light from the source. This light passes through the sample and certain frequencies are absorbed by chemical bonds, e.g. O—H bonds in water absorb IR light. The remaining light is collected by the detector (**Fig. 1**). From here a spectrum is produced with wavenumbers in cm^{-1} (675-6000 cm^{-1}) on the x-axis and absorbance on the y-axis. A water peak can be observed generally in the wavenumber range 2800 to 3700 cm^{-1}. The exact wavenumber range and the intensity of IR absorption varies depending on the composition of the mineral being analyzed.

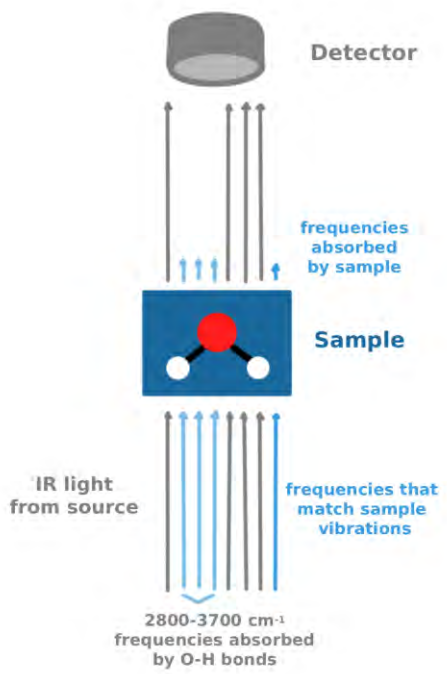


Figure 1. How FTIR generally works for our research.

For this project, I have focused on plagioclase feldspar, a solid solution series mineral with the endmembers of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). Plagioclase is a biaxial anisotropic mineral, meaning that its refractive index varies with orientation, so it absorbs IR light differently depending on orientation. Previous studies have established that measurements of IR absorbance in three perpendicular directions (Libowitzky and Rossman, 1996) can be used to calculate total water concentration in plagioclase by FTIR (Johnson and Rossman, 2004). The need to measure water absorbance in three perpendicular directions means that sample preparation for FTIR measurements is challenging and labor intensive, requiring the preparation of blocks polished on four sides or the preparation of multiple slabs (polished on two sides) in

perpendicular orientations. The preparation is difficult to perform on smaller samples, e.g. volcanic phenocrysts less than a few hundred micrometers in diameter. Since it is difficult to prepare these samples, the number of samples that can be prepared over the course of a typical research project is limited, leading to less data collected.

Methods for preparing minerals for analysis by FTIR include: 1) the traditional block method; 2) random sampling of slabs in many orientations, Kovacs et al. (2008); and 3) the Gies Tetrahedron Holder method.

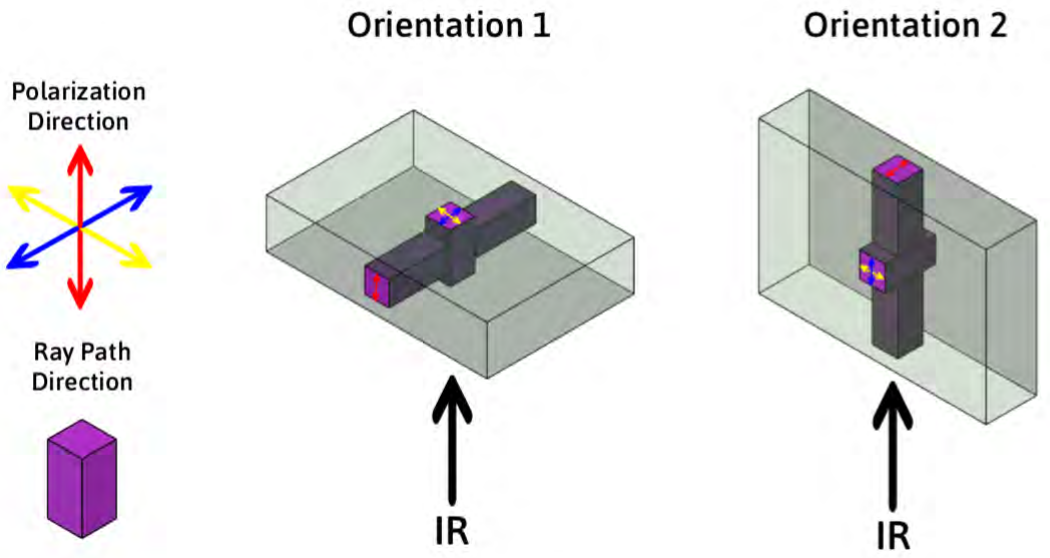


Figure 2. Diagram of block method showing polarization and ray path direction.

The traditional block method involves polishing a mineral block on four sides and taking spectra in three perpendicular directions using the FTIR spectrometer (**Fig. 2**). The integrated areas of the OH peaks in three perpendicular directions are summed together and used in the Beer-Lambert equation to calculate the water content of the sample. (Johnson and Rossman, 2004).

Another method presented in Kovacs et al. (2008) uses doubly polished crystals, or slabs, and unpolarized light. Many slabs are made from the sample that hopefully have the crystallographic axes in many different orientations. A single spectrum is taken using unpolarized light for each slab. The area of the water peak of each spectrum collected is multiplied by three and used to calculate the water concentration of that slab. This is done many times and then averaged to get an accurate concentration for the sample as a whole. If 10 randomly oriented grains are used, there is an uncertainty of ~20%. The uncertainty decreases as more grains are used (Kovacs et al. 2008).

The method that will be used for this study is the Gies Tetrahedron Holder (GTH) Method. This is not the official name as Nils B. Gies at the University of Bern has not yet

published a paper using his technique. This method uses a slab polished on 2 sides and a 3D printed holder developed by Gies that sits at a 55° angle from the surface (**Fig. 3**). The initial stage of this project involved the design of a 3D printed lid and a 3D printed stage that orients the Gies holder (**Fig. 3**). The newly designed lid enables small crystals to be attached to the Gies holder, and the newly designed stage allows the holder to be oriented precisely on the FTIR. Gies has not measured any feldspar samples with this holder, so the goal of this thesis is to test whether this method can be used to obtain accurate water concentration measurements in plagioclase phenocrysts by FTIR.

