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DOI: 10.1016/j.vibspec.2014.08.002

# **Fine-scale determination of OH in radiation-damaged zircon using Synchrotron Fourier Transform Infra Red spectroscopy (FTIR) and Attenuated Total Reflectance (ATR).**

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## **ABSTRACT**

The crystal structure of zircon is gradually broken down by the decay of small amounts of U and Th present in zirconium lattice sites. It has been observed that, with increasing radiation damage, zircon can lose radiogenic Pb and at the same time gain water from the environment. The disturbance of the U-Pb system is a major problem in zircon U-Pb geochronology. Water penetration appears to be an important factor in Pb loss but to explore this further a technique is needed for making fine-scale in situ measurements of water on the polished surface of radiation damaged zircons. Our research has shown that Attenuated Total Reflectance Fourier Transform Infra Red (ATR-FTIR) spectroscopy with a synchrotron source and thermal analysis can be successfully used to map the fine-scale distribution of OH/H<sub>2</sub>O in radiation damaged zircons. The radiation damaged zircons were found to have an OH/H<sub>2</sub>O content varying from 0.4 to 5 % with maxima occurring in the heavily damaged (metamict) zones noted for their disturbed U-Pb systems. Whilst thermal analysis confirmed the presence of OH and possibly H<sub>2</sub>O the infrared spectra did not distinguish between them.

## **KEYWORDS**

Synchrotron ATR, infrared microscopy, water zircon interaction, detection of trace water, radiation damaged zircon, in situ water detection.

## **1. INTRODUCTION**

Zircon ( $\text{ZrSiO}_4$ ) is nominally an anhydrous mineral. However, there have been a number of reports of the presence of hydroxyl groups in hydrothermally synthesised zircon [1, 2, 3]. Frondel and Collette [1] reported infrared spectra of hydroxylated synthetic zircon and attributed a broad band at  $3515\text{ cm}^{-1}$  to 4(OH) replacing  $\text{SiO}_4$  tetrahedra. Trail et al. [3] determined water contents of  $\sim 90 - 200$  ppm in zircon synthesized under water saturated conditions and suggested the possibility of using the hydroxyl content of zircon as a record of the water activity in the magma at the time of crystallisation. In addition to reports of water of crystallization in synthetic zircon it has long been recognised that water species can be present in zircons that have accumulated significant radiation damage, e.g. Aines and Rosman [4]; Woodhead et al. [5]; Nasdala et al. [6]; Pidgeon et al. [7]. The influx of water into the radiation damage zircon can take place during hydrothermal treatment [8, 9] or weathering processes [7]. In many instances radiation damaged zircons have discordant U-Pb ages, excess common Pb and other trace elements and altered oxygen isotopic compositions. The role of water in facilitating these structural and chemical changes is poorly understood. Previous investigations of OH in radiation damaged zircon have been made using transmission infrared measurements on specially prepared zircon plates (e.g. Woodhead et al. [5]). This technique has the great advantage that OH contents can be determined quantitatively [3]. However, to investigate the role of water in the disturbance of the chemical and isotopic systems of radiation damaged zircons it is necessary to determine the OH content on the same part of a zircon grain that has been analysed for its degree of radiation damage using Raman spectroscopy and its U-Pb system, oxygen isotopic ratios and trace elements using secondary ion mass spectrometry (SIMS).

For SIMS measurements zircon grains are mounted on the surface of standard resin cylinders and polished to half their thickness. SIMS measurements can target specific parts of the zircon grains but, the sensitivity of spot analyses for OH is low due to the significant OH background in the source chamber. Also, whereas the SIMS analytical spot size of a 10 to 20  $\mu$  diameter is adequate to answer general questions on water presence, a higher spatial resolution is needed to examine the detailed relationship between water content, the degree of radiation damage and the loss of Pb within a zircon grain. Consequently, the *in-situ* investigation of the OH content of resin embedded zircon chips that have been measured on ion microprobes requires greatly improved spatial resolution and sensitivity. Transmission infrared spectroscopy on specially prepared plates is not suitable for such *in situ* determinations. Our initial investigation using a conventional source infrared spectrometer in reflectance mode to determine water in radiation damaged zircon in resin mounts was not successful. The aim of this research was to investigate whether infrared reflectance or attenuated total reflectance (ATR) spectroscopy with a synchrotron source would be

more successful for in situ OH determinations. With this technique a spatial resolution of 5  $\mu\text{m}$  is readily achieved, the source is orders of magnitude brighter than a glow-bar source and ATR has been used successfully to assess trace water content in materials such as silicate glasses [11]. In the following we show that ATR Synchrotron Fourier Transform IR spectroscopy (FTIR) can be successfully applied to determine  $\text{H}_2\text{O}/\text{OH}$  in selected areas of resin mounted zircons. Preliminary results are also presented on the calibration of the infrared analytical technique for water content using thermo-gravimetric analyses of selected Sri Lankan zircons.

