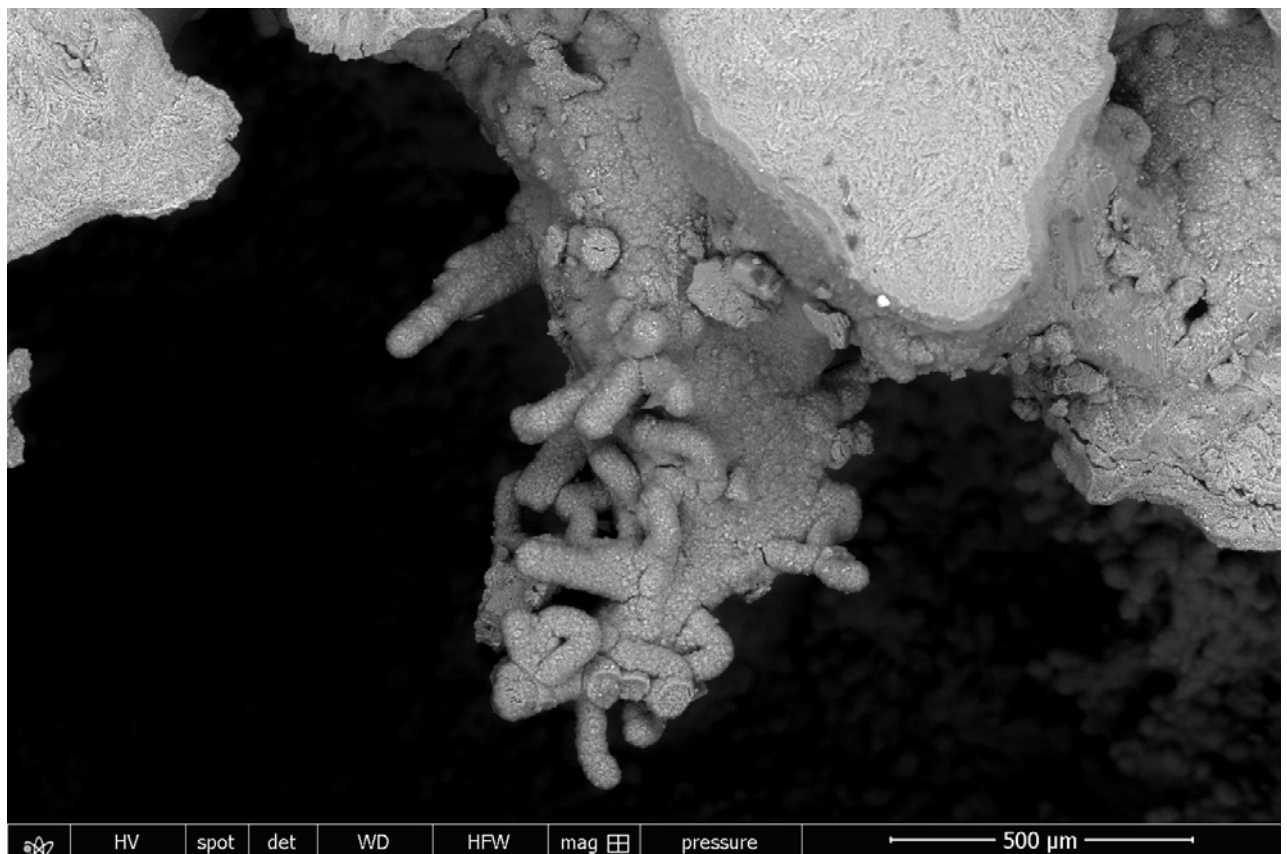


Geological and geochemical conditions controlling microbial colonization in igneous oceanic crust; implications for life on Mars

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Abstract

The igneous oceanic crust has long been considered as an inhabitable place on Earth. Research has revealed that deep-sea sediments, and even the igneous crust underneath it, harbours vast quantities of microbial life, and that prokaryotic organisms in the deep-biosphere may contain as much carbon as all plant life found at the Earth's surface. Detailed studies of the microbiological ecosystem in the deep-biosphere should therefore give us information about past, present and future environments, since changes in the ocean chemistry, temperatures, topography, and climate have a direct impact on the biotic components, such as diversity, abundance, and morphology.

This study has focused on fossilised microbes found in open and sealed pore spaces in pillow lavas from the Troodos ophiolite in Cyprus. The aim was to understand the geological and geochemical conditions that are needed for microbes to survive under the extreme conditions found in the oceanic crust, and was done by investigating the surrounding mineralogy as well as the morphology and chemical composition of fossilized microbes. Quantitative fluid composition, temperature and pH during the time of microbial colonization, as well as fossilisation was evaluated based on the mineralogy and fluid inclusions found in secondary calcite veins.

In this study, it is found that the microbial abundance increases towards higher temperatures, more pervasive hydrothermal alteration, and that colonization is favoured in volcanic rocks that are in close association with ore deposits. For their metabolism, they seem to have preferred colonization around K and Fe rich minerals, vesicle and veins that have had a high abundance of fluids. Fossilization of the microbes has mainly been done by Fe and Mg rich montmorillonite, where some fungi show precipitated, or preserved, goethite in the central strand, and rutile crystals in vacant sites in the clay. Elements such as Mg, Ca, and Na seems to have come in with the oceanic water, and Ti with the primordial water. Fossilization seems to have been initiated during temperature and pH changes of later hydrothermal activity, where at least three hydrothermal events can be seen in total in the samples.

1. Temperatures $<50^{\circ}\text{C}$ precipitated celadonite and saponite in open vesicles and veins, as well as introduced microbial life into open pore spaces.
2. A later second hydrothermal event with temperatures $<100^{\circ}\text{C}$ precipitated Na and Ca zeolite, increasing the pH from 4-6 to 7-8, stressing the microbes into starting to adhere clays as possible protection.
3. Fossilization was finalized with a last hydrothermal event with temperatures $>75^{\circ}\text{C}$, precipitating Ca carbonates, increasing pH to $>8-9$, as well as making the environment inhabitable for the microbes.

From this study, it is concluded that microbial colonization in basaltic pillow lavas favours open pore spaces that have had access to a high abundance of fluids, giving rise to more dissolved elements. These elements have come from both the oceanic and primordial water, as well as the host rock, and are essential for the microbes' metabolism. The microbes seem to prefer temperatures $<50^{\circ}\text{C}$ and a pH below 7-8.

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Introduction

The igneous oceanic crust has long been considered as an inhabitable place on Earth. Research within geomicrobiology has however revealed that this in fact may harbour one of the world's largest potential microbial habitats under extreme conditions (Schrenk et al. 2010). The vast volumes of oceanic crust present, where the upper 500-1000 meters is characterised by sub-seafloor basalt, has a high porosity of 10%, which makes this geological setting the world's largest aquifer system (Alt and Bach 2004; Orcutt et al. 2011). The main problem that has been encountered previously is that the oceanic crust is covered by oceans with average depths of 4000 m, making this geological setting out of reach in a geomicrobiological view. New technology has helped to investigate this deep biosphere via various ocean drilling programs, but have mainly focused on living microbes present in the sediments. Most studies within geomicrobiology have determined taxonomy, RNA and DNA sequences, or the morphology of fossilised microbes and ichnofossils, and their connection to paleoenvironments (Einen et al. 2008; Mason et al. 2010; Schrenk et al. 2010; Ivarsson et al. 2013). But the direct connection between microbes and their surrounding geological environment needs to be further explored.

This study will focus on fossilised microbes in vesicles and cracks in the oceanic crust from the 91 Ma Troodos ophiolite in Cyprus (Osozawa et al. 2012). The aim is to understand the geological and geochemical conditions that are needed for microbes to survive under the extreme conditions found in the oceanic crust. The study will investigate the surrounding mineralogy with alteration minerals and textures, as well as the morphology and chemical composition of possible fossilized microbes. Quantitative fluid compositions, temperature and pH during the time of microbial colonization will be evaluated based on the mineralogy. This might help us to understand why some fluid pathways becomes colonized with microbes while others reseal with traditional secondary alteration minerals, and how the microbes can be preserved. If we can understand the conditions microbes need for living in the deep biosphere on Earth, we might be able to understand where life would be expected on other planets.

Geological background

Igneous oceanic crust is created along spreading ridges, found at diverging plate boundaries, where hot magma rises along fissure zones due to thinned crust and buoyancy. Sheeted dykes are created at the axis of the fissure, or very close to it, while lava flows extend from the fissure zone and some kilometres away. Active faulting of the dykes occur after the intrusion is almost done, while faulting of the lava flow occurs both during deposition as well as after the completion, resulting in the possibility for hydrothermal fluids to enter the crust. Hydrothermal fluids are considered to be an off-axis attribute, that goes on some ten to twenty million years after the crystallization age (Pirajno, 2010). The oceanic crust is to a lesser extent also affected by hot spot plumes. Such hot spots reheat the oceanic crust and contributes with additional lava flows, heat and recirculation of hydrothermal fluids, which can contribute to new microbial diversity in old oceanic crust (Ivarsson et al. 2008).

Cyprus is located in the Mediterranean Sea, on the Anatolian plate, where northerly subduction of the African plate under the Eurasian plate is ongoing. This subduction has emplaced oceanic crust onto continental crust, making the area tectonically unstable and seismically active. The island can be divided into four geological terrains which are from

south to north: Marmonia Terrain, Troodos Terrain, Circum Troodos Sedimentary Terrain and Keryneia Terrain. This study will investigate rocks from the Troodos ophiolite found in the Troodos Terrain.

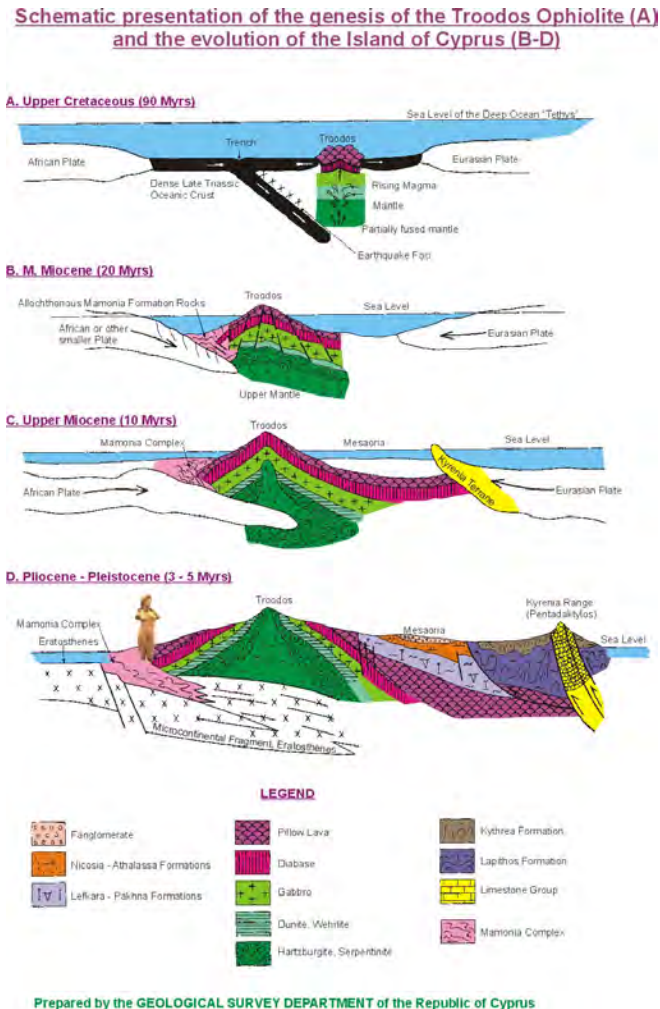


Figure 1: Tectonic evolution of Cyprus (Cyprus Geological Survey, 2016)

Cyprus is considered to have been developed in a supra-subduction zone as an ocean spreading ridge in the Thetys Ocean during the upper Cretaceous (figure 1). This is based on the chemical composition of the basalts that are more siliceous, ranging from basaltic andesite to dacite, (Robinson et al. 1983; Pearce et al. 1984) consistent with an island arc setting rather than a mid-ocean ridge setting (Wilson, 2007; Osozawa et al. 2012). After formation, the ophiolite was below the carbonate compensation depth, and parts of the ophiolite was covered with siliceous sediments, followed by carbonate sediments during late Cretaceous. Active spreading ceased during the mid-Miocene when the oceanic crust was pushed up onto the African plate, giving rise to the Marmonian and Troodos Terrains (Moores and Vine, 1971). Continued movement during upper Miocene, Pliocene and Pleis-

tocene contributed to accreted sedimentary sequences and the Circum Troodos Sedimentary and Keryneia Terrain.

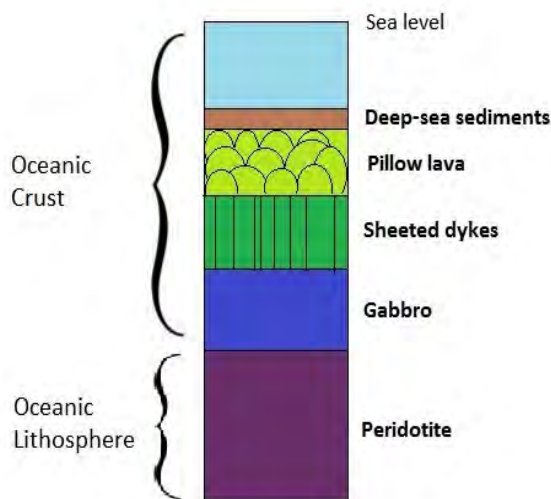


Figure 2: Schematic cross section of the oceanic crust

The Troodos Ophiolite is considered to be one of the worlds best preserved ophiolite sequences, and thus also one of the most well studied. There is no metamorphic overprint and the alterations found are of low hydrothermal character. The ophiolite has a traditional sequence with; plutonic mantle comprised of harzburgite, dunite, pyroxenites; intrusive rocks comprised of gabbros and sheeted dykes; extrusive rocks comprised of pillow lavas; and deep-sea sediments comprised of chalk, marls and umbers (figure 2). Troodos is also known for its massive sulphide deposits, containing mostly S, Cu, and Zn, where more than 30 mines have been actively mined or recognized as potential mining sites, with ore deposits ranging between a few thousands to fifty million tonnes (Adamides 1990; Hannington et al. 1998).