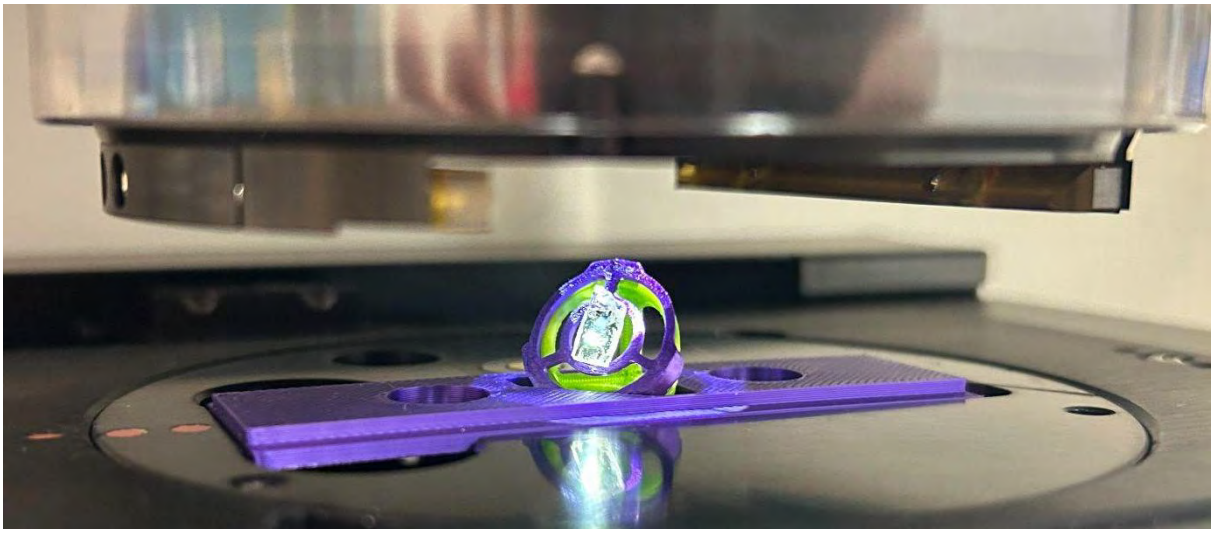


Figure 3. The GTH with 3D printed lid and stage plate.

OBJECTIVES OF RESEARCH AND BROADER IMPLICATIONS

With current FTIR methods, it is difficult to determine water concentrations of small samples like volcanic phenocrysts. In this thesis, I tested whether a tetrahedron holder can be used to obtain accurate water concentration measurements in plagioclase phenocrysts by FTIR. If the tetrahedron holder method is shown to be accurate within error (as assessed by comparison to water concentration measurements using traditional methods), this could significantly reduce the sample preparation burden for making measurements of water in plagioclase by FTIR, which could increase the amount of data that can be collected in future studies.

NULL AND ALTERNATIVE HYPOTHESES

H0: Using a Fourier Transform Infrared (FTIR) spectrometer, the total water content determined from measuring 3 perpendicular directions within a slab of plagioclase on a tetrahedron holder and the water content found from measuring 3 perpendicular directions of a polished block will be the same.

H1: Using a Fourier Transform Infrared (FTIR) spectrometer, the total water content determined from measuring 3 perpendicular directions of a slab of plagioclase on a tetrahedron holder and the water content found from measuring 3 perpendicular directions of a polished block will be statistically different.

EXPERIMENT DESIGN

Sample Selection

The first sample tested was an oligoclase (An_{22}) from the Hawk Mica Mine located in Bakersville, North Carolina (NMNH ID: 102979). Four additional samples with varying compositions were tested: (1) albite (An_{01}) sampled from Rutherford Mine in Amelia, Virginia; (2) labradorite (An_{58}) from Labrador, Canada; (3) bytownite (An_{88}) from Pacaya Volcano in Guatemala; and (4) anorthite (An_{95}) from Great Sitkin in Alaska. All these gem quality samples were obtained from the Smithsonian National Museum of Natural History (NMNH). The NMNH labels the bytownite from Pacaya Volcano as an anorthite, but EMPA work performed by S. Desikamani report an anorthite content of 88% (**Fig. 4**) and previous literature refers to this sample as a bytownite (Johnson & Rossman, 2004). Each sample has a NMNH ID: (1) C 5391 18; (2) 45011; (3) 122261; (4) 136231.

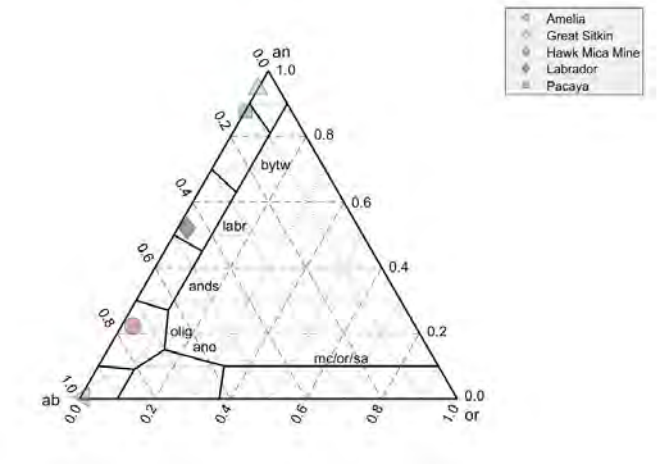


Figure 4. Feldspar ternary diagram of the four samples tested.

Block Method

Preparing the Sample

The oligoclase sample (NMNH 102979) we selected was a museum quality sample provided to us by the Smithsonian National Museum of Natural History located in Washington, DC. It was selected due to its lower water content compared to other samples in the lab's possession. A block of this sample was cut using the Princeton Scientific WS-25 wire saw located in the UMD Planetary Volcanism Lab. The sample was then placed on a glass slide and secured to it using Crystalbond. This block was polished on 4 sides using polishing papers starting at 220 grit down to 5 µm. The next smallest grit size was used when all the scratch marks look to be the same size or new grit size has removed all the larger scratches from the previous. The polishing wheel located in the lab or the Minimet 1000 was then used for the last two grit sizes of 3 µm and 1 µm.

Cleaning the Samples

The sample must go through a series of baths to remove the crystal bond, organics, or other surface contaminants. The chemical order is first acetone, then toluene, and finally isopropyl alcohol. Each bath is 30 minutes long and three baths are conducted of each chemical.

Taking Spectra

The instrument being used is the Nicolet iN10 MX Infrared Imaging Microscope for the FTIR spectrometer and the OMNIC Picta Software. The sample is oriented N-S on the FTIR spectrometer and spectra are taken using 0° polarized light (0°P) and 90° polarized light (90°P). This is two of the three perpendicular directions. The block is then rotated up on its side and spectra are taken using 90°P to obtain the third perpendicular direction (**Fig. 2**). The areas of these peaks are measured in the software (**Fig. 5**) and used in the Beer-Lambert equation to calculate the water content of the sample (Johnson and Rossman, 2004).