## 2. EXPERIMENTAL

### 2.1 *Sample preparation*

Zircon grains were separated from rock samples using conventional heavy liquid and magnetic techniques. Grains were fixed to double-sided adhesive tape enclosed in a 2.5 cm Teflon ring. Resin and hardener were added to cover the grains within the ring and left to set. The resin button was removed from the Teflon ring and polished to expose the centre of the grains. Zircons in the present study had been subjected to U-Pb isotopic analyses and oxygen, OH isotopic measurements using Secondary Ion Mass Spectrometry (SIMS). In preparation for Infrared measurements the mounts were lightly re-polished to remove the carbon coating that was applied to reduce charging during SIMS measurement. The high U, metamict zones in grain W388 are clearly shown in reflected light in Figure 4A (darker grey).

### 2.2 *Infrared spectroscopy*

Infrared spectra were obtained on the infrared microspectroscopy beamline at the Australian Synchrotron using a Bruker Hyperion 2000 microscope coupled to a Vertex V80v FTIR spectrometer. A germanium (Ge) micro Attenuated Total Reflectance (ATR) accessory and a liquid nitrogen-cooled MCT detector were used. The tip of the ATR crystal has a diameter of 100  $\mu\text{m}$ . The aperture of the microscope was set at 20 x 20  $\mu\text{m}$ , giving a 5 x 5  $\mu\text{m}$  measurement spot size (as the refractive index of Ge is 4). The tip pressure selected (medium) was the one that gave good signal strength with minimal denting of the sample by the tip. With a raster scan used for mapping it is essential that denting be minimised so that as near as possible uniform contact is made at all sample points. Preliminary ATR spectra were recorded to ensure the ATR crystal face was making good contact with the sample prior to recording maps. Where necessary, adjustment was made to the sample support to improve contact across the ATR crystal face.

The spectra and backgrounds were recorded in reflectance mode at a resolution of  $6\text{ cm}^{-1}$  and 128 scans were accumulated in the range of  $4000\text{-}800\text{ cm}^{-1}$ . Spectra were truncated to the  $4000\text{-}2800\text{ cm}^{-1}$  region and each individual spectrum was corrected for water vapour using a separately collected water vapour spectrum before integrating the  $\text{H}_2\text{O}/\text{OH}$  peak from  $3640$  to  $3025\text{ cm}^{-1}$ . The integration limits were chosen to take into account the variation in baseline slopes encountered (from positive to negative), minimise uncertainties introduced by water vapour subtraction and the possibility of resin peaks being present. The upper limit is at the point where a valley occurs in samples with low  $\text{OH}/\text{H}_2\text{O}$  content and a negative background, and is at the edge of the water vapour spectrum, whilst the lower limit is at an asymptote for these samples before any CH bands appear. A linear baseline was employed between these points (Figure 2B). Maps were generated from spectra measured in rectangular grids at  $5\text{ }\mu\text{m}$  intervals, corrected for water vapour, and assembled into the grid pattern in which they were collected. All spectra acquisition, manipulation and processing was performed using Opus 7.2 software (Bruker Optics).

### 2.3 *Thermal analysis*

Thermal analysis was carried out on powders from two clear pebble-sized crystals of Sri Lankan zircon. Data was obtained using a TA Instruments SDT2690 simultaneous DSC-TGA instrument. Thermograms were run from ambient to  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Results shown in Figure 2 form the basis of a preliminary calibration of water content in zircon using the ATR technique.

## 3. RESULTS AND DISCUSSION

### 3.1 *The ATR technique*

Infrared spectra of embedded materials can be obtained by reflectance or Attenuated Total Reflectance (ATR) techniques. With ATR the infrared beam is totally internally reflected in a high refractive index crystal, germanium in this case, which is in intimate contact with the sample. An evanescent wave penetrates  $\sim 0.5\text{-}1.5\text{ }\mu\text{m}$  from the crystal into the sample. This leads to spectra that are analogous to transmission spectra of thin samples. The depth of penetration is wavelength dependant and is  $\sim 0.6\text{ }\mu\text{m}$  in to zircon in the  $3500\text{ cm}^{-1}$  region. If spectra are to be compared to transmission spectra they need to be corrected for wavelength dependent depth of penetration. That correction has not been applied in this work as no such comparisons have been made.

For the zircon samples used we found that ATR gave a significantly stronger OH stretching band (ca.  $3500\text{ cm}^{-1}$ ) relative to the  $\text{SiO}_4$  band near  $1100\text{ cm}^{-1}$ , when compared to measurements made in reflectance mode. Hence ATR spectra were used to assess the presence of OH/ $\text{H}_2\text{O}$  in the samples. Furthermore, the  $\text{SiO}_4$  stretch band shape is not affected by refractive index changes, as was the case with reflectance spectroscopy.