Hydrothermal processes in the deep subsurface

There are various types of hydrothermal processes and systems related to the bedrock and the geological setting. For this work, hydrothermal systems in the deep subsurface associated with Volcanogenic Massive Sulphide (VMS) deposits will be considered. In this system, both oceanic water, magmatic fluids and primordial fluids are responsible for physical and chemical alterations of the host rock. Hydrothermal fluids in contact with the host rock creates a chemical and thermodynamic disequilibrium in the fluid/rock system, which will respond with dissolution and precipitation of mineral assemblages in its strive for equilibrium. Such a change is highly dependent upon temperature, pressure, composition, and the origin of the fluids, the composition of the host rock, as well as the overall structure of the hydrothermal system, i.e. recharge, circulation and discharge. Old hydrothermal systems that is no longer active can be preserved in the host rock in the form of quartz and calcite veins, or other secondary mineralizations that normally occur geologically fast along spreading ridges. VMS deposits are such settings that gives us information about previous hydrothermal processes, and which can be compared to venting of spreading ridges in the modern oceanic crust (Pirajno, 2010).

There are different types of hydrothermal metasomatism, depending on tectonic setting. In low temperature and pressure environments such as spreading ridges, and often in association with VMS systems, it is common to find propylitic, argillic, sericitic or phyllic alterations (Robb, 2005). These alterations can be caused by hydrogen ion metasomatism or

base cation exchange. Hydrogen Ion metasomatism is characterized by anhydrous minerals, such as feldspars, reacting with H^+ or OH^- from H_2O in the fluids, creating hydrous clay minerals, dissolving metal ions into the solution, as well as precipitate quartz. The reaction causes a pH change of the solution, which affects the possibility of the solutions to dissolve or precipitate cations, where K^+ , Na^+ and Ca^{2+} is readily exchanged between the solution and the surrounding minerals (Pirajno, 2010).

Geobiology

Geobiology is the broad term for the interdisciplinary study of the connection between the biosphere and the geosphere. A branched part of this area is geomicrobiology. While microbiology has had far more attention during the last centuries due to medical, industrial and environmental uses, geomicrobiology has just been recognized within the last two decades, even though deep-sea drilling programs extends some sixty years back (Ehrlich, 1996). The understanding of our deep-biosphere seen in a microbial and geological view has been somewhat limited due to technological challenges and the depth of the oceans. Mars surface has for example been far better mapped than our own seafloor (Schrenk et al. 2010). New research has revealed that deep-sea sediments, and even the igneous crust underneath it, actually harbours vast quantities of microbial life (Johnson and Priuis, 2003; Schrenk et al., 2010). Whitman et al. (1998) calculated that prokaryotic organisms in the deep-biosphere may contain as much carbon as all plant life found at the Earth's surface. Detailed study of the microbiological ecosystem in the deep-biosphere should therefore be able to give us information about past, present, and future environments, since changes in the ocean chemistry, temperatures, topography, and climate have a direct impact on the biotic components such as diversity, abundance, and morphology.

Classification, metabolism and reproduction

Life as we know it consists of relatively simple building blocks. Depending on how these building blocks are organized, larger biomolecules are created that can control metabolism, reproduction, and cell reparation which are essential functions for survival. A living cell consists of four major biomolecules; amino acids $H_2NCH(R)CO_2H$ that help build proteins, carbohydrates $C_xH_yO_z$ that gives the cell its energy, nucleotides $C_{10}H_xN_5O_yP_z$ that are the building blocks for the cells genetic material, and lipids $CH_3(CH_2)_xCO_2H$ that are needed for the cell membranes (Raven et al. 2016).

Living organisms can be divided into the domains Archea, Bacteria and Eukarya. Where the first two belongs to the Prokaryotes, and the last belongs to the Eukaryotes based on their cellular structure. All three domains are found within the deep-biosphere and studies shows that bacteria dominates the microbial diversity on exposed seafloor basalt, with mainly Proteo- and Actinobacteria (Einen et al. 2008; Mason et al. 2008; Santelli et al. 2008). Archaeal communities consist mainly of Crenarchaeota or Euyrarchaeota (Thorseth et al. 2001; Fisk et al. 2003; Mason et al. 2007; Orcutt et al. 2011), and ascomycetes and basidiomycetes are the dominant species from the Eukarya domain (Connell et al. 2009). Microbes found in this setting are classified as endoliths (rock-dwelling), or extremophiles

due to the extreme environments they live in. Endoliths can in turn be sub-classified based on the environment they occupy or directly create (Golubic et al. 1981; Marlow et al. 2015):

- Chasmoendoliths colonize preexisting cracks and veins
- Cryptoendoliths colonize preexisting vesicles and structural cavities
- Euendoliths are boring organisms that form tunnels, usually found as ichnofossils, due to active penetration into mineral and glass
- Autoendoliths construct their habitable environment by using surrounding mineralogy, leading to filled pore spaces that may be sealed off for future habitability of other micro-organisms

Endoliths can be either lithotrophs or autotrophs, meaning that they live on inorganic or organic compounds, or dissolved elements in the fluids. Lithotrophs usually use iron, manganese or sulphur as an energy source that is consumed directly from the surrounding bedrock, while autotrophs generate organic compounds from inorganic compounds by manufacturing biomass including biofilm or slime (Connell et al. 2009; Lear and Lewis. 2012).

Reproduction of microorganisms in subseafloor environments has been determined to be relatively slow, having cycles ranging from hundreds to thousands of years (Lomstein et al. 2012). The low reproduction occurs because the organisms have a limited source of nutrients and fluids, and most of their energy is instead of growth aimed towards maintenance such as i.e. cell repair. The long cycles for cell division could be a way for the organisms to survive during long glacial periods on the surface, when nutrition supply is cut off or limited.

Environmental conditions vary for the endoliths. Some extremophile organisms are known to live and reproduce in environments with temperatures up to 122°C and with pH ranging between 3 and 9 (Takai et al. 2008; Pettipther et al. 1997; Horikoshi, 1999). Other extremophiles are also known to live in extreme anaerobic, haline, radioactive or metal rich environments (Ito et al. 1983; Oren 2002; Danovaro et al. 2010).

Methods

Sampling and thin section preparation

Grab-and-bag sampling was made during a one week field excursion to Cyprus in December 2015. Sampling was made from the mantle and progressively upwards in the ophiolite sequence, with focus on the upper oceanic crust where microbes should be more abundant. Locality descriptions were made in the field, and macroscopic descriptions were made both in the field and on hand samples.

A total of thirty-one samples from seven different localities were taken for this study, where twenty-six samples were prepared for thin sections (figure 3, appendix A0). Each sample was sawed parallel to the lineation and perpendicular to the foliation, and coarsely grinded with silicon carbide (SiC180). Final thin section was made by Vancouver Petrographics Ltd and ABC Ahead, where nine samples were polished with a thickness of 30 microns, and twenty-two samples were doubly polished for fluid inclusion study, with a thickness of 150-200 microns.

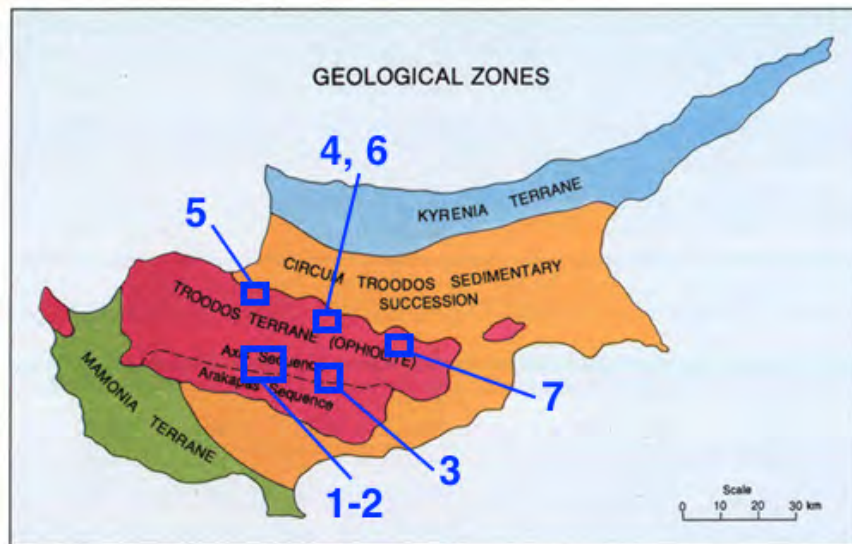


Figure 3: Sampled localities in the Troodos Terrain (Cyprus Geological Survey, 2016)

Macroscopic and microscopic study

Optical magnification can be used to determine mineralogy, deformation and secondary alterations, giving us information about temperature, pressure, origin or provenance as well as tectonic evolution. The method assumes that the data found in the hand sample or the thin section, thus a very small part of the overall bedrock, can be applied for the whole rock unit. However, local changes in mineralogy and deformation might occur, and may not be applicable to the rest of the studied area. A good understanding of the overall locality and detailed bedrock mapping can help constrain the geological history, and validate the macroscopic and microscopic data.

Macroscopic descriptions of each locality were made by using a 10x handlens both in the field and on hand samples, as well as a Dino-Lite Edge X universal serial bus micro-

spectroscopy on the hand samples. Locality descriptions include a general overview of the geology, mineralogy and possible later hydrothermal or tectonic events.

Microscopic descriptions of the thin sections to determine main mineralogy, microbial fossils and ichnofossils were made with a Leitz polarization microscope. For opaque mineralogy, a Leica polarization microscope with reflective light was used. Textures and deformation in the thin sections are described per the approach of Passchier and Trouwe (2005), and morphology of microbes and ichnofossils are described per the approach of Murray et al. (2013) and Erwig and Gow (2016).

Pictures of the hand samples were taken with a 5-mega pixel camera built in the USB-microscope that has an extended depth of field, EDOF, which gives focus in a depth view, making it suitable for studying vesicles or cavities. The microscope also has an extended dynamic range, EDR, which enables the software to stack multiple pictures with different exposure, decreasing any reflections from the object in the picture. Magnification ranges between 5X-140X, giving the microscope a lower maximum magnification, but a much wider working range in comparison to a traditional microscope. Pictures of the thin sections were taken with a 10-mega pixel camera mounted to a trinocular head of the polarization microscope.

Environmental Scanning Electron Microscope

Environmental Scanning Electron Microscope, ESEM, can be used to make chemical and morphological images as well as determine element oxide composition in minerals and their densities. The microscope uses low vacuum where a micro atmosphere around the sample works as a conductive layer so no carbon coating is needed. Because the samples contain fossilized microbes, later analyses of the samples where carbon needs to be determined, can thus still be done using this method.

The ESEM uses a tungsten filament that is heated and the electrons are deflected towards the sample and decelerated with a known voltage. Secondary electrons leaving the sample surface after collision with the primary electrons can then be detected via either an energy-dispersive spectrometer or a wavelength-dispersive spectrometer. The element oxide composition is calculated using Bragg's law for constructive interference, the electrons momentum and the elements density (Rouessac and Rouessac, 2007; Jönsson and Nilsson, 2009).

For this study a Philips XL-30-ESEM-FEG650 and energy-dispersive spectroscopy (EDS) was used. The electron beam was set to 20 kV and the probe current to 6.00 nA at a working distance of 10 mm.

Raman spectroscopy

Raman spectroscopy gives information about the molecular structure, molecular bonds and density in solid, liquid and gaseous phases. A laser beam generated from an argon source is focused towards the sample via an objective lens. The illuminated spot sends out electromagnetic radiation that is collected in a lens, and the wavelength corresponding to the laser beam is filtered out. Remaining wavelengths are then sent to a detector.

Raman spectra were collected using a confocal laser Raman microspectrometer (Horiba instrument LabRAM HR 800; Horiba Jobin Yvon, Villeneuve d'Ascq, France), equipped with a multichannel air-cooled (-70°C) 1024 x 256 pixel CCD (charge-coupled device) detector. Acquisitions were obtained with an 1800 lines/mm grating. Excitation was provided by an Ar-ion laser ($\lambda = 514$ nm) source. Spectra were recorded using a low laser power of 0.1-1 mW at the sample surface to avoid laser induced degradation of the samples. Sampling was carried out using an Olympus BX41 microscope coupled to the instrument and the laser beam was focused through 80x (hand specimens, working distance of 8 mm) and 100x (thin sections) objectives to obtain a spot size of about 1 μm . The spectral resolution was 0.3 cm^{-1} /pixel, with a typical exposure time of 10 s and with 10 accumulations. The accuracy of the instrument was controlled by repeated use of a silicon wafer calibration standard with a characteristic Raman line at 520.7 cm^{-1} . The Raman spectra were achieved with LabSpec 5 software. Minerals in thin sections and hand specimens of collected samples were identified by Laser Raman spectroscopy and comparisons with reference spectra in the RRUFF database (Downs, 2006). The bands in the Raman spectra are related to various types of vibration modes and were used to distinguish between different mineral structures and mineralogical transformations by alteration.

Fluid inclusion study

Fluid inclusions can be trapped in growth irregularities during crystallization or recrystallization of minerals. The trapped fluids represent the composition of the fluids during time of mineral formation; they contain information about the growth conditions and are considered to have had no exchange with the surrounding environment. Analyses (microthermometry) of fluid inclusions are carried out using a heating/freezing stage mounted on a microscope. Determinations of the composition are done by freezing and heating the fluid inclusions and observe phase changes. After freezing the inclusions, melting of the inclusion content is noted. The melting temperatures provides information of the composition from the first ice melting temperature (T_{fm}) which is typical for the eutectic temperature of a specific salt-water system and the concentration of dissolved salt (eq. mass % NaCl) from the final ice melting temperature (T_{m}). To get an indication of the formation temperature, the inclusions are heated until the inclusion content homogenize in to a single phase, this is the homogenization temperature (T_{h}) that is assumed to represent the temperature at the time of entrapment.

There are however some difficulties with this method; the first is to determine the timing for the fluid entrapment and confirm that these are contemporary with the microbial activity or a part of the secondary mineralization contributing to the fossilization of the microbes, the second is diffusion of elements occurring between the fluid inclusion and the surrounding minerals. Elements with small ionic or molecular radii (H_2 or He) could diffuse and affect the fluids composition and/or the isotopic ratios (Wilkinson, 2001). The first problem can be addressed with detailed petrographic studies where secondary alteration minerals as well as microtextures can confirm the relative timing of the fluid inclusion (Van den Kerkhof and Hein, 2001). The second problem can be disregarded in this study since the area is not considered to have been subjected to strong potential chemical gradients that is found in

metamorphic environments, and hydrogen diffusion is not likely to have occurred (Roedder and Skinner, 1968).

A conventional microscope was used to get an overview of the samples and the distribution of fluid inclusions. Microthermometric analyses on fluid inclusions in calcite were performed with a Linkam THM 600 stage mounted on a Nikon microscope utilizing a 40x long working-distance objective. The working range of the stage is -196°C to +600°C (for details see Shepherd et al. 1985). Calibration was made using SynFlinC synthetic fluid inclusions and well-defined natural inclusions in Alpine quartz. The reproducibility was $\pm 0.1^\circ\text{C}$ for temperatures below 40°C and $\pm 0.5^\circ\text{C}$ for temperatures above 40°C.