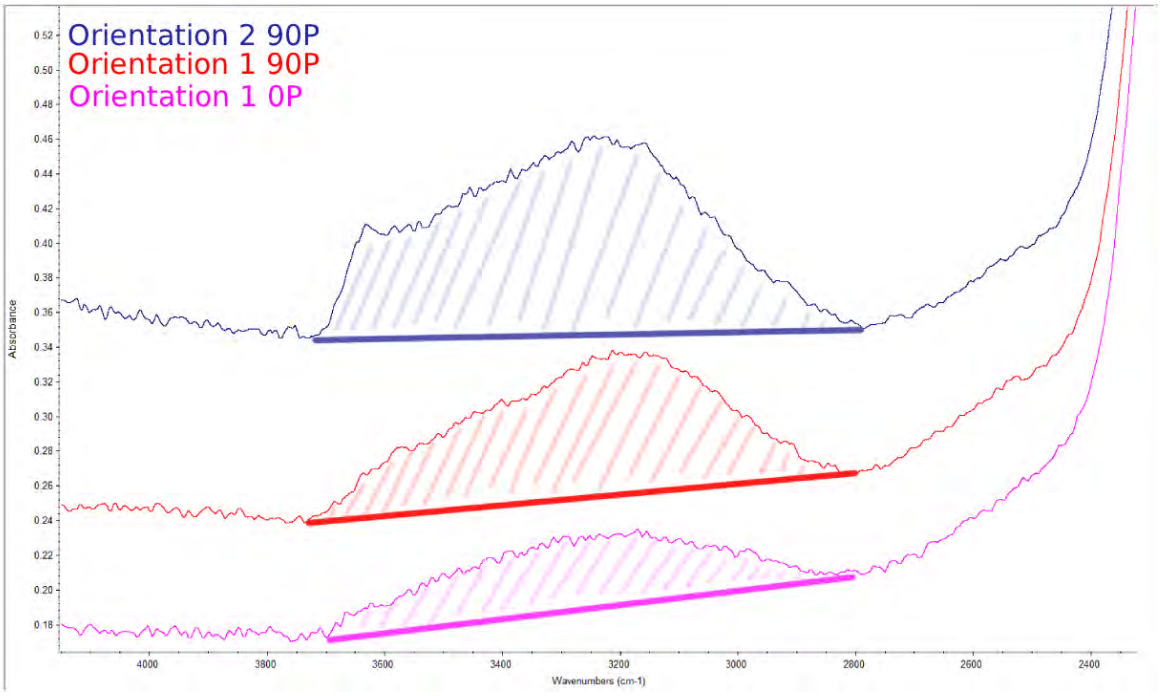


Figure 5. The diagonal lines show the area under a water peak with an established baseline. The area is then used to calculate the water content.

Calculating the Water Content

To calculate the water content in parts per million (ppm), the Beer-Lambert equation (variation #1) is used.

$$C_{H_2O} = \frac{A * mw}{\rho * \varepsilon} * 10^6$$

$$A = \frac{A_1}{d_1} + \frac{A_2}{d_1} + \frac{A_3}{d_2}$$

A is the total integrated area of OH- related bonds (**Fig. 5**). In the example shown in **Fig. 5**, the areas under the peaks at the wavenumbers 2800 to 3700 cm^{-1} are used for $A_{1\text{-}3}$. The three spectra shown are Orientation 1 (O1) with 0°P, O1 with 90°P, and Orientation 2 (O2) with 90°P. The thickness of the crystal in centimeters is represented by $d_{O1,O2}$. Two thicknesses are needed because two orientations are used (**Fig. 2**) This is measured using a micrometer thickness gauge. The density of plagioclase (ρ) is 2650 g/L. $\boldsymbol{\varepsilon}$ is the integral absorbance coefficient, which is 202,600 ± 20,260 L mol^{-1} H_2O cm^{-2} (Mosenfelder et al. 2015). Everything is then multiplied by 10^6 or 1,000,000 to convert from weight fraction to parts per million.

Gies Tetrahedron Holder (GTH) Method

Preparing the Sample

The sample used comes from the same larger oligoclase sample from the Hawk Mica Mine in North Carolina. A small piece of this sample was already broken off but a new one could be cut using the Princeton Scientific WS-25 wire saw. The sample was then placed on a glass slide and secured to it using Crystalbond. The slab was then polished on 2 sides using polishing papers starting at 220 grit down to 5 µm. The polishing wheel or the Minimet 1000 was used for the last two grit sizes of 3 µm and 1 µm. Preparation of this sample is quicker than preparation of the block.

Cleaning the Samples

The sample went through the same series of baths to remove anything that could affect the spectra collected. The chemical order, length of time of each bath, and the number of baths remained the same.

3D Modeling and Printing

The original GTH (100% size) was too large to fit on our FTIR. To solve this issue, it was decreased to 50% of the original size. To allow for smaller crystals to be attached to the holder, lids were created using Fusion 360 with a circle as the attachment point (**Fig. 6**). Since crystals vary in size, lids with different circle sizes were created to accommodate any sample. To orient the holder in the same position for each measurement, a new stage plate was designed and printed that lines up a leg of the holder in the N-S direction every time.

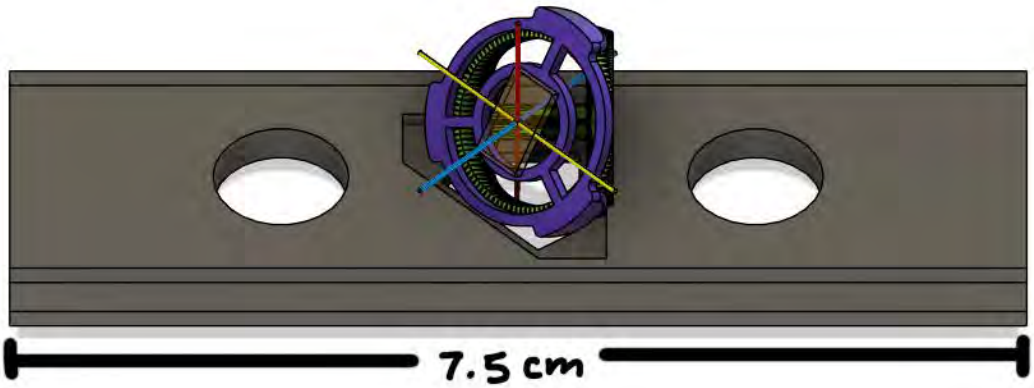


Figure 6. GTH with 3D printed lid on 3D printed stage plate in Fusion 360.

Attaching the Crystal to the Lid

The sample is attached to the 3D printed lid using Crystalbond. It is important to minimize the Crystalbond used to attach so it doesn't coat the crystal and affect the spectra. To begin the process, a glass slide with crystal bond on it was placed on a hotplate and heated up to about 85°C. Using tweezers, little dollops of crystal bond were pulled out of the larger clump and placed on the glass slide. Once enough dollops were made, the slide was pulled off the hotplate. Using a razor blade, dollops were scraped off and placed directly on the crystal where you would like to attach the lid to it. The crystal that is on a clean glass slide was then placed on the hotplate to melt the crystal bond. Once it was hot enough (the crystal bond is not sticking to the tweezers), the glass slide with the crystal was pulled off the heat. After a couple of seconds, the lid was placed on the crystal and a popsicle stick was utilized to make it flat and even. Once it felt secure and had cooled for around 3 minutes, the lid was placed on the tetrahedron holder to fully cool. It was important to place the lid on the holder quickly so it would not pop off. It was also important to minimize acid and heat exposure of the lid because it would cause warping and/or deterioration.

Taking Spectra

Once the crystal-lid-holder system had cooled, it was placed in the 3D printed stage plate for spectral analysis. After the sample on the holder was loaded on the stage plate and FTIR, the condenser needed to be optimized over air (the right or left hole of the stage plate). Next, the z-position of the center of the crystal needed to be found. It was found that one value of z-position doesn't always equal a micron. This is due to the condenser optimized for each type of light. To figure out the conversion, the top and bottom ledges of the stage plate were used. The height difference between these ledges was a known value (1.435 mm). The top ledge of the stage plate

was focused on, that z- position was recorded. This was then repeated for the bottom ledge. These numbers were subtracted to get the thickness and compared to the known thickness in microns. A conversion was calculated if the numbers differed by more than 50. The middle of the crystal sat 8 mm above the stage plate. The z-position of the top of the stage plate and an additional 8 mm focused the FTIR on the middle of the crystal. The 3D printed stage plate oriented a leg of the GTH in the N-S direction each time on the FTIR spectrometer. Spectra was then taken (at 1-20 spots) using 0°P and 90°P in an orientation, then rotated to the next orientation. There were three orientations in total that are collected (**Fig. 7**).