Heterogeneous zircon samples gave spectra typical of zircon containing OH/ $\text{H}_2\text{O}$  and showed significant variation in the intensity of the  $3500\text{ cm}^{-1}$  band (Figure 1). These spectra also illustrate the overlap of atmospheric water vapour bands with the zircon OH/ $\text{H}_2\text{O}$  stretching band and their intensity variation with the changing atmosphere in the dried air flushed microscope enclosure. It clearly indicates the need for their subtraction before the broad band arising from the condensed phase can be reliably integrated. The spectra also showed little or no evidence of resin having been smeared across the sample during the re-polishing process. In a few spectra very weak CH stretching bands ( $< 0.001$  absorbance units) were observed in the  $2900\text{ cm}^{-1}$  region.

Figure 1. Near here

The spectra of homogeneous zircon samples, after water correction, are shown in Figure 2B. Whilst attempts to obtain spectra with a global source and  $50\text{ }\mu\text{m}$  aperture were unsuccessful, similar spectra were obtained for bulk powdered samples using a diamond ATR cell. Unfortunately, because of the difference in depth of penetration with germanium and diamond ATR elements and powders versus polished flat surfaces it is not possible to make quantitative comparisons of the spectra.

The backgrounds in the homogenous and heterogeneous zircon spectra are also different, negative as opposed to positive. Hence the selection of integration parameters was crucial in obtaining consistent results. The background changes maybe a reflection of changes in crystallinity and refractive index. As zircon becomes more damaged (amorphous/metamict) its refractive index decreases.

Integration of the OH stretching band (Figure 2B) shows that the peak area reflects the mass loss obtained from thermal analysis (Figure 2A). Thermal analysis data show a mass loss of 0.72% and 0.36% from ambient to 500°C for WZ1 and WZ32 respectively. The initial loss from ambient to ~50°C is possibly due to adsorbed atmospheric water. The second and third losses, ~50 -300°C and ~300 -500°C, are due to dehydroxylation or H<sub>2</sub>O loss. Whilst it is tempting to attribute the second loss to H<sub>2</sub>O removal this cannot be done with certainty, but in view of its higher temperature range the third loss is definitely attributable to dehydroxylation. Irrespective of the attribution, there are at least two different OH/H<sub>2</sub>O environments in these zircons. The infrared peak was integrated between 3640 and 3025 cm<sup>-1</sup>, the limits being chosen to be as near as feasible to minima or inflection points in the spectra. The peak areas (2.26 and 1.16 for WZ1 and WZ32 respectively) correlate well with the mass losses and suggests that the method is suitable investigation OH/H<sub>2</sub>O content in these, and possibly other, minerals. The detection limit (Signal/Noise = 3) would appear to be ~ 0.2%.

Figure 2. Near here

The OH stretch is broad and without other features and hence sheds no further light on the presence or absence of H<sub>2</sub>O in the crystals. It simply suggests that there is a range of OH environments. The HOH bending band at ~1600 cm<sup>-1</sup> could not be identified with certainty due to overlap by the water vapour spectrum and thus sheds no further light on the subject. The position of the OH stretching band at 3525 cm<sup>-1</sup> (cf. liquid H<sub>2</sub>O at ~3300 cm<sup>-1</sup>) indicates that the Si-O --- H-O hydrogen bonding is weak, as would be expected in radiation damaged crystals where the unit cell has increased in size [6].

A critical aspect of the FTIR-ATR mapping technique is that good/consistent contact is made between the ATR crystal and the sample. This is illustrated quite clearly in Figure 3 where the edge of a SHRIMP spot was deliberately included in the measurement grid of a visually uniform area of a heterogeneous zircon. It clearly shows the lack of contact at the SHRIMP crater on the left of the grid and possibly a minor loss of contact near the edges in the middle of the grid. It must again be emphasized that spectral intensity is critically dependant on contact and hence the local topography, and that care must be taken in assessing results when there are imperfections in the surface under investigation.

This sample (W155) gave large peak areas (~12-15), suggesting an OH/H<sub>2</sub>O content of 4 – 5%. As we have not been able to generate standards with OH/H<sub>2</sub>O levels as high as this that estimate is based on a simple extrapolation of the WZ1 and WZ32 data.