X-ray fluorescence

X-ray fluorescence spectrometry (XRF) uses X-rays to excite electrons and thus ionize the atom. During this excitation, secondary x-rays are created and measured for both energy and intensity, to determine what element and what amount of the element is available in the analysed sample. This method is commonly used to determine major and trace element chemistry in rock samples and sedimentary cores (Rollinson, 2013).

For this study, XRF was done on all the samples by analysing rock samples from each sequence, but from different localities. This gives relative information about elemental changes found in a rock. A more accurate method would be to analyse samples from each section taken from the same drill core. Whole rock analysis with X-ray fluorescence was made on the rock chips left over from the thin section preparation. This gave the major and trace elemental composition of the samples from each locality, where relative elemental changes in the host rock could be determined. Actual elemental concentrations were calculated using a natural olivine (Fo₉₄, North Cape Minerals, Norway) with a known composition as a standard. XRF was made with a ZSX Rigaku Primus II X-Ray Fluorescence spectrometer, where sampling was made with a Mo tube set to 30 kV and 25 mA, and an analytical time of 10 seconds. The XRF spectrometer was set to 200 μm and a scanning width of 80 mm.

Isotope ratio mass spectrometry

Isotope ratio mass spectrometry is used to determine mixtures of natural isotopes in solid and liquid materials. The more common isotopes measured with this technique are C, O, H, N, and S, where variations in the abundance is given as a ratio between the heavier and the lighter isotope in the sample. The ratio is then compared to a carbon standard, originally a Pee Dee Belemnite (PDB) from South Carolina, USA. Because ratios are close to 1, recalculation of the results are done into delta values with $\delta = \left[\frac{[^{13}\text{C}/^{12}\text{C}]_{\text{sample}}}{[^{13}\text{C}/^{12}\text{C}]_{\text{standard}}} - 1 \right] \times 1000$, making it easier to interpret any variation. Samples that are depleted in the heavy isotope will give a negative delta value.

Carbon isotope analysis was done on 18 samples from the whole ophiolite sequence. Each sample was crushed and grinded in a mortar, and $\sim 5\text{--}22$ mg of each sample was weighed. The samples were then mixed with 99% H_3PO_4 to react with any possible CO_2 . A GasbenchII coupled to a Finnigan MAT 252 mass spectrometer was used to analyse the carbon isotopes.

Qualitative and quantitative results

Geology and geochemistry

Mount Olympus, DTC151201, coordinates N34°56'52.7 / E32°51'43.9

The first locality is situated on the northern slope of Mount Olympus, approximately two kilometres NNE from the road. The area consists of coarse grained mantle peridotite, classified as harzburgite, with veins, dykes and xenoliths of fine grained dunite. Both the harzburgite and the dunite are cross cut by coarse grained pyroxenite veins. Patches of harzburgite are also found within the dunite in places (figure 4), and contacts are found both as sharp and more diffuse. The dunite could have crystallized due to early differentiation of the olivine, melting of the harzburgite or complete melting of the orthopyroxene in the harzburgite. Serpentinization is more abundant closer to the road and decreases towards the sampled locality. A chrome mine is found approximately 4 kilometres north from the road.



Figure 4: Fine grained dunite as a xenolith in coarse grained harzburgite. Photo taken towards north west. (Photo Iain Pitcairn)

Sampling was made of the harzburgite and the hand sample shows a dark greenish tint, with a yellow/brownish weathering (appendix A1). It is a medium grained crystalline rock containing olivine, pyroxene and plagioclase (appendix A2). The olivine has a dark green colour and occurs as individual crystals in domains and in thin parallel cracks and veins in the hand sample. Pyroxene is found in a connected network between the olivine and the plagioclase. The plagioclase seems somewhat recrystallized.

Microscopy shows that the main minerals are olivine, orthopyroxene, hornblende, plagioclase and serpentinite with accessory minerals clay, opaque minerals and occasionally epidote. Dark phases ranges between 20% and 50%. The samples have an inequigranular to seriate texture with interlobate grain boundaries. Dynamic recrystallization is coarse grained with medium deformation. Subhedral olivine is abundant in the sample, and has a typical mesh texture, where cracks are filled with secondary serpentine and clays (appendix A3). Orthopyroxene, with the composition of enstatite, is found as subhedral crystals, highly fractured in a similar mesh texture as the olivine. Exsolution lamellas of augite is found along the {100} cleavage plane, consistent with a Buschveld intrusion type. Inverted pigeonite is also found in some crystals. Hornblende has a green-brown colour and is found as interstitial crystals in the wehrlite-pyroxenite. Plagioclase, with a composition of An₆₀₋₇₀ is found as euhedral to anhedral laths, and commonly shows Carlsbad twinning. Alterations of olivine to serpentine and clays are common, as well as olivine recrystallized into orthopyroxene and then into hornblende.

Chandria, DTC151202, coordinates N34°55'13.9 / E32°56'40.8

This locality is a well exposed road cut containing multiple magmatic intrusions (figure 5). These are, from old to young, wehrlite-pyroxenite, pale gabbro, olivine gabbro, plagiogranite and mafic dykes. The locality gives insight into how the upper plutonic section is created and the complexity of the magmatic events. This locality lies in close proximity to the contact with the sheeted dykes towards the north.

Sampling was made of the wehrlite-pyroxenite (appendix A4), the olivine gabbro (appendix A5) and the pale gabbro (appendix A6). The wehrlite-pyroxenite has a steel blue colour with a brownish weathering. It is a coarse grained crystalline rock containing pyroxene, olivine and somewhat recrystallized plagioclase (appendix A7). The olivine gabbro has a dark blue colour with a dark brown/reddish weathering surface. It is a medium to coarse grained crystalline rock containing olivine, pyroxene and plagioclase (appendix A8). The plagioclase occasionally occurs as laths, but are mostly recrystallized. The pale gabbro has a light blue colour with a reddish tint weathering. It is a coarse grained crystalline rock containing pyroxene and recrystallized plagioclase (appendix A9).

Microscopy shows that the main minerals in the wehrlite-pyroxenite are orthopyroxene, olivine, hornblende and plagioclase, with epidote as accessory mineral. Dark phases ranges between 20% and 30%.

The wehrlite-pyroxenite has an inequigranular texture with interlobate to amoeboid grain boundaries. Olivine is found partly recrystallized into orthopyroxene. Primary orthopyroxene is common in the sample and has a composition of enstatite. Some orthopyroxene contains inverted pigeonite and are found as subhedral crystals, while others are found partly recrystallized into hornblende (appendix A10). Hornblende has a green-brown colour, is found as interstitial crystals and are moderate to common in the sample. Plagioclase with a composition of An_{60-70} is found as euhedral to anhedral laths and Carlsbad twinning is common.

The main minerals in the gabbros are olivine, orthopyroxene, hornblende and plagioclase, with accessory minerals serpentine, opaque minerals, and where epidote and clinozoisite is only found in the pale gabbro. Dark phases ranges between 10% and 20%.

The gabbros have an inequigranular to seriate texture with polygonal to interlobate grain boundaries. Orthopyroxene, with a composition of enstatite, is found as anhedral to subhedral crystals, and are common in the samples. Olivine crystals are only found in the olivine gabbro (appendix A11). The pyroxene is often recrystallized into serpentine or



Figure 5: Several magmatic events, where the olivine gabbro is found as bodies within the pale gabbro. The plagiogranite has a sharp contact towards the olivine gabbro, and mafic dykes cross cut both the plagiogranite and the pale gabbro. The red box indicates sampled area for DTC151202A. Photo taken towards the east. (Photo Iain Pitcairn)

have a mesh texture with recrystallized serpentine, possible lizardite. Epidote-clinozoisite is also found within the serpentinized cracks in the pale gabbro. Exsolution lamellas of augite is found parallel to the $\{100\}$ cleavage plane in the pyroxenes, and pyroxenes are more Fe-rich in the pale gabbro based on their colour (appendix A12). Possible ilmenite, with skeletal texture, is found as inclusions in the pyroxenes. Hornblende has a green-brown colour, is found as interstitial crystals and occur from sparse in the pale gabbro, to abundant in the olivine gabbro. Possible light brown oxyhornblende is seen in the olivine gabbro. Plagioclase, with a composition of An_{45-50} , is found as euhedral to anhedral laths, as well as subhedral crystals. Carlsbad and albite twinning is common, while pericline twinning occurs sparsely, and always on one-hand side of the Carlsbad twinned crystals.

Palaichori, DTC151203, coordinates N34°54'58.6 / E33°05'32.0

This locality is a well exposed road cut containing basaltic sheeted dykes ranging from centimetres to meters in width (figure 6). Chilled glassy margins are found both symmetrical and asymmetrical along the dykes, and the dykes are separated by long vertical joints or shear faults. Less prominent are the short horizontal joints within the dykes. A later magmatic intrusion of coarse grained pale gabbro is found to the west.



Figure 6: Sheeted basaltic dykes separated by vertical jointing or shear faults. The red box indicates sampled area for DTC151203A and the photo is taken towards the north (Photo Diana Carlsson)

Sampling was made from E to W of the sheeted dykes, and the hand samples has a light grey colour with brownish weathering (appendix A13-15). It is a fine grained crystalline rock containing plagioclase and pyroxene/amphibole. Thin veining ranges from sparse to abundant, with a parallel or anastomosing texture, and are filled with secondary calcite (appendix A16-17). The plagioclase is recrystallized, and there are both smaller and larger xenoliths of coarse grained clast, presumably gabbro, within the basalt dykes.

Microscopy shows subhedral epidote clusters with possible chlorite and clays in a mesostasis of plagioclase and oxides (appendix A18). The opaque minerals are commonly found as small euhedral crystals, evenly distributed throughout the whole sample. They are also found as rims around the vesicles, but rarely within the veins.

Akaki River, DTC151204, coordinates N35°00'41.2 / E33°09'18.1

This locality is a natural river outcrop where hyaloclastite is overlaid by pillow lavas and is cross cut by vertical and inclined dykes (figure 7). Horizontal sills can also be seen at this locality. Both the dykes and the sills are characterised by perpendicular jointing.

Sampling was made on the lower pillow lavas found to the west of figure 7. The pillow lavas consist of fine grained basalts with a green colour, and weathered surfaces shows a green/brownish colour (appendix A19-22). Microscopy shows a mineralogy of clay, plagioclase and oxides, where the oxides consists of anhedral to subhedral pyrite, recrystallized into hematite and magnetite at the edges (appendix A23-26, appendix B1).



Figure 7: Sheeted basaltic dykes separated by vertical jointing or shear faults. The photo is taken towards the north (Photo Diana Carlsson)

Skouriotissa copper mine, DTC151205, coordinates N35°05'50.7 / E32°53'28.8



Figure 8: The Phoukasa main ore deposit to the right, the Skouriotissa fault lies roughly parallel along the NW going road, and the Phoenix deposit lies to the left. The dark brown/black sedimentary layer is the sulphide lying on top of the stockwork. The red box indicates sampled area for DTC151205. Photo is taken towards the north. (Photo Diana Carlsson)

This locality is currently the only active open pit mine on Cyprus, mining mainly Cu (figure 8). The mine is divided into two deposits by the Skouriotissa fault; the Phoukasa to the east and the Phoenix to the west. A second fault, the Phoukasa fault, lies just east of the Phoukasa deposit. Mineralization of the stockwork was done by oxidative remobilization of the primary ore and contains Cu, Au and Ag. Cu is leached from this low-grade ore with acidic S and bacterium breakdown and transported away from the leaching site via electrolysis, giving a final product containing high concentrations of copper.

Sampling was made on the upper pillow lavas found in the western part of the Phoukasa deposit, just above the main ore

body. The samples were taken in a short profile of 10 meters, where the samples east of the ore body have less abundant vesicles but are more commonly fractured (appendix A27-29). Fractures are filled with calcite, and vesicles are commonly filled with red/brown clays. The sample to the west have abundant vesicles that are partly recrystallized into zeolite minerals. All the samples are very fine grained and the hand samples have a green/grey colour

with a green/brown weathering that occurs in domains.

Microscopy shows that clinopyroxene, and relict possible olivine crystals, are found in a mesostasis of clay, plagioclase and oxide minerals (appendix A30). EDS shows that plagioclase has a composition of An_{50-75} , and alkali exchange between orthoclase and albite with a composition of Ab_{20-30} has occurred (appendix B2). The clinopyroxene has a composition of diopside and the crystals have an euhedral to anhedral habit, containing both zoning as well as parallel twinning (figure 9, appendix A31). Total recrystallization of olivine into Fe rich clays, Ca carbonates and iddingsite are modest to common in the samples (appendix A32). The opaque minerals consist of anhedral magnetite to subhedral pyrite recrystallized into hematite and magnetite at the edges. Chromite to hercynite spinel are also found as round crystals in augite, where the augite is partly recrystallized into calcite and iddingsite (appendix B3).

*Kamara River, DTC151206,
coordinates N35°00'42.2 / E33°09'13.6*

This locality is a natural canyon with large pillow lavas found on each side of the small river. The pillows ranges from a few decimetres to several meters in width, where the mega-pillows could have formed due to higher magma input. Further in along the canyon and towards the SE, columnar jointed lava flows are found, which have been cross cut by dykes.

Sampling was made on the lower pillow lavas along the hiking trail in the canyon, found approximately 50 meters from the road and approximately 200 meters from the Akaki river locality (appendix A33). The sample is very fine grained with a green/grey colour and a green/brown weathering surface (appendix A34). Vesicles are sparse and no secondary filling minerals can be seen. Because these samples was only made as double thick thin sections, optical microscopy was limited (appendix A35).

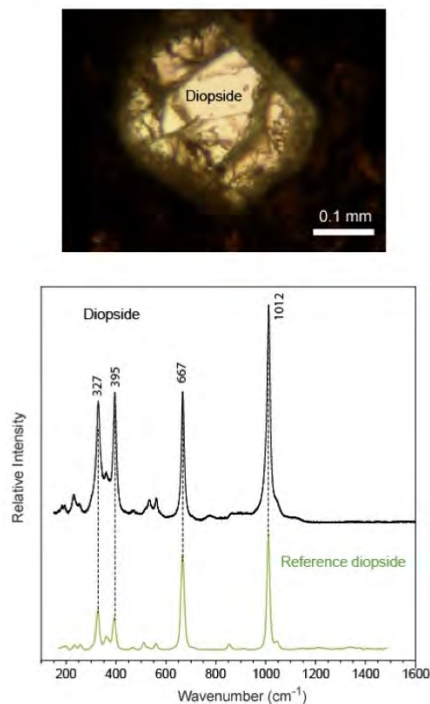


Figure 9: Raman spectrum in the spectral range $100 - 1600\text{cm}^{-1}$ of a diopside crystal in sample DTC151205C. Reference spectrum is from Downs (2006). (Photo Curt Broman)

Mathiatis mine, DTC151207,
coordinates N34°58'33.8 / E33°20'53.0 to N34°58'35.1 / E33°20'43.8



Figure 10: Pillow lavas at the Mathiatis mine, hammer for scale (Photo Diana Carlsson)

This locality is an old open pit mine, used to mine low grade Cu. The mine ceased its operation in 1987, leaving waste heaps and a groundwater filling pit. The stockwork is found at the very bottom of the mine, where some of the pyrite rich quartzite was still visible during the excursion in 2015. This stockwork is successively overlaid by brecciated and chloritized basalts, a clay altered basalt layer followed by a younger unmineralized lava flow (figure 10).