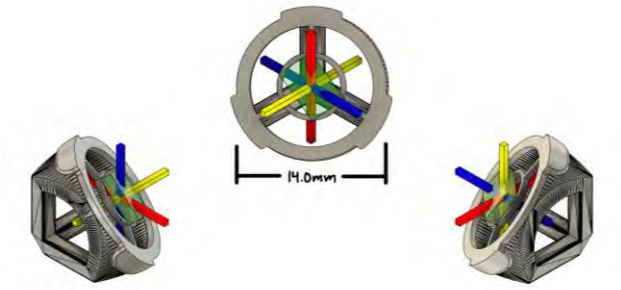


Figure 7. GPH with 3D printed lid oriented in three orthogonal directions.

Calculating the Water Content

The areas of these peaks with a straight baseline were measured in the software (**Fig. 7**) and used in the Beer-Lambert equation (variation #2) to calculate the water content of the sample (Johnson and Rossman, 2004).

$$C_{H_2O} = \frac{A * mw}{\rho * d * \varepsilon} * 10^6$$

The thickness of the crystal (d) is actually the path length passing through the sample. Since the holder oriented the slab up to a 55° angle, a refracted beam path length had to be calculated using Snell's Law and simple trigonometry.

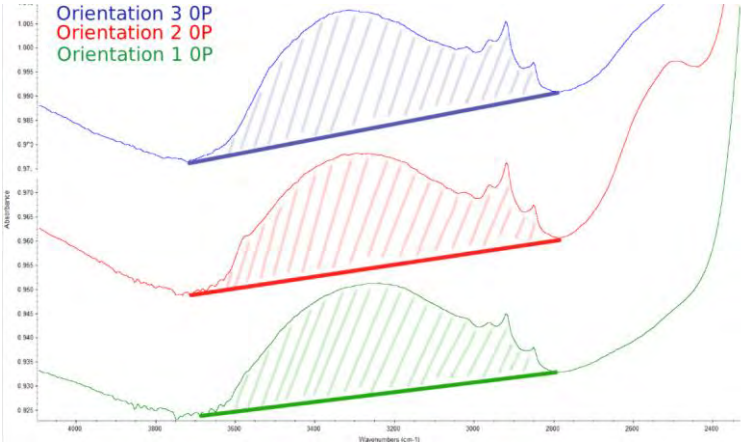


Figure 8. The diagonal lines show the area under a water peak with an established baseline. The area is then used to calculate the water content. The spikes on the right side of the area are thought to be organics (Johnson and Rossman, 2003).

RESULTS

Block Method

In each orientation, we took measurements at both the bottom/top of the crystal and as close to the middle as possible. The uncertainty of the baseline for each area is relatively small, with the highest being 0.633 and the lowest being 0.003 (**Table 1**). There might also be error on total integrated area due to background subtraction (Bell et al. 1995). By taking spectra in both 0°P and 90°P in Orientations 1 and 2, multiple calculations can be used to determine the water content of the sample. For example, O1 0°P + O1 90°P + O2 90°P can be used and then O1 90°P + O2 90°P + O2 0°P as well (**Fig. 2**).

Albite

The block of albite from Amelia, VA had a thickness of 0.0721 cm in O1 and 0.0955 cm in O2. After averaging the water contents calculated using the two combos, albite was found to have an average water content of 199 ± 63 ppm H_2O (**Table 2**, **Fig. 9**).

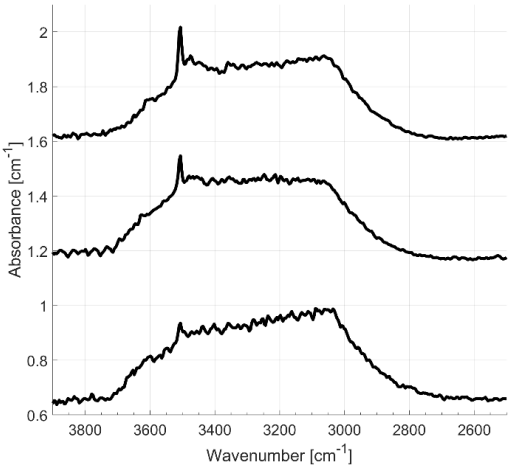


Figure 9. Albite Block C1, O1 0°P on bottom, O2 90°P on top.

Oligoclase

The block of oligoclase from North Carolina had a thickness of 0.2103 cm in O1 and 0.3417 cm in O2. After averaging the water contents calculated using the two combos, oligoclase was found to have an average water content of 14.7 ± 2.1 ppm H_2O. (**Table 2**, **Fig. 10 (LEFT)**).

Labradorite

The block of labradorite from Labrador, Canada had a thickness of 0.2480 cm in O1 and 0.3010 cm in O2. After averaging the water contents calculated using the two combos, labradorite was found to have an average water content of 424 ± 69 ppm H_2O. (**Table 2**, **Fig. 10 (RIGHT)**).

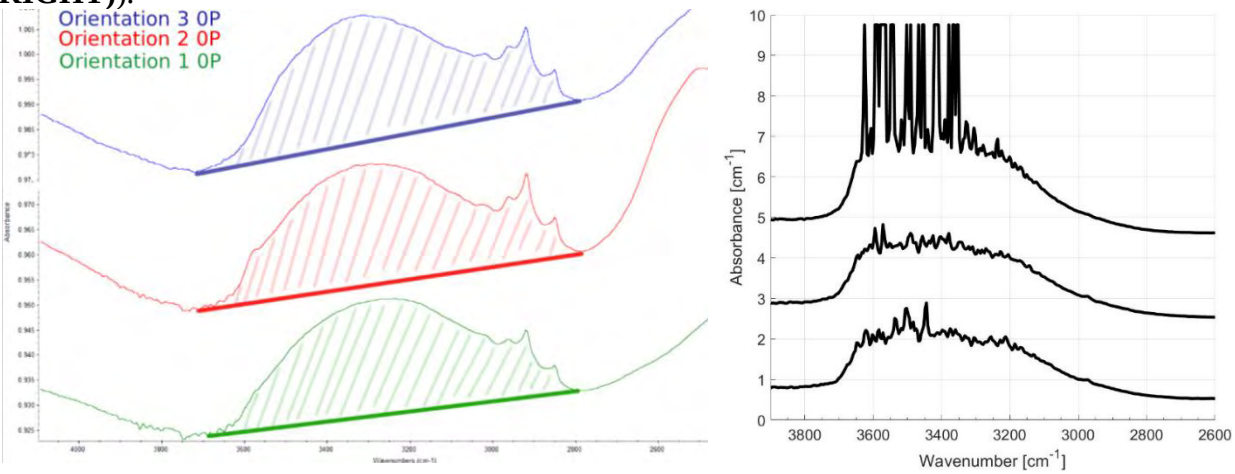


Figure 10. (LEFT) Oligoclase Block (RIGHT) Labradorite Block C1, O1 0°P on bottom, O2 90°P on top

Table 1. Block method reported thicknesses, thickness corrected mean peak areas, mean water contents, and average water content. C stands for combination, C1: O1 (0P) + O1 (90P) + O2 (90P), C2: O1 (0P) + O2 (0P) + O2 (90P). C1 and C2 were focused in the middle of the crystal when taking spectra. Two blocks were made and analyzed from the Great Sitkin anorthite sample. d_{O1} is the thickness of the crystal in Orientation 1. d_{O2} is the thickness of the crystal in Orientation 2.