Figure 3. Near here

### 3.2 *Traverses across zoned zircons Archaean granite (W388) from Western Australia*

The capability of the ATR technique is well illustrated by the traverses made on two zoned grains from the zircon population of granite sample (W388). These grains had previously been analysed for U-Pb isotopes using a SHRIMP ion microprobe at Curtin University and oxygen and OH content using a Cameca 1280 ion microprobe at UWA [7]. These measurements have detected OH in the grains which has been attributed to the penetration of water into the radiation damaged zircon during low temperature weathering. The grains broadly consist of a central core of low but variable U and Th content, and hence low radiation damage, and a narrow zone near the margin of grains that is high in U and Th and radiation damage to the degree of being amorphous. The outer rim of the grains is low in U and Th. This is shown on Figure 4 where expansion of the radiation damaged zone (seen as a darker grey area) has resulted in radiating fractures in the less damaged outer rim. The distribution of OH/H<sub>2</sub>O in this traverse is shown in Figure 4B. It mirrors the damage pattern and indicates that it is not surface moisture contamination that is being detected and that it arises from OH/H<sub>2</sub>O in the zircon lattice. Low OH/H<sub>2</sub>O (~0.4 %) is observed in the section of the traverse on the low U outer rim of the grain and a definite peak of ~3 % OH/H<sub>2</sub>O is observed over the metamict zircon area. Smaller irregular peaks in OH/H<sub>2</sub>O occur towards the centre of the grain indicating that water has penetrated into the lower radiation parts of the grain. The fine structure in the pattern of OH/H<sub>2</sub>O along the traverses (Figures 3B, 4B) demonstrates the sensitivity of the technique. Detailed cathodoluminescence images show that the extent of penetration is controlled by the degree of radiation damage within the grains.

Figure 4. Near here

The decay of U to Pb in zircons is probably the most widely used technique for dating igneous and metamorphic rocks. Highly crystalline zircon is extremely resistant to chemical and mechanical abrasion however the zircon structure breaks down over time due to radioactive decay. With



progressive radiation damage incompatible radiogenic Pb, that was previously tightly held in the zircon structure, becomes vulnerable to migration into amorphous zircon pathways where it can relocate within the zircon or be removed entirely. The entrance of water into the radiation damaged zircon has been shown to profoundly affect the rate of Pb loss [8, 9, 10]. However, the mechanisms of water interaction with the radiation damaged zircon and the dissolution and transport of radiogenic Pb are not well understood. Consequently the present successful demonstration of the FTIR-ATR technique for fine scale mapping of OH of complexly radiation damaged zircon is an important step in advancing this understanding. The advantage of the FTIR-ATR technique is that it can be applied “in situ” to selected grains and parts of grains that have been analysed by other isotopic, structural and chemical techniques. There is great scope for further FTIR-ATR analyses of water in natural zircons with specific radiation damage and U-Pb discordance properties and also for investigating zircons that have been subjected to hydrothermal experiments.

#### 4. CONCLUSIONS

Attenuated Total Reflectance Fourier Transform Infra Red (ATR-FTIR) spectroscopy using a synchrotron source FTIR-ATR microscopy produced spectra that can be used to determine the distribution of OH/H<sub>2</sub>O in resin mounted zircon grains that have been, or are to be used, for determining their U-Pb system, oxygen isotopic ratios and trace elements by secondary ion mass spectrometry (SIMS). Whilst the spectra did not enable us to determine whether OH or H<sub>2</sub>O or both were present in the samples thermal analysis showed that OH was definitely present. The detection limit for OH/H<sub>2</sub>O is ~0.2 % and we have observed content as high as ~5 % in highly radiation damaged (metamict) zones. To obtain more precise values standards with an OH/H<sub>2</sub>O content up to at least 5% are required. To date we have not been successful in obtaining or generating them.

Due care must be taken when employing ATR to ensure that good/uniform contact is made with samples embedded in resin mounts as the infrared beam decays exponentially from the ATR crystal and only penetrates 0.5-1.5  $\mu\text{m}$  in to the sample. As the ATR tip has a diameter of 100  $\mu\text{m}$  and the measurement area is 5 x 5  $\mu\text{m}$  undulating sample surfaces and/or skewed contact may result in a decrease of spectral intensity (absorbance) and lead inconsistent results.

The high sensitivity and spatial resolution of the ATR-FTIR technique provides a new capability for investigating the role of water in the removal of radiogenic Pb from radiation damaged zircon. The technique is also widely applicable to other minerals where sample heterogeneity data is sought.

## ACKNOWLEDGEMENTS

Part of this research was undertaken on the infrared microspectroscopy beamline at the Australian Synchrotron, Clayton, Victoria, Australia. The authors thank the Australian Synchrotron for support for undertaking the project and Dr D. Martin and Dr. M. Tobin of the Australian Synchrotron for their expert help and support. WvB and RTP acknowledge research support from Curtin Research and Development.

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#### CAPTIONS TO FIGURES

Figure 1. Variations in the OH stretching region showing changes attributable to sample enclosure atmospheric H<sub>2</sub>O vapour changes and zircon condensed phase OH/H<sub>2</sub>O content (sample W155). The spectra have been off set for clarity.

Figure 2. Thermal analysis mass loss (A) and ATR-FTIR spectra (B) of homogenous Sri Lankan zircons WZ1 and WZ32. OH/H<sub>2</sub>O peak integration base lines (- - -) are shown in B.

Figure 3. FTIR-ATR map of the OH/H<sub>2</sub>O band for zircon W155 showing lack of ATR element contact with the SHRIMP crater on the left side of the map.

Figure 4. FTIR-ATR map showing increased OH/H<sub>2</sub>O content in the radiation damaged areas of zircon W388.