A profile was sampled from the bottom to the top, with one sample from the stockwork zone and the rest taken on the lower clay altered pillow lavas and the younger un-

mineralized pillow lavas at the top (appendix A36). The stockwork has a dark grey colour with a gold metallic luster and an orange/red weathering surface (appendix A37). It contains euhedral and anhedral pyrite crystals in a fine-grained matrix. Large, 1-5 cm, subhedral red/brown jasper crystals are also seen, where some jasper shows evidence of a late stage intrusion of quartz veining, giving the jasper a mesh texture. The pillow lavas are fine grained crystalline rocks and hand sample shows a light grey/green colour with a brown/green weathering surface (appendix A38-41). Samples close to the stockwork have abundant thick cracks commonly filled with clays, calcite and zeolite. Further from the stockwork the cracks get thinner and less abundant and at the top of the sequence, no cracks are visible but vesicles are instead abundant.

Microscopy shows domains of pervasive hydrothermal alteration in the samples (appendix A42). Less altered domains have a relict igneous texture preserved containing subhedral feldspar laths in a mesostasis of clay and oxide minerals (appendix A43-44). EDS shows that the feldspars has a composition of An_{40-65} or orthoclase (appendix B4). Pervasive hydrothermally altered domains consists of fine grained clays and oxides. Some relict crystals are seen that have been totally recrystallized into clays.

The acquired Raman spectra of an altered orthoclase in sample DTC151207Ba reflect a gradual transition from orthoclase, $KAlSi_3O_8$, to analcime $NaAlSi_2O_6 \cdot H_2O$ (figure 11). The strongest Raman bands from the orthoclase that appear at $513cm^{-1}$, $475cm^{-1}$ with a shoulder at $455cm^{-1}$ and $285cm^{-1}$ are believed to result from the main T-O-T and O-T-O vibration modes where T=Si and/or Al (Freeman et al. 2008). Other weaker bands (755 , 805 and $1124cm^{-1}$) are also associated with structural changes in the T-O-T and O-T-O region due to varying bond lengths and angles in the tetrahedral (Freeman et al. 2008). A weaker band at $157cm^{-1}$ is assigned to Si-O vibrations involving larger cations like K and Na (Me-O in figure 12) in the structure (Frogner et al. 1998). In figure 11, spectra A-E, it can be seen that the replacement by analcime causes the band at $513cm^{-1}$ to disappear and

the band at 475cm^{-1} to shift to a higher wavenumber at 482cm^{-1} . The band at 455cm^{-1} shifts towards a lower wavenumber at 389cm^{-1} in analcime, whereas the moderately strong band at 285cm^{-1} for orthoclase shifts upwards to 299cm^{-1} . In analcime an additional band at 3560cm^{-1} appear that can be assigned to O-H stretching of structurally bonded water (Frost et al 2014). The intensity of this band is gradually increasing from the intermediate phase in spectrum B, this band is of course absent in the unaltered part (A) of the orthoclase. The clinopyroxene has a composition of diopside and the crystals have an euhedral to anhedral habit that shows zoning as well as parallel twinning. Recrystallization of possible olivine into Fe rich clay, iddingsite and Ca carbonates are modest to common in the samples. The opaque minerals consist of anhedral magnetite to subhedral pyrite, where the pyrite sometimes is recrystallized into hematite and magnetite at the edges. Titaniferous magnetite with skeleton texture, as well as magnetite vein structures in micro cracks in the clay is also seen (figure 12).

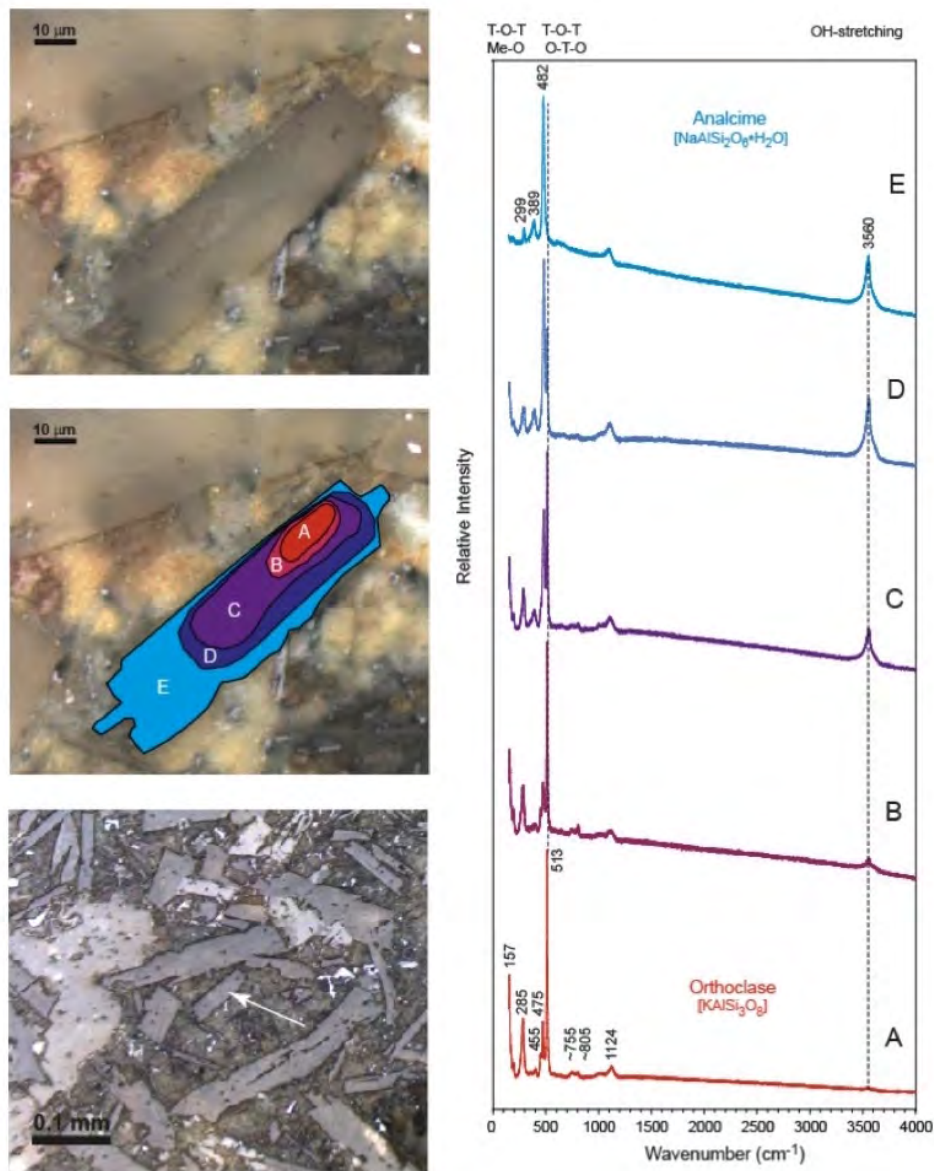


Figure 11: Raman spectra in the spectral range $100 - 4,000\text{cm}^{-1}$ of an altered orthoclase crystal shown in the uppermost photo and its position in the sample (lowermost photo). The Raman spectra A-E illustrate the transition from the endmember feldspar identified as orthoclase (red spectrum A) to the endmember zeolite identified as analcime (blue spectrum E) with intermediate phases represented by red- to blueviolet spectra B to D. Band positions are indicated by wavenumbers (cm^{-1}) on the red spectrum for orthoclase and on the blue spectrum for analcime. The spectral range for vibrational bands Me-O (Me = K, Na), T-O-T and O-T-O (T = Si, Al), and OH is given on top of the diagram. The spectra in the diagram correspond to the areas marked A-E (with the same color) in the middle photo. These areas represent different zones of the gradual transition from the original orthoclase still left in the core to the final phase analcime along the margin of the crystal. (Photo Curt Broman)

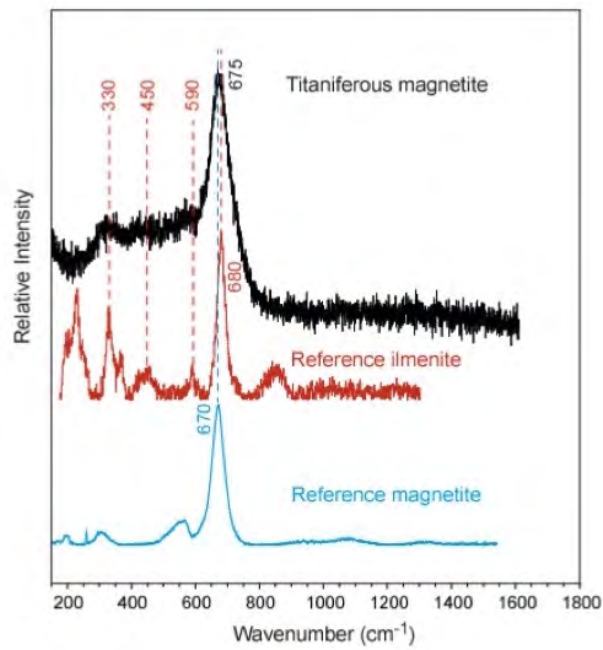
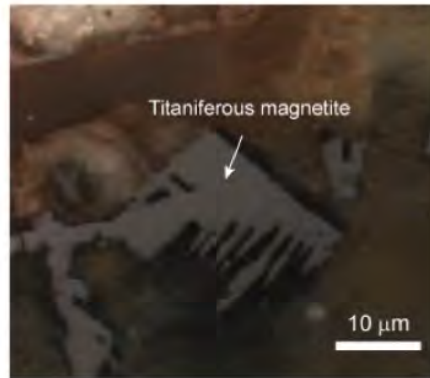


Figure 12: Raman spectrum in the spectral range $150 - 1,800\text{cm}^{-1}$ of a dendritic iron oxide (see photo), identified as titaniferous magnetite [general formula $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ with $x=0-1$]. Reference spectra in blue for magnetite Fe_3O_4 and in red for ilmenite FeTiO_3 from Downs (2006). (Photo Curt Broman)

*Theotokos Monastery, DTC151208,
coordinates N35°00'24.7 / E33°16'09.8 to N35°00'27.5 / E33°16'11.5*

This locality shows the typical succession of volcanics, umber and chinks found in the upper oceanic crust. The area has several faults dipping to the east, indicating that this area should have been situated to the left of the spreading ridge during ocean floor faulting.

Sampling was made on umbers at this locality (figure 13). This umber was somewhat different from umber seen at other localities due to the higher abundance of cracks and veins. The umber is a very fine grained sedimentary rock with a dark brown colour where cracks and veins have an anastomosing texture and are filled with secondary minerals. Because these samples were only made as double thick thin sections, optical microscopy was limited. EDS shows that the umber contains Fe and Mg-rich smectites, Mn oxides, hematite and minor quartz (appendix B5).



Figure 13: Umbers, photo taken to the S. Sampled area for DTC151208B is on the right hand side of the photo. (Photo Iain Pitcairn)

Whole rock analysis

XRF-data of the ophiolite shows clear elemental changes between the different sequences, as well as local variations within the sequences (figure 14-16). Figure 14-16 shows elemental change to analyse point, and can be seen as relative depth of each sequence. Samples within each sequence is however from high to low hydrothermal alteration, and cannot be seen as a depth relationship, since each profile is taken in either/both horizontal and vertical direction from magmatic or ore deposit intrusions. K has a higher variation in the lower part of the ophiolite, while the general trend is that K increases towards the upper part with a decrease in the sediments. This trend is also seen for Cu. S is more abundant in the lower parts of the ophiolite as well as in the rather unaltered pillow lavas, while it is less abundant in lavas that are hydrothermally altered, and in the sediments. This same trend is again seen for F, Ca, V, Ti, and to some extent Mn and Ni. Si and Fe is fairly stable from the mantle and upwards through the whole sequence, but is highly depleted in the vein mineralogy.