Sample Compositions	C1	C2	d_{O1} (cm)	d_{O2} (cm)
Albite			0.0721	0.0955
Peak Area (cm^{-2})	6573	5245		
Water content (ppm)	221	176		
	Average water content (ppm): 199			
Oligoclase			0.2103	0.3417
Peak Area (cm^{-2})	459	415		
Water content (ppm)	15.4	13.9		
	Average water content (ppm): 14.7			
Labradorite			0.248	0.301
Peak Area (cm^{-2})	11912	13366		
Water content (ppm)	400	449		
	Average water content (ppm): 424			
Bytownite			0.1977	0.3778
Peak Area (cm^{-2})	2473	2386		
Water content (ppm)	83.0	80.1		
	Average water content (ppm): 81.5			
Anorthite			0.0580	0.1013
Peak Area (cm^{-2})	2525	2307		
Water content (ppm)	85	77		
			0.0576	0.1253
Peak Area (cm^{-2})	2378	2223		
Water content (ppm)	80	75		
	Average water content (ppm): 79			

Bytownite

The block of bytownite from Pacaya Volcano in Guatemala had a thickness of 0.1977 cm in O1 and 0.3778 cm in O2. After averaging the water contents calculated using the two combos, the bytownite was found to have an average water content of 81.5 ± 2.1 ppm H_2O.

Anorthite

Two blocks of anorthite from Great Sitkin Island, Alaska were analyzed. Block one had a thickness of 0.0580 cm in O1 and 0.1013 cm in O2. Block two had a thickness of 0.0576 cm in

O1 and 0.1253 cm in O2. After averaging the water contents calculated using the two combos and two blocks, anorthite was found to have an average water content of 79 ± 8.6 ppm H_2O.

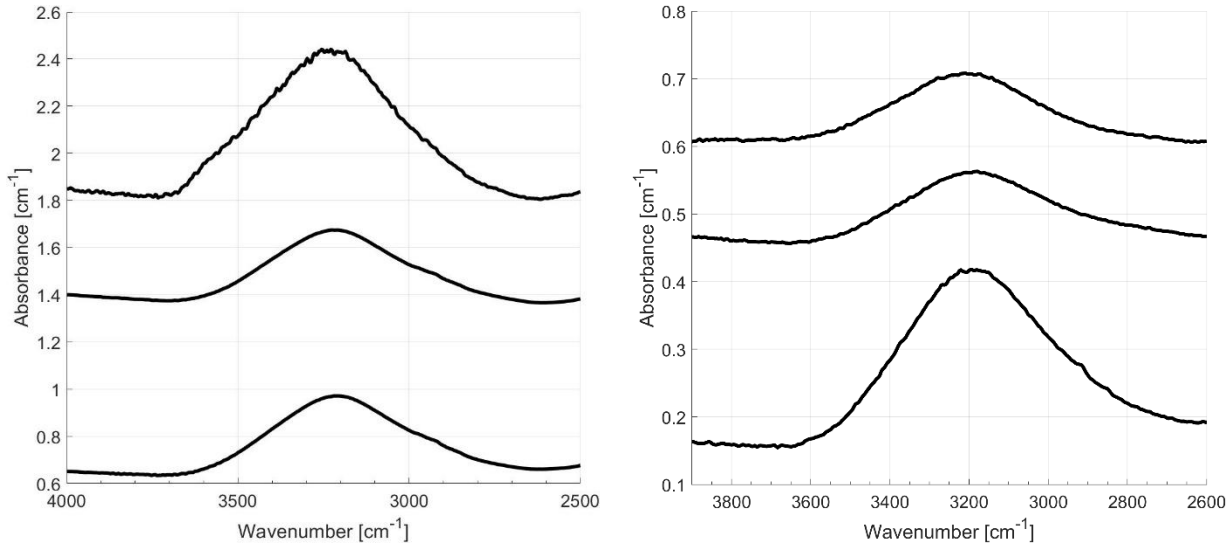


Figure 11. (LEFT) Bytownite Block C1, O1 0°P on top, O2 90°P on bottom. (RIGHT) Anorthite Block C1, O1 0°P on bottom, O2 90°P on top

Gies Tetrahedron Holder Method

This method was first tested on oligoclase during the Fall 2025 semester. While performing the method, there were difficulties aligning the GTH in the proper orientation each time. To solve this issue the stage plate was created to align a leg of the holder in the N-S direction each time. Due to failure to properly orient the crystal when taking spectra, this value was not included.

In each orientation, we took spectra using both 0P and 90P. This allows us to calculate the water content of the sample using multiple combinations including O1 0P + O2 0P + O3 0P and O1 90P + O2 90P + O3 90P. A standard straight baseline was used for the area of the peaks.

Albite

Two slabs from the large sample of the Amelia, VA albite were created and analyzed. The first slab analyzed was 0.1308 cm thick, and the second was roughly half of that with a thickness of 0.0657 cm. The average water content of the thicker slab was 226 ± 20.6 ppm H_2O. The thinner slab had an average value of 131 ± 4.5 ppm H_2O. The mean area peaks and water contents were pretty similar between 0°P and 90°P (**Table 2**).

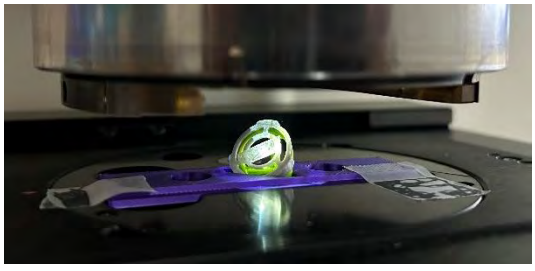


Figure 12. An albite slab on the GTH on the FTIR spectrometer.

Table 2. GTH method reported thickness (d) of the crystal, average peak areas of 0° polarized light and 90° polarized light, water contents for 0° polarized light and 90° polarized light, and the average water content of the sample. The refracted beam path length is used to calculate the water content. Two albite slabs of different thickness's were created from the same sample and both analyzed.