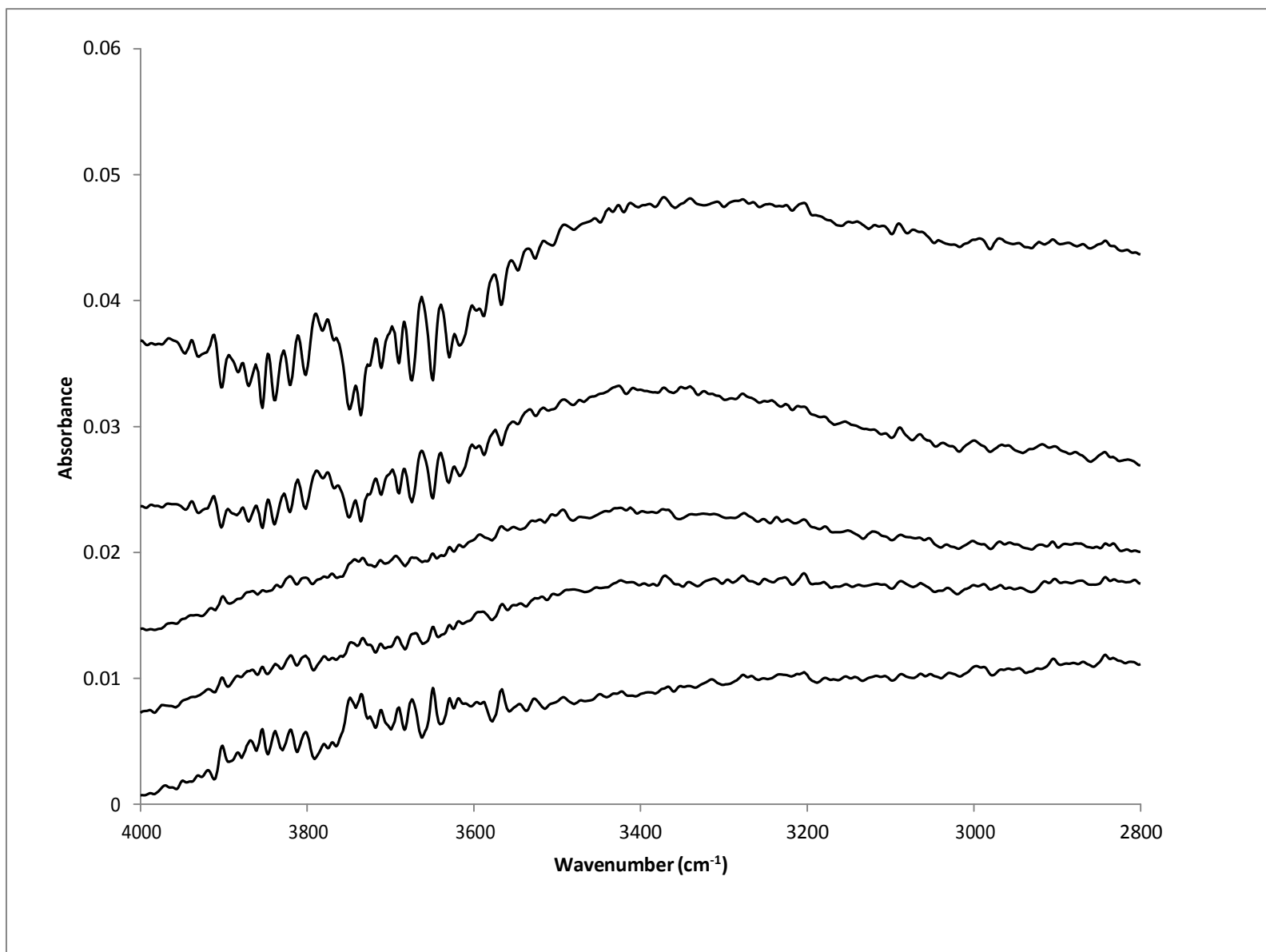


Figure 1

Figure(s)