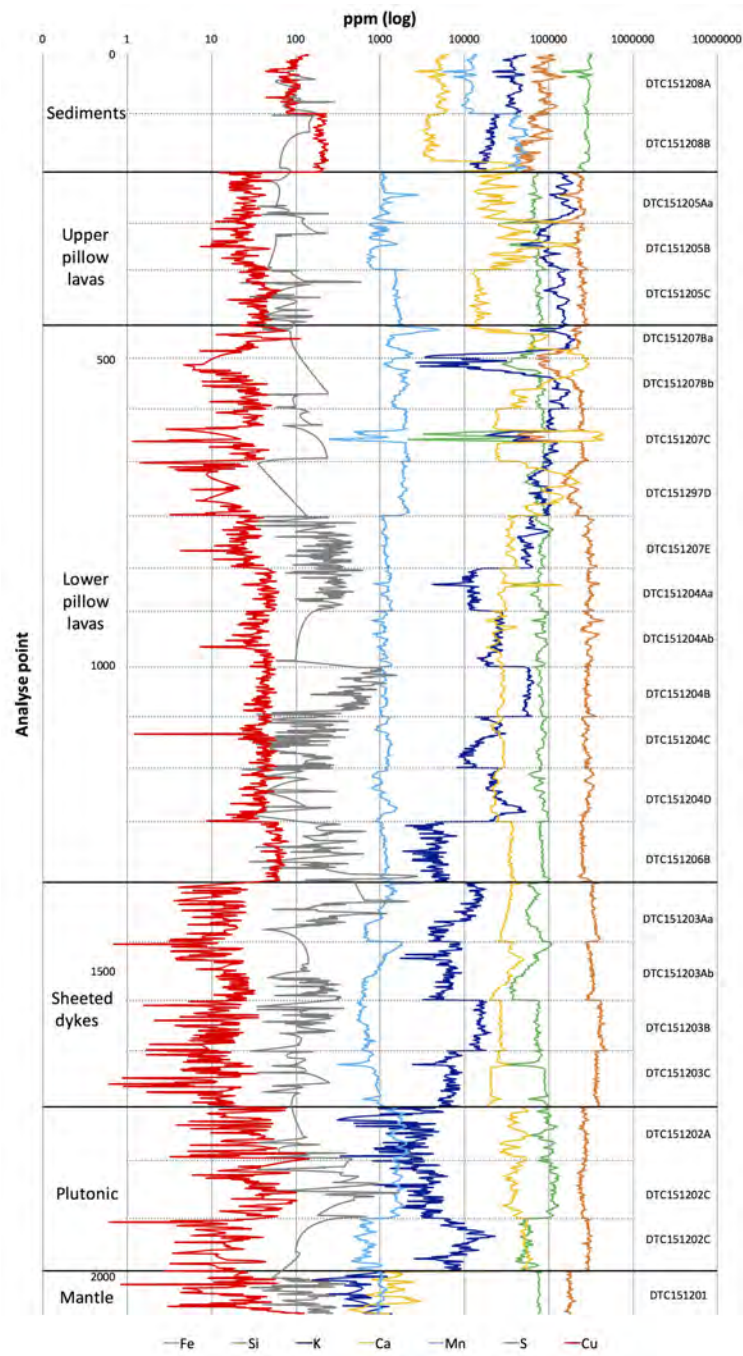


Figure 14: XRF-data of rock chips

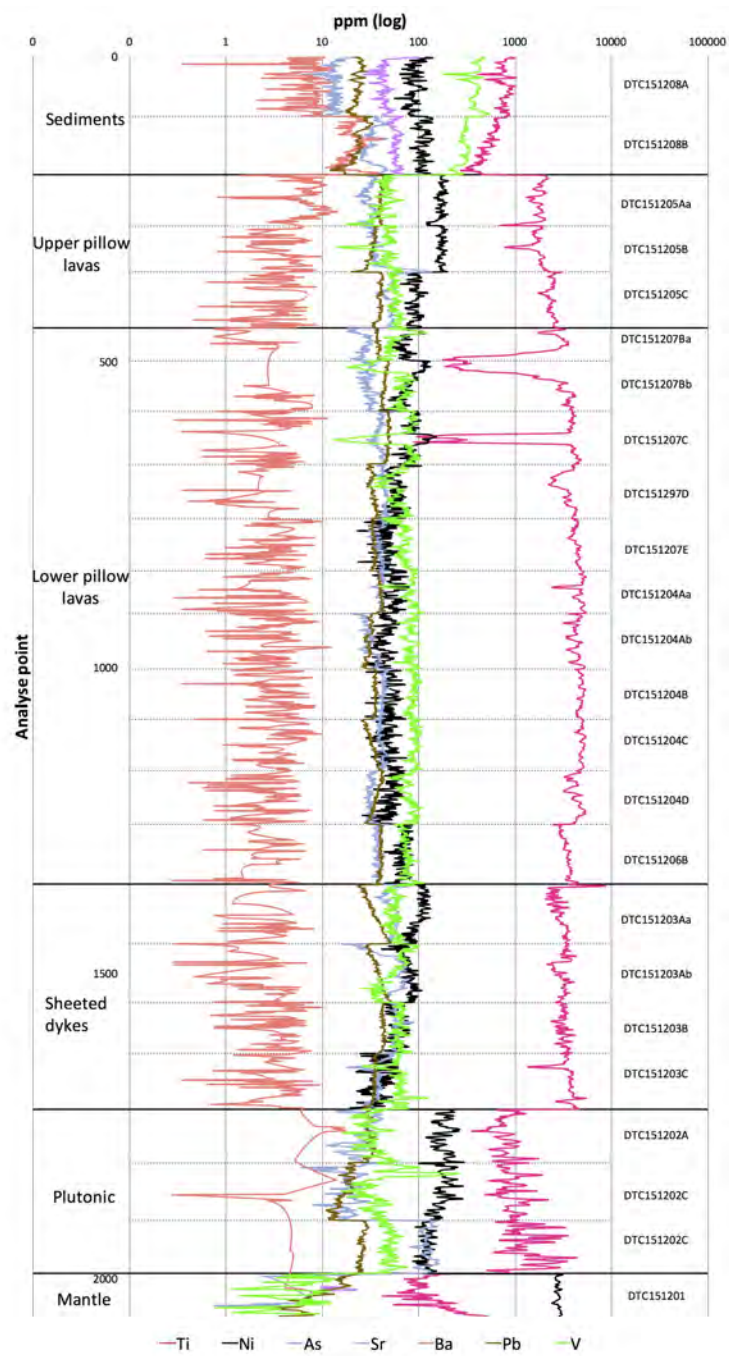


Figure 15: XRF-data of rock chips

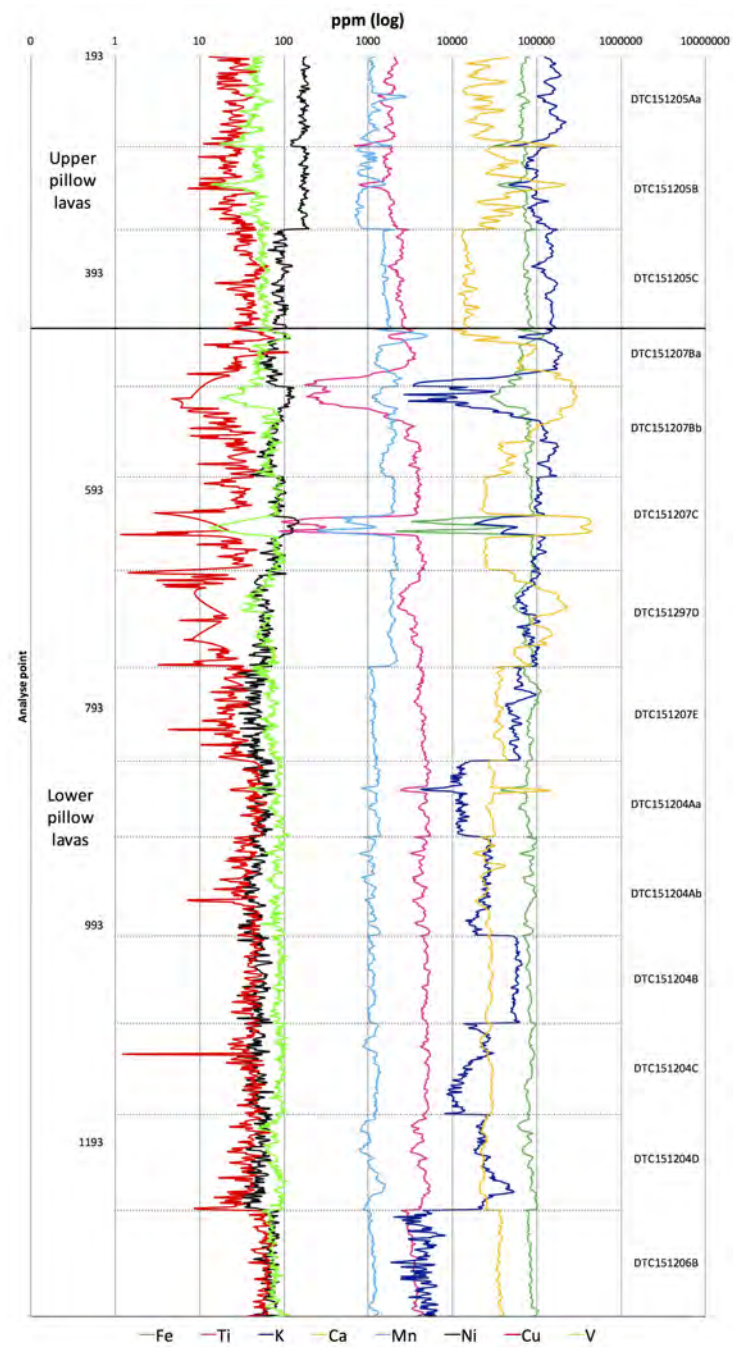


Figure 16: XRF-data of pillow lavas, and elements changing with veining

Carbon isotopes

Isotope data from the ophiolite sequence show very little biological carbon, and no direct trend is seen. The pillow lava samples show a $\delta^{13}C$ signal ranging between ~ -21.5 to -26.9 , where the sedimentary umbers that contains the highest amount of carbon, still only shows $\delta^{13}C$ values around ~ -23.1 to -23.7 .

Table 1: Isotope data from the ophiolite sequence

Analysed sample	Stuff	Rock type	Weight (mg)	Reaction with HCl	$\delta^{13}C$ vs PDB (‰)	% C	$\delta^{15}N$ vs air (‰)	% N
Bulk	DTC151202C	Mantle	21.66	No	-26.872	0.05	n.d.	n.d.
Bulk	DTC151203A	Sheeted dykes	14.549	No	-25.077	0.047	n.d.	n.d.
Bulk	DTC151206B	Lower pillow lava	15.08	No	-25.923	0.045	n.d.	n.d.
Bulk	DTC151204A	Lower pillow lava	15.069	No	-19.256	0.058	n.d.	n.d.
Bulk	DTC151204A	Lower pillow lava	15.0305	No	-26.03	0.057	n.d.	n.d.
Bulk	DTC151207A	Ore	14.821	No	-22.959	0.066	n.d.	n.d.
Vein	DTC151207B	Lower pillow lava	15.102	Heavy	-24.61	0.046	n.d.	n.d.
Bulk	DTC151207B	Lower pillow lava	15.303	No	-24.673	0.06	n.d.	n.d.
Clay	DTC151207B	Lower pillow lava	15.101	Heavy	-25.565	0.025	n.d.	n.d.
Vein	DTC151207C	Lower pillow lava	15.421	Heavy	-25.653	0.043	n.d.	n.d.
Bulk	DTC151207C	Lower pillow lava	15.616	Little	-25.762	0.085	n.d.	n.d.
Vein	DTC151207D	Lower pillow lava	15.693	Heavy	-21.464	0.018	n.d.	n.d.
Bulk	DTC151207D	Lower pillow lava	15.28	No	-23.539	0.023	n.d.	n.d.
Bulk	DTC151207E	Lower pillow lava	15.652	No	-25.188	0.027	n.d.	n.d.
Vein	DTC151205A	Upper pillow lava	15.70;15.356	Heavy	-26.858	0.051	n.d.	n.d.
Bulk	DTC151205A	Upper pillow lava	15.36	Medium	-26.071	0.059	n.d.	n.d.
Bulk	DTC151208A	Sediment	5.34	No	-23.233	0.145	n.d.	0.013
Bulk	DTC151208B	Sediment	5.683	No	-23.695	0.119	n.d.	0.005

Textures and secondary mineralization in vesicles and veins in the pillow lavas

Akaki and Kamara River

Veining in these samples are sparse, with an irregular or anastomosing texture (appendix A23). Secondary minerals are zeolite, quartz and clay. Fine grained calcite as well as larger calcite crystals with distinct twinning is seen in late secondary veins, cross cutting zeolite filled vesicles. EDS and Raman shows that the zeolite have a composition corresponding to mordenite (figure 17, appendix B6), and that the clays ranges from illite to smectites. Veins are usually <1 mm in width, but larger cracks combined with vesicles are found to be <4 mm in width.

Vesicles are sparse to common, <6 mm, with round to subhedral shapes and are rimmed by saponite and oxides, and filled with acicular mordenite (figure 18a, appendix A23). Some vesicles are also rimmed by calcite or quartz instead of clays as secondary minerals. Globular quartz inclusions are found at the edges of the larger zeolite filled vesicles, with diameters <20 μm . Clay alteration is sparse, and is commonly found around the zeolite filled vesicles, occasionally within the centre of the filled vesicles, as well as in individual domains.

Hollow tubes in zeolite is found in one of the larger veins in the sample taken furthest from the dyke intruded area (figure 18b). The morphology of the tubes is curvi-linear, <2 μm , extending from the edge of the vein towards the centre. In the other sample, filaments are instead found extending from the edges of the zeolite filled vesicles, where the vesicles have a Mg to Fe rich clay rim, with increasing Fe towards the vesicle center (figure 18c-d). The filaments consist of Fe rich smectites, they have a lobate morphology, are sparse in the samples, and the width of the filaments are increasing closer to the dyke intruded area, with widths of <5 mm to <20 mm. The filaments are short and fairly straight; some are found branched and some have a terminal globular swelling with diameters <20 μm (figure 18e). Fe-rich globules are also seen at the edges in some zeolite filled vesicles, with diameters <20 μm (figure 18f).

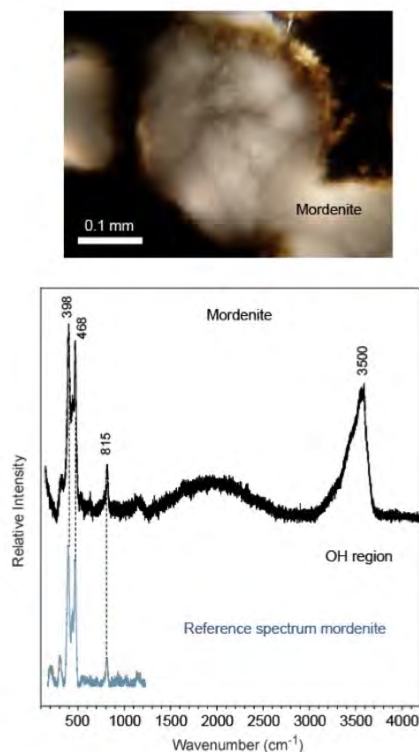
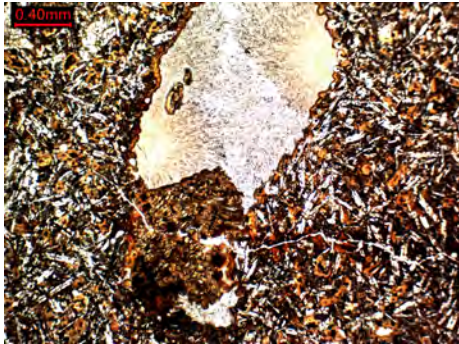


Figure 17: Raman spectrum in the spectral range $100 - 4200\text{cm}^{-1}$ of a zeolite in a cavity in sample DTC151204B, identified as mordenite $\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$. Reference spectrum ($100 - 1300\text{cm}^{-1}$) is from Downs (2006). The band at 3500cm^{-1} is due to the presence of OH groups in the structure. (Photo Curt Broman)