Sample Compositions	0°P	90°P	d (cm)
Albite			0.1308
Peak Area (cm^{-2})	992	1084	
Water content (ppm):	216	236	
	Average water content (ppm): 226		
			0.0657
Peak Area (cm^{-2})	309	300	
Water content (ppm):	133	129	
	Average water content (ppm): 131		
Oligoclase			0.0838
Peak Area (cm^{-2})	51.1	44.1	
Water content (ppm):	17.3	15.0	
	Average water content (ppm): 16.1		
Labradorite			0.0637
Peak Area (cm^{-2})	684	695	
Water content (ppm):	305	310	
	Average water content (ppm): 307		
Bytownite			0.0324
Peak Area (cm^{-2})	72.4	81.2	
Water content (ppm):	63.5	71.7	
	Average water content (ppm): 67.6		
Anorthite			0.0293
Peak Area (cm^{-2})	113	104	
Water content (ppm):	109	101	
	Average water content (ppm): 105		

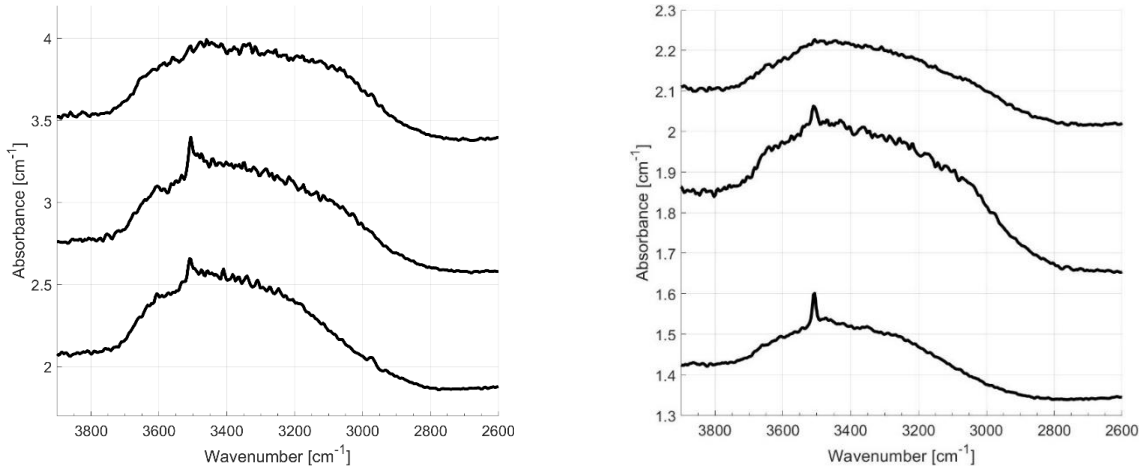


Figure 13. (LEFT) Thick is 0°P, O1 on the bottom, O3 on the top. (RIGHT) Skinny is 90°P, O3 on the bottom, O1 on the top.

Oligoclase

The oligoclase slab from North Carolina that was analyzed was 0.0838 cm thick. The average water content of the slab was 226 ± 20.6 ppm H_2O. Mean area peaks and water contents were pretty similar between 0°P and 90°P (**Table 2, Fig. 14**).

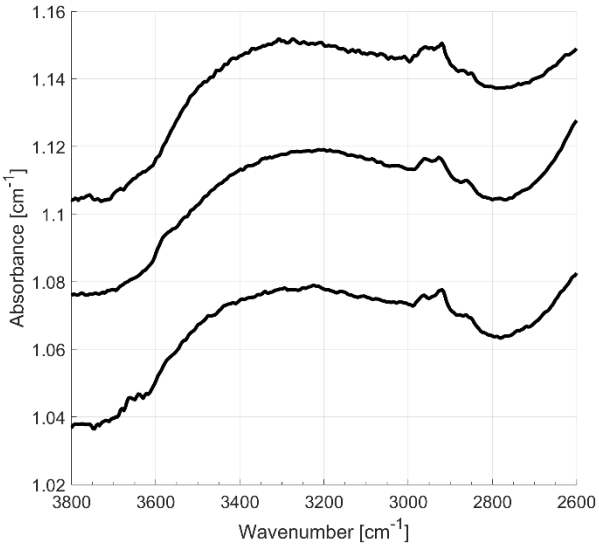


Figure 14. Oligoclase 0°P, O1 on bottom, O3 on top.

Labradorite

The labradorite slab from Labrador, Canada that was analyzed was 0.0637 cm thick. The average water content of the slab was 308 ± 5.4 ppm H_2O. Mean area peaks and water contents were pretty similar between 0°P and 90°P (**Table 2**). After looking closer at the sample, inclusions and many different phases could be seen (**Fig. 15**).

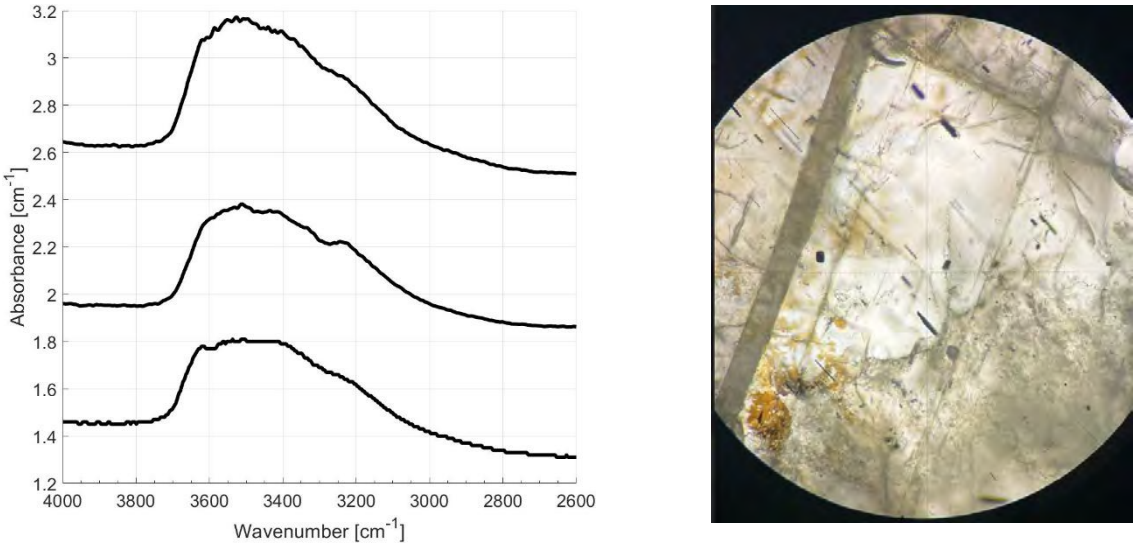


Figure 15. Labradorite 0°P, O1 on bottom, O3 on top. Under magnification (20x, field of view of 1.00 mm from top to bottom of the circle), many phases including dark inclusions can be seen.

Bytownite

This heavily fractured sample from Pacaya Volcano in Guatemala was analyzes using a 0.0324 cm thick slab. The average water content of the slab was 67.6 ± 8.5 ppm H_2O (**Table 2**, **Fig. 16 (LEFT)**).

Anorthite

A slab from the Great Sitkin Island, Alaska anorthite sample that was 0.0293 cm thick was analyzed. The average water content of the slab was 105 ± 9.1 ppm H_2O (**Table 2**, **Fig. 16 (RIGHT)**).