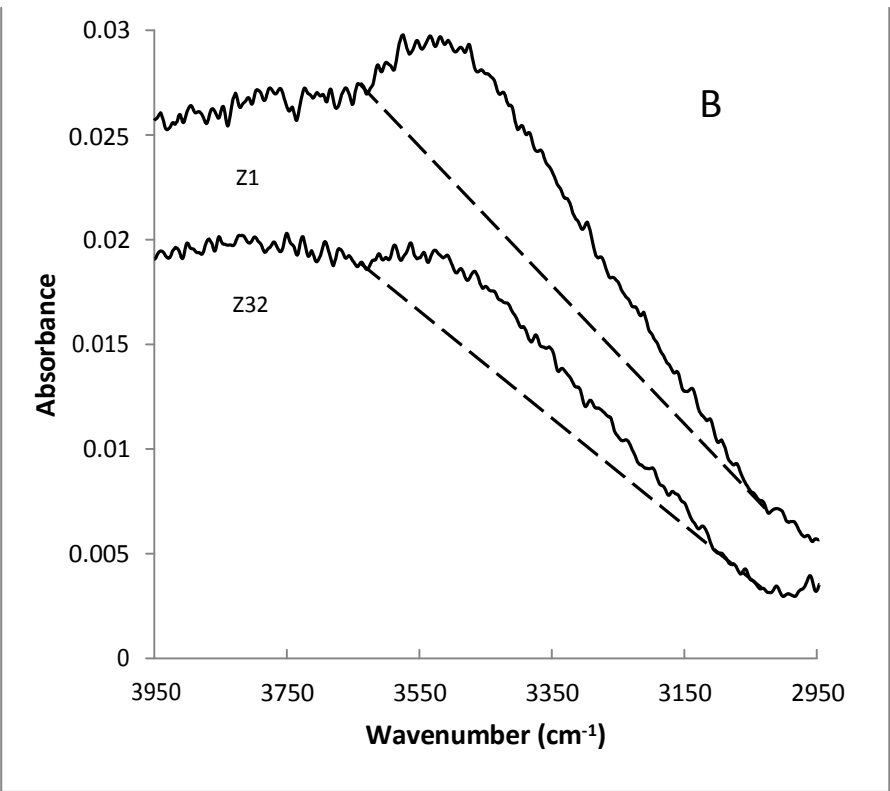
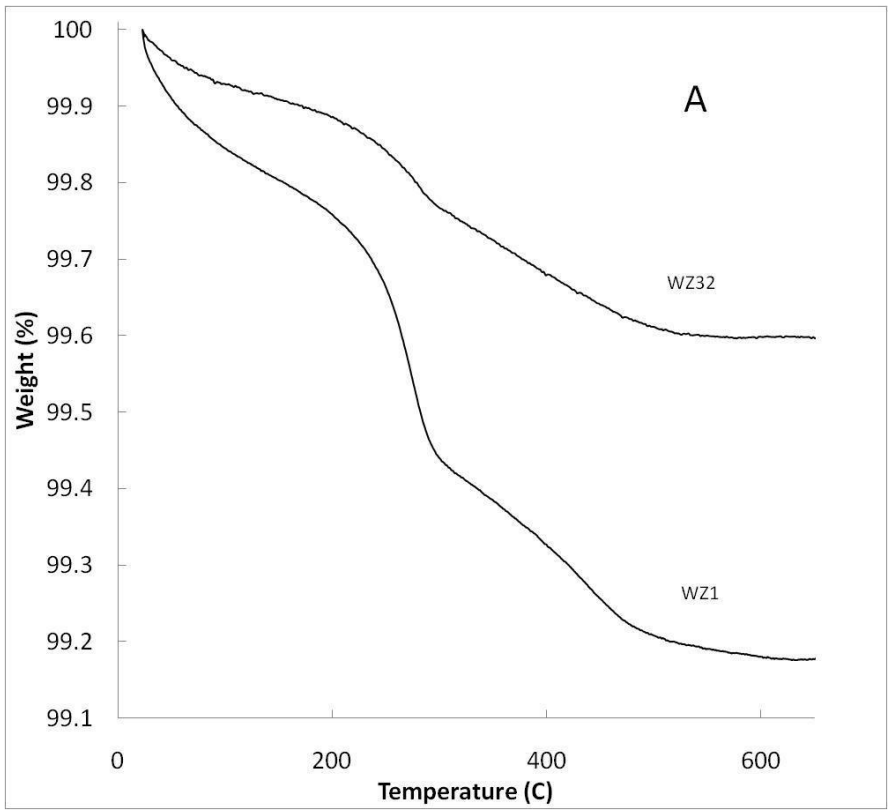