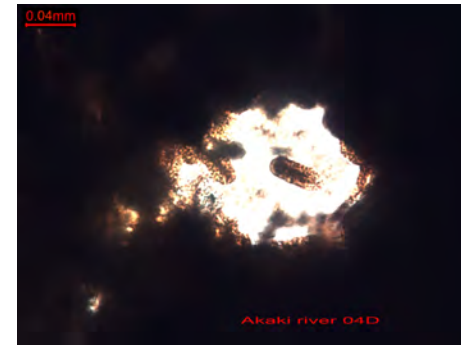
(a) Zeolite and clay filled vesicle



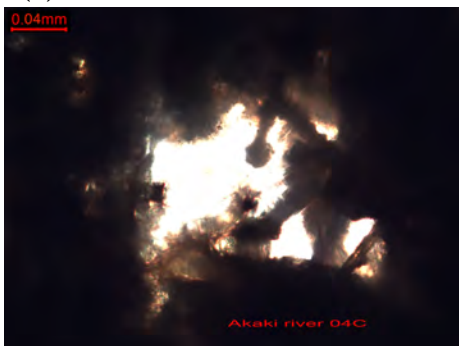
(b) Hollow tubes in zeolite



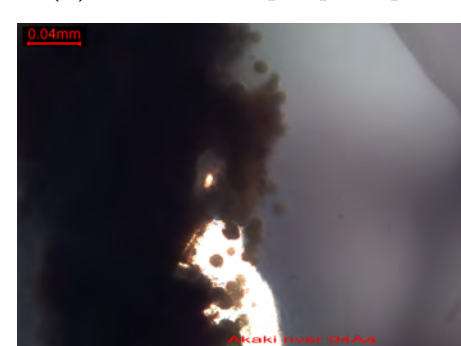
(c) Filaments in zeolite filled vesicle



(d) Filaments in open pore space



(e) Swelling at the tip of a filament found in an open vesicle



(f) Fe-rich globules

Figure 18: a-f) optical microscopy and analyser out, samples from Akaki River

Skouriotissa Mine

Veining is modest to common within the samples, with mainly anastomosing texture (appendix A30). Veins are usually <1 mm in width and are filled with secondary calcite. Wider cracks contain radiating zeolite or massive calcite. The calcite crystals show distinct twinning of higher grade than the calcite from the Akaki and Kamara river. Individual euhedral grains of blue silicate carbon are found within the vein, and are residues from the thin section preparation. Green alteration clays, with a composition of smectite to celadonite, are common in the larger veins in the samples closer to the main ore, ranging from Fe-rich in the core to more Mg-rich in the outer rims (appendix B8).

Vesicles are sparse to common in the samples, <3 mm, with round to subhedral shapes (appendix A30). EDS and Raman shows that secondary filling consists of calcite and zeolite with a composition of analcime and mordenite (appendix B9). Some vesicles show layered crusts, characterized by stromatolite-like arched sections, rich in Fe and Ti clays and oxides, with minor C according to the EDS (figure 20a-d, appendix B10).

Filaments are sparse in the thin section samples, usually short and stubby with an undulating morphology at the edges of the vesicles. Only one well defined filament is seen in the thin section from the least altered area, taken furthest from the main ore body (figure 20e). The filament has a width of <35 μm , shows swelling, and protrudes out from the mineral film at the edges into the empty vesicle. Globular textures, <90 μm , are sparse to moderate, and is found along the edges of the veins or the vesicles. They have an undulate or punctiform morphology. Globules are often found in contact with the green clays.

This locality also has a high abundance of filaments visible to the naked eye in the hand sample DTC151205C, where some filaments have been horizontally cut, and a recrystallized center can be seen along the whole filament. The filaments ranges from short and stubby to

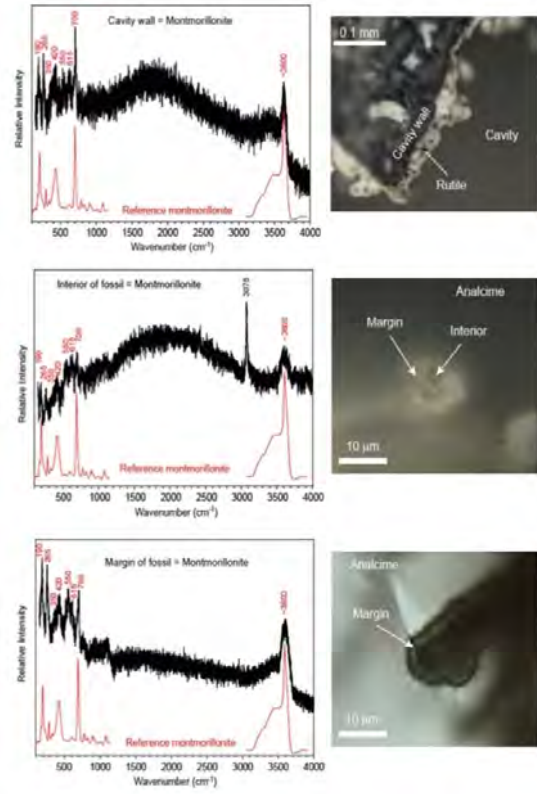
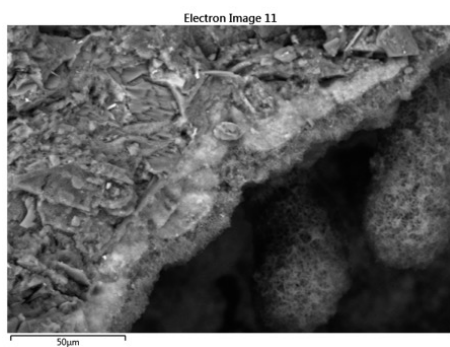


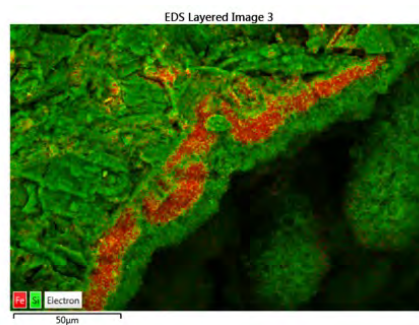
Figure 19: Raman spectra in the spectral range $100 - 4000\text{cm}^{-1}$ of a cavity wall and filament in an analcime-filled vesicle in sample DTC151207Ba. The spectra with peak positions in red numbers show that both the cavity wall and the filaments are composed of a Fe-rich montmorillonite. The spectra from the interior of the filament indicate that hydrocarbons are present with the peak at 3075cm^{-1} . Reference spectra of montmorillonite after Wang et al. (2015) have been incorporated in each diagram. Rutile grains are incorporated in the cavity wall of montmorillonite. (Photo Curt Broman)

long and branching. Some seems to have a secondary recrystallization, of possible zeolite, forming a mushroom shaped crystal terminating the filament (figure 20f). EDS shows that the center of the filaments have been recrystallized into clays, with a brownred Mg-rich core and an outer rim that is Fe-rich (appendix B11). Raman further shows that the clays have a composition of montmorillonite (figure 19). Raman spectra of clays may be problematic to obtain owing to the ultra-fine grain nature of the material and low degree of crystallinity (Wang et al. 2015). However, figure 19 shows a set of acquired spectra from the clay in the filaments with discernible peaks at 190, 265, 420 (with a shoulder at 360), 550, 615 and 700cm^{-1} together with the strong wide band around 3600cm^{-1} . The wavenumbers are close to published data for typical montmorillonite $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with strong bands near 200, 425 (broad band) and 700cm^{-1} with a less intense peak around 270cm^{-1} together with a wide band around 3600cm^{-1} (Bishop and Murad 2004; Wang et al. 2015). The peaks at 190, 265, 420 and 700cm^{-1} arise from SiO_4 tetrahedral unit vibrations. The peak at 550cm^{-1} and the downshifted 270cm^{-1} peak to 265cm^{-1} indicates a Fe-rich composition, the peak at 420cm^{-1} is influenced by an Al-rich composition and the peak that appear as the shoulder at 360cm^{-1} is an indicator for some Mg (Wang et al. 2015).

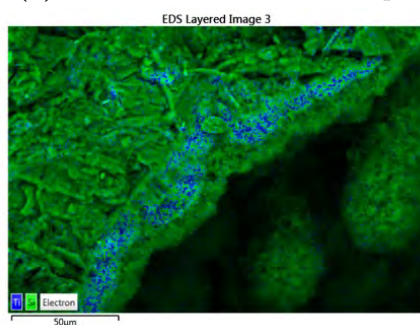
The extra band at 615cm^{-1} is normally not found in montmorillonite spectra, but matches the 604cm^{-1} peak caused by interference of Fe^{3+} with Si-O-Si groups in the spectrum of glauconite $(\text{K,Na})(\text{Fe}^{3+},\text{Al,Mg})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$ (Wang et al. 2015) and may suggest that the Fe-rich nature of the montmorillonite is due to the presence of a glauconite-like structure formed by replacement reactions of the montmorillonite. Mixture of smectite and mica is a common clay association in marine sediment (Charpentier et al. 2011). This may also explain why the measured Raman spectra are identified as montmorillonite and not nontronite. The wide band around 3600cm^{-1} is assigned to OH vibrations. The appearance of an additional strong peak at 3075cm^{-1} compared to the margin suggest the presence of hydrocarbons and bands in the range $3000 - 3100\text{cm}^{-1}$ can be assigned to C-H stretches in aromatic compounds (Orange et al. 1996). Raman spectroscopy on the walls inside the cavities reveals that they are covered by similar montmorillonite as the filaments are composed of. The Raman analysis also shows organic species (hydrocarbons) in a few filament cores.



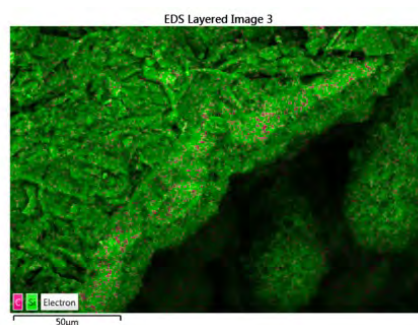
(a) Rim structure in hand sample



(b) Fe enrichment



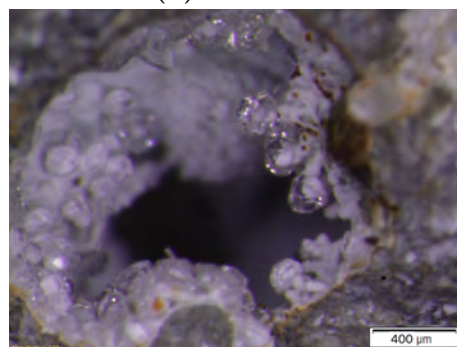
(c) Ti enrichment



(d) C content



(e) Filament with swelling textures found in an open vesicle



(f) Fossilized filaments in open vesicle with zeolite crystals at the tip

Figure 20: a-d) EDS, detailed data in appendix B e) optical microscopy, analyser out, f) handsample

Mathiatis Mine

Veining is common in the samples and has an irregular texture (appendix A36). The width of the veins range from less than a millimetre to a few centimetres and are filled with secondary calcite, zeolite and clays. Radiating acicular zeolite occurs in larger domains in some samples and blue silicate carbide residues from thin section preparation are found in some veins. Domains with calcite have inclusions of ferroan calcite and hematite, and the calcite crystals shows distinct twinning similar to the calcite found from the Akaki and Kamara river.

Vesicles are sparse to common, <80 μm , usually with increasing abundance further from the main ore body (appendix A36). They have a round to anhedral shape, where the majority are filled with analcime or mordenite zeolite, and calcite given by the Raman analysis. Early clay alteration is modest to common in the samples and occurs either in larger domains or as saponite and Fe rich oxide rims around the zeolite crystals and the vesicles. Pervasive clay alteration is more common closer to the main ore body.

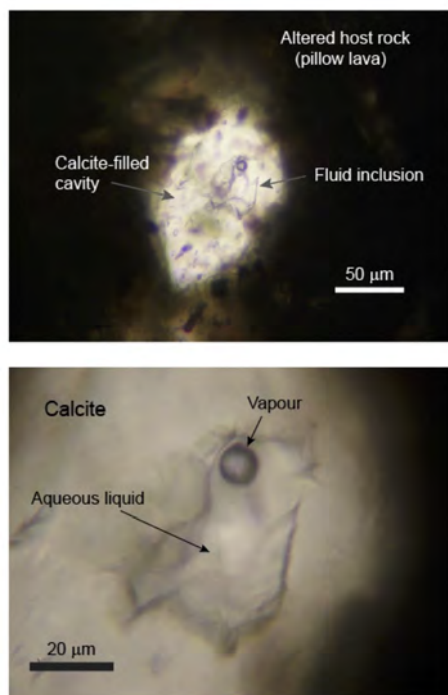


Figure 21: The photos show a large aqueous fluid inclusion in a calcite-filled cavity within the surrounding altered pillow lava (sample DTC151207D). (Photo Curt Broman)

A few fluid inclusions were recognized in the calcite, most of the calcite crystals have irregularly feathery-like dark and empty inclusions mainly radiating from the center. These probably reflect a rapid growth of the calcite. However, six inclusions that contained an aqueous liquid and a vapour bubble were distinguished in sample DTC151207D (figure 21). Five of these that were found in calcite veins, varied in size from 5 to 20 μm and were irregular with angular shapes. Such inclusions may have suffered post-entrapment modifications like stretching or leakage, which can result in a shift to higher homogenization temperatures. The recorded homogenization temperatures from these inclusions, 109 °to 131°C (to liquid), should be used with caution and are probably somewhat too high. However, one large fluid inclusion (40 μm) that was found in a cavity filled with well-preserved calcite has survived without leakage. The small size of the cavity and the surrounding basaltic host rock has protected the fluid inclusions from deformation and leakage. Homogenization temperature of this inclusion was measured at 75 °C (to liquid) which is a minimum value for the formation temperature. First melting of all six inclusions was observed at temperatures around -35°C indicating a mixed composition dominated by Mg^{2+} , Fe^{2+} , Ca^{2+} and Na^+ (Shepherd et al. 1985). Final ice melting occurred between -2.4°C and -2.7°C, corresponding to salinities from

4.0 to 4.4 eq. mass % NaCl. Salinities have been estimated from data in Bodnar (2003).