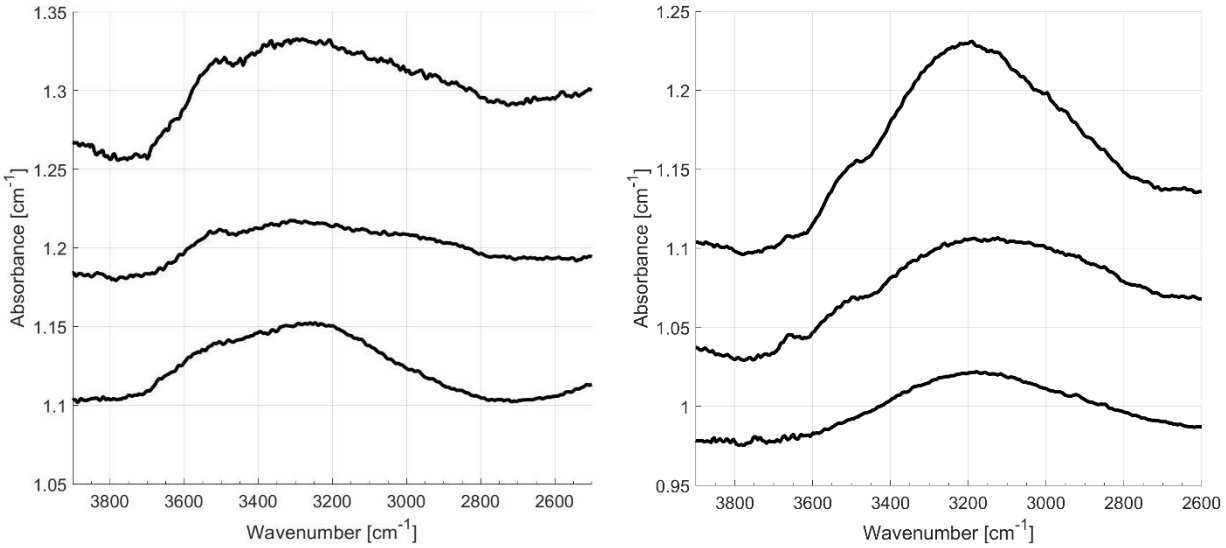


Figure 16. (LEFT) Bytownite 90°P, O2 on top, O3 in the middle. (RIGHT) Anorthite 0°P, O3 on bottom, O2 on top.

DISCUSSION

Block Method vs. GTH Method

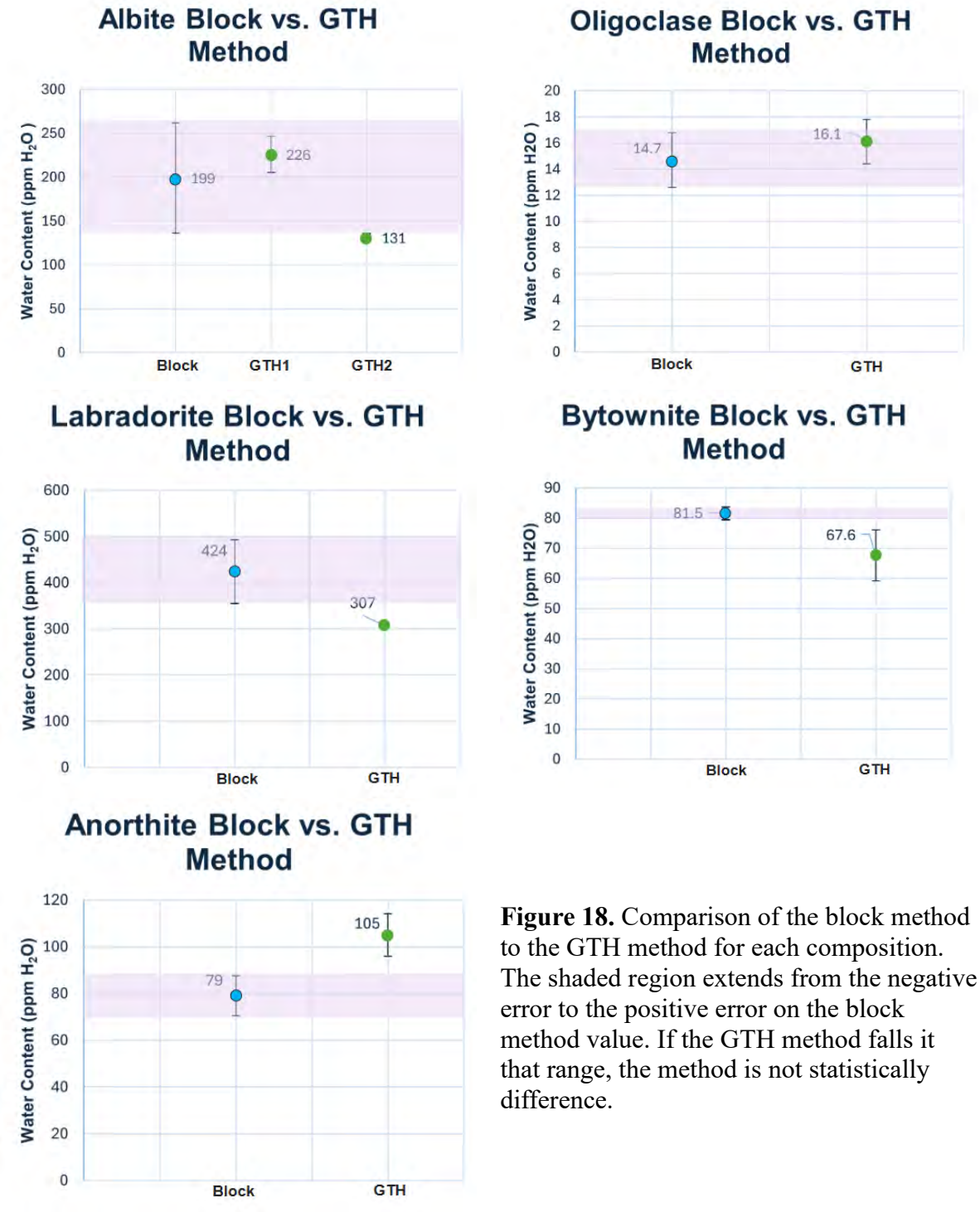


Figure 18. Comparison of the block method to the GTH method for each composition. The shaded region extends from the negative error to the positive error on the block method value. If the GTH method falls it that range, the method is not statistically difference.

The GTH method seems to be a promising method based off the data collected. For the Amelia, VA albite, the block method produced a value of 199 ± 63 ppm H_2O. The GTH method was tested on two slabs of this composition. The thicker slab that reported a value within the error bars of the block method. The second slab produced a much lower value that falls outside the error. This albite is riddled with fluid inclusions and due to this, it is most likely heterogeneous. If more blocks and slabs were tested, many different water contents would be found. This sample is not useful for comparing methods since it is not homogeneous and the same water content can't be produced using different parts of the sample.

Next is the oligoclase from North Carolina. The block method produced a value of 14.7 ± 2.1 ppm H_2O. The GTH method resulted in 16.1 ppm H_2O which falls in that range of the block method. The oligoclase sample was a nice homogeneous sample and didn't cause any troubles. This sample is useful for comparing the methods. This sample shows agreement between the two methods.

The third composition used was the labradorite from Labrador, Canada. The block method produced 424 ± 69 ppm H_2O for the water content of the sample. The spectra for this composition is very noisy and has large spikes. This is most likely due to thickness of the block being too high. The GTH method yielded a value of 307 ppm H_2O. This number falls outside of the acceptable range. The thickness of the slab was much better than the block thickness based off the cleaner spectra. Both methods may be overestimating the true amount of water in the sample. After looking at the sample with a microscope, some of the inclusions might be biotite or other minerals. This will increase the water content of the sample significantly. The spectra of the slab supports this idea since it doesn't have a normal water peak shape. The inclusions alter this shape. This sample is not great to use to compare the methods due to its heterogeneity and heavy influence from inclusions.