Figure 2

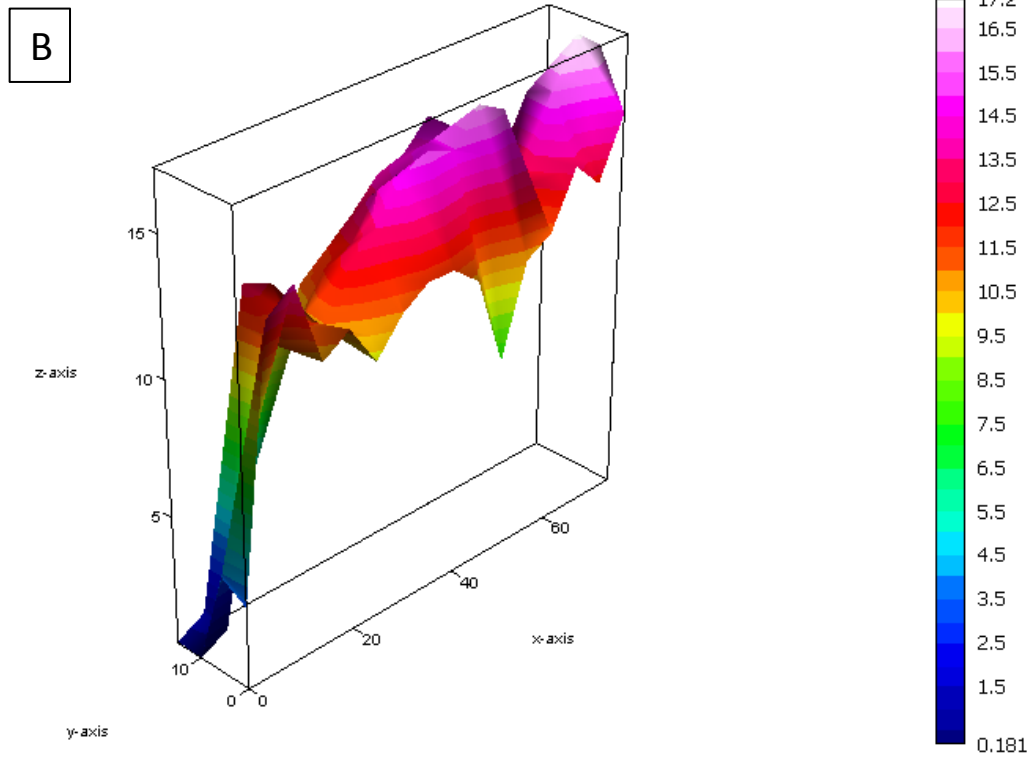
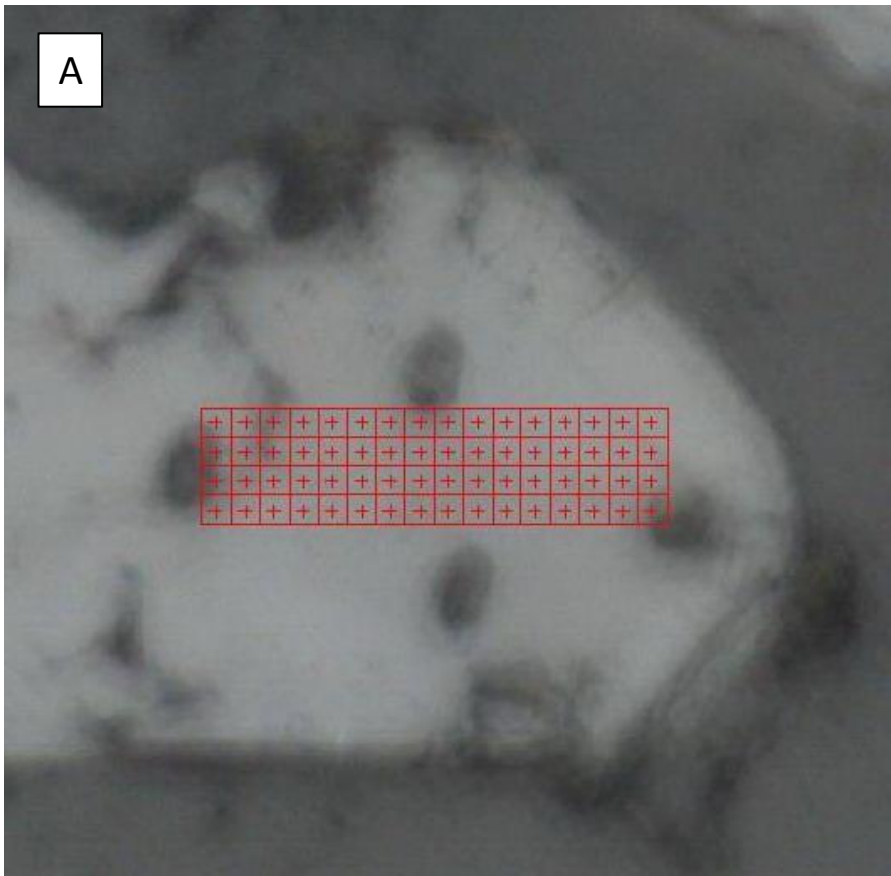