Thick filaments are common and more abundant closer to the main ore body. They have a filamentous or lobate morphology where thicker filaments have a diameter $<15\text{ }\mu\text{m}$ (figure 23a, b). Secondary mineralization in the centre is easily distinguished in the thicker filaments, taking up more than half of the filaments diameter (figure 23c). EDS shows that these filaments have a composition of smectite with minor Ti, Mn and V. Raman confirms a composition of Fe-rich montmorillonite for both the interior and the margin of the fossils. EDS and Raman both shows a Mg rich core, encapsulated by an Fe rich outer rim (appendix B12). The Raman analysis also shows organic species (hydrocarbons) in a few filament cores. In calcite-filled vesicles, a few filaments were found that contained goethite with strong Raman peaks at $246, 300, 386, 483$ and 550cm^{-1} in the interior of the structures (figure 22). Some filaments have several successive rims of clay, where K enrichment is found in the Fe rim, followed by a thin Ti rich outer layer, and a more massive Mg rich final layer (figure 23c). Small fragments of rutile are found in the clay during the Raman analysis, and could be the reason for the Ti enrichment seen in the EDS. Branching filaments show swelling structures or spore like textures, with new filaments occasionally protruding from these structures (figure 23d). Thinner filaments, $<5\text{ }\mu\text{m}$, usually have septa and a cell like nucleus that is phosphorus rich (figure 23e, 24a-b), and filaments $<3\text{ }\mu\text{m}$ have no strand, septa or cell like nucleus visible in optical microscopy. The thinnest filaments are found in the sample furthest from the main ore body and occur in clusters radiating from the edges in empty vesicles (figure 25a). The thin filaments rarely show any branching features. All filaments seem to grow in direct contact with the opaque minerals or at the edges of K rich orthoclase laths that protrude into the vesicles (figure 25b-c). The orthoclase is often recrystallized into Na rich Analcime at the edges. No mineral film is visible around the min-

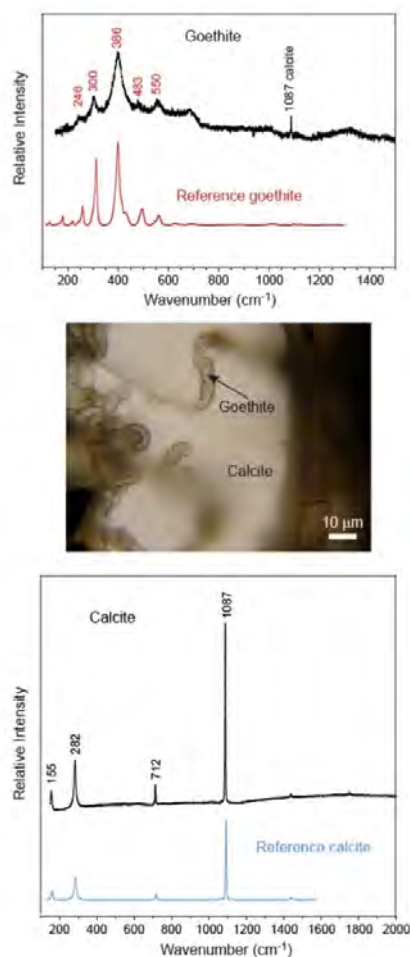
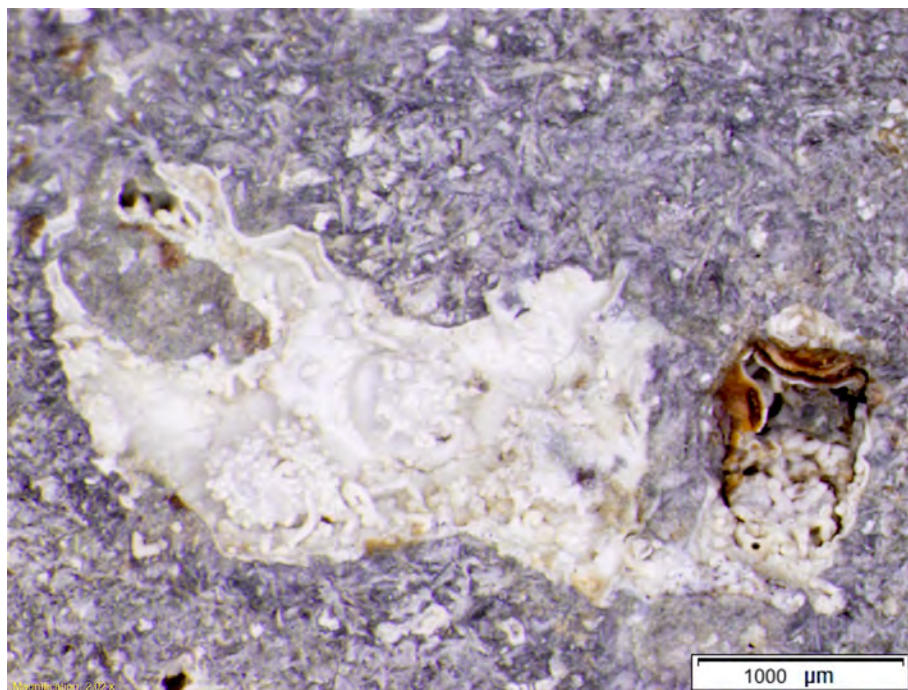
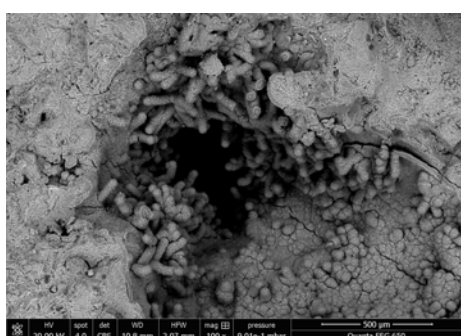


Figure 22: Upper diagram: Raman spectrum in the spectral range $100 - 1500\text{cm}^{-1}$ of the interior of the filament in a calcite-filled vesicle in sample DTC151207Ba. The spectrum shows peaks that are attributed to goethite. Lower diagram: Raman spectrum in the spectral range $100 - 2000\text{cm}^{-1}$ of a calcite-filled vesicle. Reference spectra of goethite and calcite after Downs (2006) have been incorporated in the figure. (Photo Curt Broman)

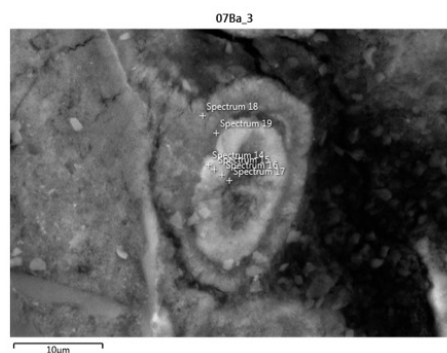
erals. Globular microtextures are found in all the samples but with different morphology and size. Samples closer to the main ore body have globules with a punctiform morphology, where some show a moniloid structure, and with diameters $<5\text{ }\mu\text{m}$ (figure 25d-e). They are sparse and are found in both empty and filled vesicles, usually in association with the filaments. Large globules are found in the least altered pillow lavas. Samples that have the largest veining and amount of secondary filling, found in the middle of the profile have a high abundance of larger globules with a punctiform morphology and a diameter of $<200\text{ }\mu\text{m}$. Globules in the veins are found along the edge of the veins and in cluster domains. A different type of globules is found in samples taken furthest away from the main ore body, these have a different morphology, with punctiform shape that has a radiating Fe-rich smectite corona around it, and a core containing magnetite. They are greenish in colour in contrast to the Fe oxide globules that are brownish. These globules are found at the edges of empty vesicles and have a diameter $<35\text{ }\mu\text{m}$ and a core $<12\text{ }\mu\text{m}$ (figure 25f).



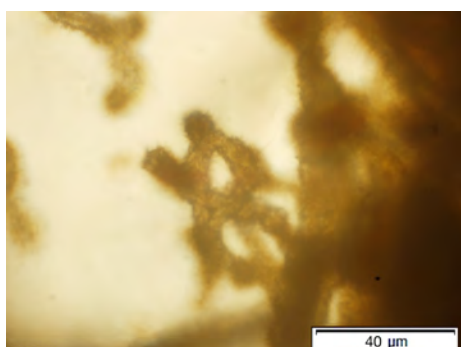
(a) Filaments in filled vesicle. Layered brown crust is seen to the right



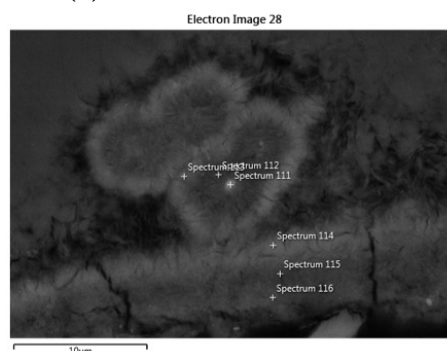
(b) Filaments in open pore space



(c) Filament in cross section

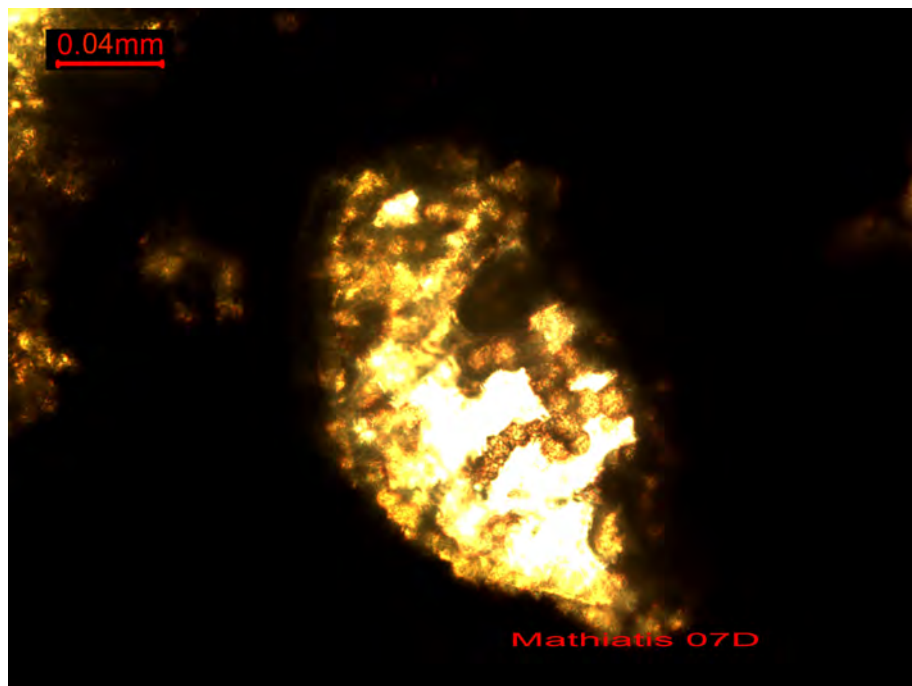


(d) Branching of filaments



(e) Phosphorus rich core, surrounded by Fe and Mg rich clay rims

Figure 23: a) hand sample; b-c, d) EDS, detailed data in appendix B; e) optical microscopy, analyser out

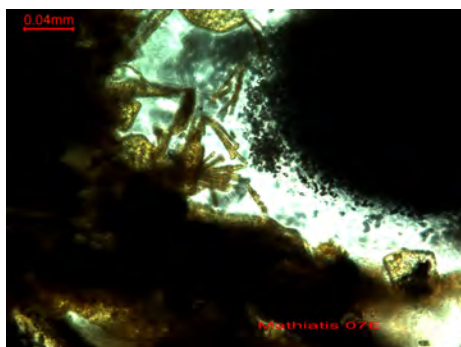


(a) Moniolid structure in a filled vesicle

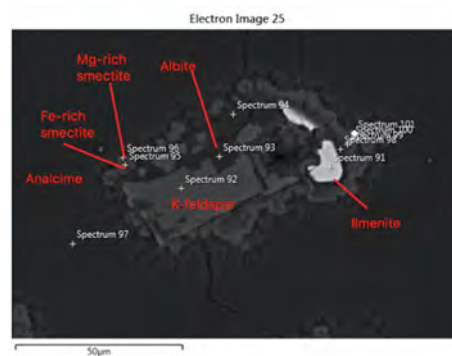


(b) White arrows show possible cell nucleus, red arrows show repetitive septa.

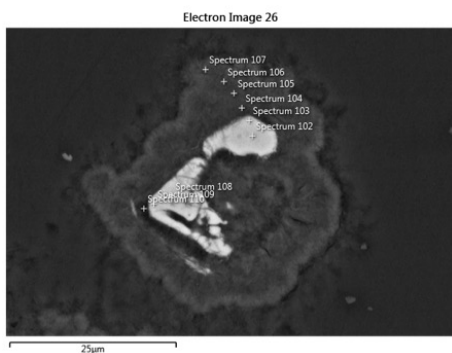
Figure 24: optical microscopy, analyser out



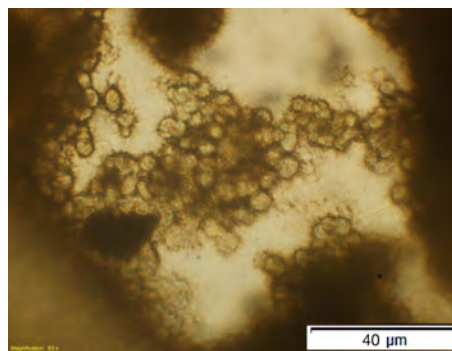
(a) Filaments in clusters along the wall of a vein



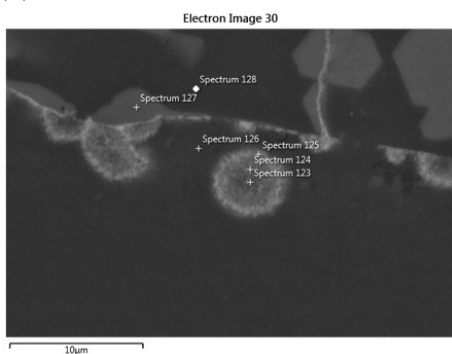
(b) Globular structures around a K-feldspar and ilmenite crystal



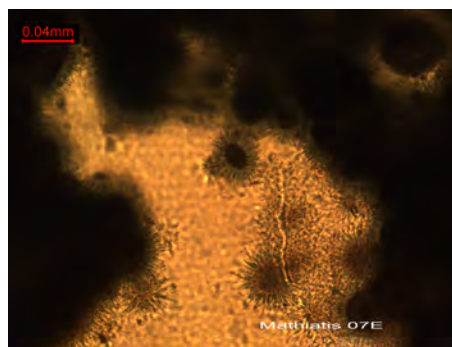
(c) Globular structures around ilmenite



(d) Initial stages of moniloid growth



(e) Fe rich globules in a zeolite filled vesicle,



(f) Fe-rich clay globules in secondary filled vesicle growing along the edge of feldspar

Figure 25: a, d, f) optical microscopy, analyser out; b-c, e) EDS, detailed data in appendix B

Discussion

Biogenicity

The biogenicity of the findings in the pillow lavas is tested against the following criteria: 1) the geological context, 2) the syngeneticity and indigenosity, 3) the morphology, and 4) the composition (Schopf and Walter, 1983; Buick, 1991; Gibson et al. 2001; Ivarsson 2006).