The fourth composition is bytownite. The block method produced a water content of 81.5 ± 4.1 ppm H_2O for this sample. The GTH method, however, produced a value of 67.6 ppm H_2O. This is much lower and is outside the acceptable range for this composition. Both spectra look clean, so the discrepance is most likely not from poor spectra. The sample itself is heavily fractured. These fractures may play a role in the difference between the values.

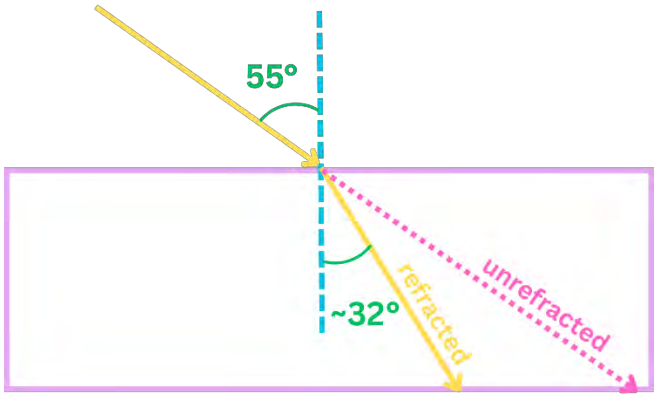
The last composition tested was the anorthite from Alaska. The block method produced a water content of 79 ± 8.6 ppm H_2O. The GTH method yielded a value of 105 ppm H_2O for its water content. The value determined using the GTH method falls outside the error bars of the block value. These numbers are statistically different. The spectra for both methods look clean and there is no clear reason as to why the values differ. To understand the picture more, additional slabs would need to be analyzed.

Based on the current data, the GTH method shows potential in being a useful method to measure water in plagioclase. Since the results show both support and evidence against my null hypothesis, I cannot except my null or alternative hypothesis. More data would need to be collected to draw a true statistical conclusion.

Snell's Law: Unrefracted vs. Refracted Beam Path Lengths

The GTH method orients the slab at a 55° angle. Due to this, the IR light enters at a 55° angle going into the crystal. Air has a refractive index of about 1 (n_{air} =1.00). Plagioclase on average has a refractive index of 1.54 (n_{plag}=1.54). Since light is moving from one medium to another, it will refract. Moving from a lower refractive index to a higher refractive index causes

the light to bend towards the normal, decreasing the angle. With this holder, the angle becomes about 32° (**Fig. 17**). Since the thickness of the crystal is know for each sample, the refracted beam path length can be calculated for each crystal using trigonometry (**Table 3**). Based off of the water content comparisons between the albite, oligoclase, and anorthite, the GTH method may be overestimating the water content. This could potentially be because the light isn't perfectly refracted. If it is behaving somewhere between the unrefracted (longer beam path length) and the refracted length, this could explain the overestimation.



$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

$$1.00 \sin 55° = 1.54 \sin\theta_2$$

$$\theta_2 = \sin^{-1}(\sin 55°/1.54)$$

$$\theta_2 = 32.135°$$

Figure 17. Snell's Law visual showing refracted and unrefracted beam path lengths and the angle created from refraction.

Table 3. GTH method beam path lengths used in the Beer-Lambert equation. Included is the composition, the thickness (d), the unrefracted path length (d_{unref}), and the refracted path length (d_{ref}). The refracted path length is the thickness used in the Beer-Lambert equation to get the water contents listed in the *RESULTS* section.

Sample Compositions	d (cm)	d_{unref} (cm)	d_{ref} (cm)
Albite			
	0.1308	0.2280	0.1545
	0.0657	0.1148	0.0778
Oligoclase			
	0.0838	0.1461	0.0990
Labradorite			
	0.0637	0.1111	0.0753
Bytownite			
	0.0324	0.0565	0.0383
Anorthite			
	0.0293	0.0511	0.0346

Uncertainties

The uncertainties reported for each value is 2σ of the population of values. For the slabs, as many as 30 values are used to calculate σ, then the value is multiplied by two. These are not the only uncertainties with the method. An overall 10% uncertainty exists due to the uncertainty of the molar absorbance coefficient from Mosenfelder et al. (2015). Another place for uncertainty is the straight baseline for the areas. It is unknown as to how much that baseline affects the calculated values, but that source of uncertainty is acknowledged none the less. There is much room for improvement with this method and hopefully these uncertainties could be reduced in future work.

CONCLUSIONS

With current methods, it is difficult to obtain a water concentration of a small anisotropic mineral sample. This research cut down on preparation time and allowed for smaller samples to be used more easily. More data can then be produced, yielding better data. The low-cost use of FTIR spectroscopy seems promising for determining the water concentration of plagioclase crystals if the samples are homogeneous. The Gies Tetrahedron Holder (GTH) method produced water contents both within the realm of uncertainty and outside of it in both directions. With refinements, time, and potentially better sample selection, this method could be very useful in determining water content in plagioclase.

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UMD HONORS CODE

I pledge on my honor that I have not given or received any unauthorized assistance on this assignment/examination.

BIBLIOGRAPHY

Bell, D.R., Ihinger, P.D., and Rossman, G.R. (1995) Quantitative analysis of trace OH in garnet and pyroxenes. *American Mineralogist*, 80, 465–474.

Hamada, M., Kawamoto, T., Takahashi, E., & Fujii, T. (2011). Polybaric degassing of island arc low-K tholeiitic basalt magma recorded by OH concentrations in Ca-rich plagioclase. *Earth and Planetary Science Letters*, *308*(1-2), 259-266.

Johnson, E. A., & Rossman, G. R. (2003). The concentration and speciation of hydrogen in feldspars using FTIR and 1H MAS NMR spectroscopy. *American Mineralogist*, *88*(5-6), 901-911.

Johnson, E. A., & Rossman, G. R. (2004). A survey of hydrous species and concentrations in igneous feldspars. *American Mineralogist*, *89*(4), 586-600.

Kovacs, I., Hermann, J., O'Neill, H. S. C., Gerald, J. F., Sambridge, M., & Horváth, G. (2008). Quantitative absorbance spectroscopy with unpolarized light: Part II. Experimental evaluation and development of a protocol for quantitative analysis of mineral IR spectra. *American Mineralogist*, *93*(5-6), 765-778.

Libowitzky, E., & Rossman, G. R. (1996). Principles of quantitative absorbance measurements in anisotropic crystals. *Physics and Chemistry of Minerals*, *23*(6), 319-327.

Libowitzky, E., & Beran, A. (2006). The structure of hydrous species in nominally anhydrous minerals: Information from polarized IR spectroscopy. *Reviews in Mineralogy and Geochemistry*, *62*(1), 29-52.

Mosenfelder, J. L., Rossman, G. R., & Johnson, E. A. (2015). Hydrous species in feldspars: A reassessment based on FTIR and SIMS. *American Mineralogist*, *100*(5-6), 1209-1221.