Figure 3

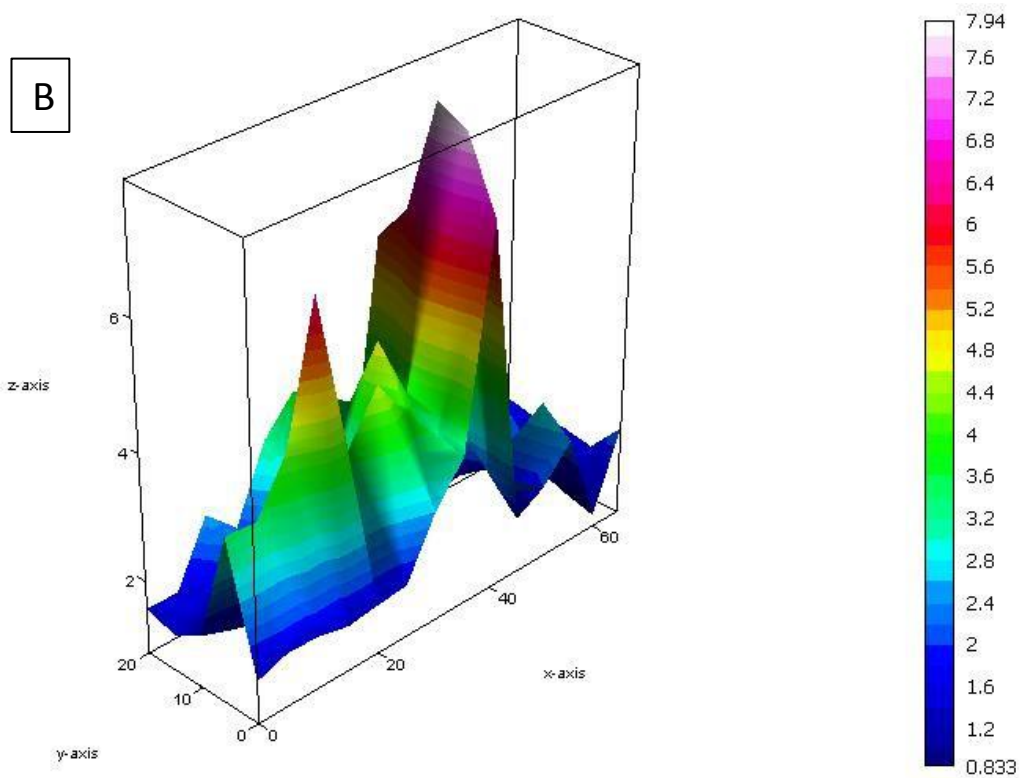
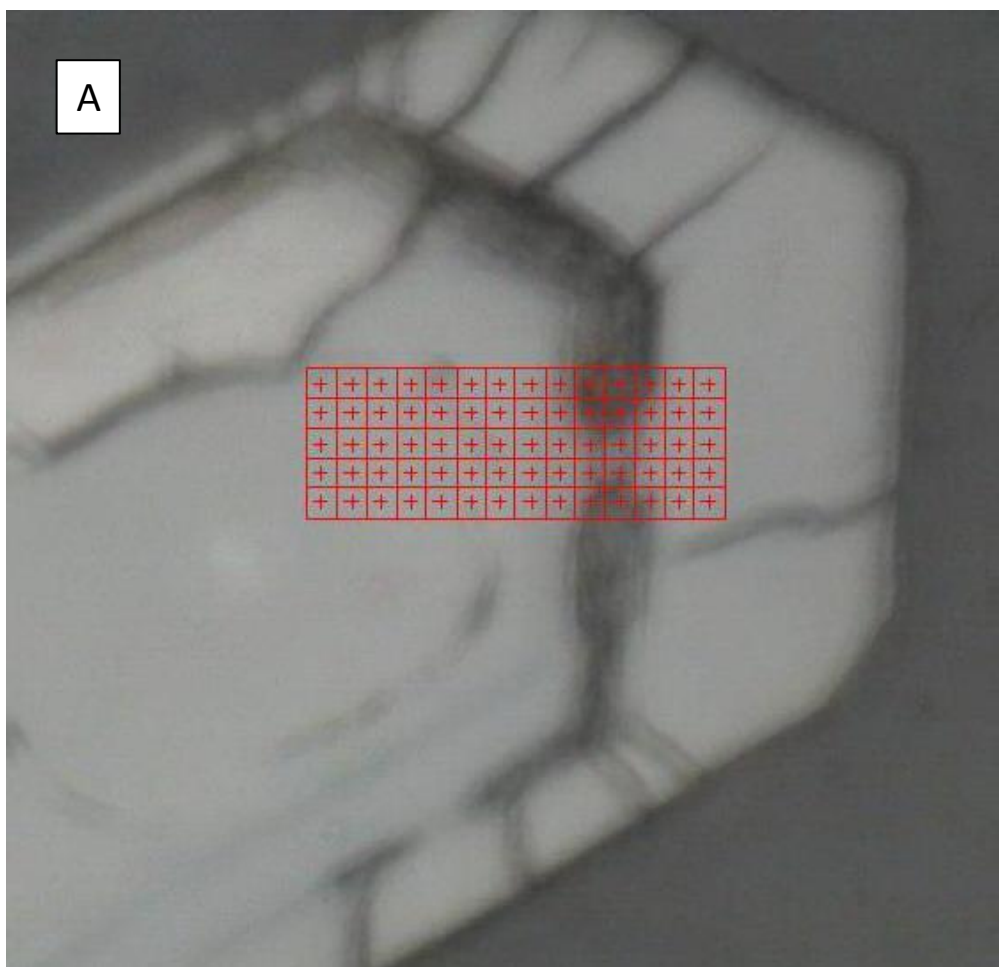


Figure 4