1) Life as we know it needs water, nutrition and heat to survive, and can survive even in environments that are extreme. The igneous crust in the deep sub-surface offers all of this. Previous studies show that both prokaryotic and eukaryotic life including fossilized life is found in the deep subsurface, within veins, vesicles and volcanic glass (Eickmann et al. 2009; Fisk and McLoughlin, 2013; Ivarsson et al. 2013; Bengtson et al. 2014). Such findings have also been coupled with biomolecules and microbial life as deep as 900 m below the seafloor (Ivarsson et al. 2012, Ivarsson et al. 2013). In this study, fossilized microbes are found in both empty vesicles and veins, as well as encapsulated by secondary zeolite or carbonates. Thus, the geological setting is compatible with microbial life.

2) Where encapsulated, secondary mineralization and filling must have occurred later than the growth of the putative microbes, since filaments protrude from minerals constituting the walls of the vesicles or veins, or are found around interstitial crystals totally encapsulated by secondary minerals. Hydrothermal alteration along the edges of the vesicles, consistent with saponite and montmorillonite, indicates that the microbes probably colonized the rock during the early first alteration. No secondary mineralization is seen occurring between the vesicle/vein walls or minerals and the microbes, indicating that secondary mineralization is younger than the putative microbes and that the microbes are indigenous. Secondary mineralization occurs when mixed warm hydrothermal fluids containing Na, Ca, Si, and metals in dissolution enters the pillow lavas. Cooling and pH changes of the fluids induce precipitation and filling of the voids, and is known to happen 10-20 Ma after crystallization of the rock (Pirajno, 2010). Previous research also shows that the ophiolite was emplaced onto land some 20 Ma ago, giving us a minimum age for the fossils (Moores and Vine, 1971). This indicates that the microorganisms are syngenetic to the early hydrothermal fluids rather than being a modern colonization.

3) All the samples collected from the pillow lavas contain filamentous structures ranging between $<2\text{ }\mu\text{m}$ to $<35\text{ }\mu\text{m}$ in width. The width of filaments cannot be used as a reliable criterion to discriminate between prokaryotes and eukaryotes (Schulz and Jørgensen, 2001), but is still used within studies of fossil microorganisms due to no better method available. Normally prokaryotes have diameters up to $2\text{ }\mu\text{m}$ but big bacteria among the sulfur oxidizers with diameters up to 1 mm are known (Schulz and Jørgensen, 2001). Fungal hyphae normally have diameters between $2\text{--}27\text{ }\mu\text{m}$, but fossilized hyphae from the ocean floor can have even wider diameters (Bengtson et al., 2014; Ivarsson et al., 2015). The hyphae in the current study, are found both as long branching filaments in open vesicles, as well as short and undulating in secondary recrystallized vesicles. Thicker and longer filaments found in the samples from the two mines, contains a secondary recrystallized center, as well as cell like walls and nucleus. Based on the overall morphology, these filaments appear to have a mycelium-like network, similar to that found among fungi (Webster and Weber, 2007). Actinobacteria are the only known prokaryotes that form mycelia, but have diameters up to $2\text{ }\mu\text{m}$, thus, are excluded due to the exceeding diameters among the current filaments, that

usually exceeds 5-10 μ m. Honegger et al. (2013) used a diameter of <1 μ m to distinguish between actinobacteria filaments and fungi hyphae. Though the fossilization process could have contributed to increasing diameters, the central core is still found larger than what is expected for actinobacteria. The filaments and the mycelium-like network they occur as bear close resemblance to previously described fossilized fungal mycelium in igneous oceanic crust (Ivarsson, 2012, 2015; Bengtson et al. 2014). The mineralized center could be a strand developed during fossilization of fungal hyphae (Ivarsson et al. 2012). Globular textures that are Fe-rich and with diameters less than 15-20 μ m could be fossilized spores or yeast cells (Taylor et al. 2015).

Layered textures at the margins of the vesicles in the hand sample from the Skouriotissa mine are similar to layered microstromatolites and, thus, an indication of bacteria. This has previously been described by Bengtson (et al. 2014) and Ivarsson (et al. 2015) as common prokaryotic fossils in igneous oceanic crust. Based on the composition of the layered structures in the current study, these structures have been interpreted as probable remains of iron oxidizing bacteria.

4) EDS and Raman shows that the filaments consist of smectite with a composition of montmorillonite. They have a Mg rich core, encapsulated by an Fe rich outer rim. Some filaments have several successive rims because of successive mineralization during the fossilization, where the Mg core and Fe rim is alternated with thin Ti and K rich layers. Rutile fragments was found with Raman and could explain the Ti content. The K-enrichment is probably due to leaching of surrounding minerals and/or from the fluids. EDS also shows phosphorus enrichment in possible cell interiors, which could be remnants of organic compounds. Cell contents like DNA for instance contain high amounts of P (Sindhu et al. 2014; Raven et al. 2016). These P enrichments are seen in several microbes, always in the center, surrounded by Mg rich smectites and an outer thinner possible cell wall of Fe rich smectite. Because the samples are glued with an epoxy resin containing carbon, Raman spectra of both the epoxy and the filaments was done to exclude carbon contamination. Some filaments have hydrocarbon content preserved in the central core, given by the Raman analysis. This shows that carbon content is indigenous to the filaments, and a biotic origin is therefore likely. The stromatolite textures seem to have a different composition, in contrast to the fungi, consisting mainly of Fe, Ti, and some C according to the EDS.

The above criteria for biogenicity have been addressed and successfully fulfilled in favour of a biological interpretation. It is further suggested, based on the morphological features and elemental composition, that the filaments represent fossilized fungal hyphae that occur in mycelium-like networks, and that the layered rim-structures are fossilized bacterial biofilms with some resemblance to microstromatolites. Hollow tubes found in samples from the Akaki river has not been evaluated based on these, or criteria for ichnofossil, since too little data have been collected for these textures. More studies are needed in order to classify these as biogenic.

Elements and isotopes

Of all the pillow lavas, the most abundant biogenetic textures are found in the samples from the mines, where the microbes prefer colonization around Fe rich oxides or K rich feldspars. Basaltic rocks, including the ones in this study, usually contains olivine, pyroxene, feldspars and oxides, minerals that are high in Mg, Fe, K, Na, Ca, Al and Si (Wilson, 2007). Because of the type of ore deposit these samples are associated with, we also have a higher abundance of S, Cu, Zn, and Pb found in pyrite, chalcopyrite, pyrrhotite, sphalerite, and galena (Robb, 2005). Hydrothermal alteration can dissolve and alter these minerals, which is seen in the samples as; olivine recrystallized into clays, Ca carbonates, and iddingsite; pyroxenes recrystallized into calcite and clays; K-feldspars recrystallized into plagioclase or zeolite; and pyrite recrystallized into hematite or magnetite. Data from the XRF and the pillow lavas confirm that secondary veining and pervasive hydrothermal alteration has depleted several elements, while Ca and Ni are enriched. Because secondary mineralization consists of carbonate minerals such as calcite and zeolite, enrichment of Ca seems evident. Ni is usually enriched in mafic magmas, and shows a good correlation with MgO, indicating olivine fractionation or accumulation (Willson, 2007). Weathering and dissolution of mafic, Ni rich rocks could therefore give rise to Ni enrichment in secondary veining, as seen in these samples. Depletion is seen for Fe, Cu, K, Mn and V, and to some extent also Ti. While Fe, K and Ti, with minor Mn and V, have been found within the fossilized microbes, Cu is likely to have been deposited as oxides, while Mn has been deposited as oxides in the umbers. Mn and Fe enrichment in umber is common, and occur in association with VMS deposits around the hydrothermal venting area, also known as black smokers (Robb, 2005). At the Mathiatis mine Ti seems more depleted, with a higher variation, and seems to correlate with the pervasive hydrothermal alteration in the area. Microscopy shows that local domains with ilmenite crystals occur in the samples closer to the ore deposit, and that Ti could have been dissolved during hydrothermal alteration from the host rock, and later recrystallized as oxides.

K and Fe are two of the most abundant cations found in all living organisms and help control biochemical functions and growth, and the uptake of these ions is thus essential for microorganisms to survive (Benson, 1997; Rodriguez-Navarro, 2000). In extreme environments, where nutrient abundance is limited, elements might need to be dissolved from the surrounding substrates. This is done by chelating compounds, such as siderophores secreted by the microbes, or by the production of organic acids that can dissolve the Fe from the substrate (Philpott 2006). In the samples from the Mathiatis mine, fossilized microbes are often found in direct contact with interstitial K-feldspar and Fe oxides. The K-feldspar has either been recrystallized at the edges due to solid solution, hydrothermal alteration with dissolution of K^+ and recrystallization with Na^+ , or biotically altered during metabolism. The Fe-oxides that are in direct contact with the microbes, shows no direct recrystallization along the edges, indicating either Fe dissolution on a smaller scale than what the methods in this study can distinguish, or microbial growth and total dissolution of the mineral. Other properties that can control microbial and mineral connections depends on the type of biofilm formation, micro-environment, surface properties of the minerals, as well as surface charges (Vaughan et al. 2002; Brown et al. 2008). The higher abundance of microbes asso-

ciated with samples from the mines, is probably due to a higher oxide content, and higher temperatures on the hydrothermal fluids, giving rise to more dissolved ions from the host rock in general. The samples show an increase of heterotrophic fungi, but their connection to the increasing metal content is probably indirect, since autotrophic prokaryotes usually are more favoured by metal availability. It is however expected to see an increase of fungal colonization, if potential biomass, and thus nutrients increases in general. Isotope data of the ophiolite shows no correlation trend with increasing microbial content from the mantle and upwards. No trend is seen for the profile taken at the Mathiatis mine either. Because the data varies within the whole sequence, these results probably indicates later biological contamination due to weathering, alteration and introduction of organic contamination. The isotope data can therefore not be used to reconstruct past environmental conditions for endolithic microbes in the oceanic crust.

Hydrothermal history

A clear distinction is seen with filaments increasing towards the main ore deposit and pervasive hydrothermal alteration, where vertical temperature gradients changes with depth. A horizontal temperature gradient is also seen in relation to the ore deposits. Modern hydrothermal vent areas have temperatures between 350°- 400°C along the active axial ridge, which decreases gradually from the spreading center (Candela, 2005). For Troodos, discharge temperatures were between 300°- 350°C (Spoonner, 1980).

A larger calcite from the Akaki river and the Mathiatis mine shows distinct twinning, indicating temperatures <200°C and twinning in calcite seen from the Skouriotissa mine indicate temperatures between 150°- 300°C (Burkhard, 1993). Homogenization temperatures of fluid inclusions in the calcite from the Mathiatis mine also show temperatures >75°C. Calcite formation in the sheeted dykes on Cyprus has been estimated to 75°- 100°C, and is considered to be somewhat higher than calcite formation in the lavas (Cann and Gillis, 2004). The crystal faces of the analcime found in the Skouriotissa samples shows a tetragonal structure and temperatures <230°C (Ghobarkar and Schäfer, 1999). Zeolite together with silica indicates temperatures <150°C, while zeolites and smectites indicates temperatures <100°C, and mordenite also indicates temperatures <100 °C in basalts with a composition of andecite to dacite (Seki et al. 1969; Miyashiro and Shido 1970; Palmason et al. 1979). Celadonite is usually formed with temperatures <50 °C, where a previous study has given a formation temperature between 15°- 20°C for celadonite on Cyprus, and celadonite found together with saponite in basaltic rocks showed formation temperatures between 50°- 90°C (Odin et al. 1988). From the Raman analysis, we found non crystalline carbon in the fossilized fungi, which indicates temperatures <150 °C (Beyssac, et al. 2002a; Beyssac, et al. 2002b; Huang et al. 2010; Pimenta et al. 2007).

There are several hydrothermal alteration stages for the upper oceanic crust along a spreading ridge, dependent on if the alteration occurs in the active spreading zone, in the passive off axis zone, and if the circulation is open or closed (Frey and Robinson, 1999). Low hydrothermal alterations of the upper oceanic crust are found in both the active and passive, off-axis part of the system, though higher grade alterations is usually found in the active part of the system. Both these types of alterations occur with open circulation and convection

of the oceanic waters. The last stage is very low hydrothermal alteration occurring due to a close convection system, that occurs when impermeable sedimentary layers closes the heat flow circulation between the crust and the oceanic waters (Frey and Robinson, 1999). A first hydrothermal alteration of the pillow lavas is given by celadonite and Fe rich oxides, followed by saponite seen in the vesicles and veins. This stage of alteration should have occurred with temperatures $<50^{\circ}\text{C}$ for celadonite, and $<75^{\circ}\text{C}$ for saponite. This alteration sequence is seen in most of the samples, though celadonite is sparse, and saponite is much more abundant. Secondary filling suggests two additional later events with hydrothermal fluids, where the first precipitated Na or Ca zeolites with temperatures below 100°C . The last event precipitated Ca carbonates with temperatures $>75^{\circ}\text{C}$.

Organisms in these samples seems to have thrived in the open vesicles prior to secondary precipitation of zeolite or calcite. Thus, this gives a temperature window of a few degrees for oceanic water up to 75°C in which the microorganisms could have occurred. If hydrothermal fluids, warmer than 80°C enters the system, the eukaryotes die, and all type of eukaryotic metabolism ceases (Tansey and Brock, 1972). Though some prokaryotes have been found to survive up to 130°C under limited time, such microbes are usually found in geothermal areas (Kashefi and Lovley, 2003).

Basaltic fluids have a general pH between 8-10 (Von Frenkenstein et al. 1988), but hydrothermal alterations can change the pH in the host rock, where decreasing Mg increases the pH (Stakes and Scheidegger, 1981; Alt and Honnorez, 1984). Cold oceanic water with a pH between 7-8 mixes with magmatic and primordial fluids usually with a pH between 4-6 (Robb, 2005), during its rise to the ocean floor, pH and/or redox changes will precipitate the elements in dissolution, creating new minerals. The high clay content in all the samples indicates pH higher than 5 (Henin, 1955). Mordenite is usually found in environments with a pH between 7-9 (Mariner and Surdam, 1970), analcime is found in environments with pH higher than 8 (Savage et al. 2001), while Ca carbonates is found in environments with pH higher than 8-9 (Gudbrandsson et al. 2011). Living fungi in aerobic environments have been cultivated and shows a preference for pH around 4.5-8.3 (Rousk et al. 2009), and studies of living fungi from subterranean environments shows that they can survive in extreme environments with pH up to 10 (Reitner, 2006).

Fossilization

Fossilization of microbes, their morphology and even their organic matter, can be preserved by petrification and/or permineralization (Taylor et al. 2015). The preservation potential of organic material and soft tissue is dependent on the type of biomolecule, where macromolecules and lipids are easier preserved in contrast to carbohydrates, proteins or nucleic acids (Tegelaar et al. 1989). Both types of fossilization require enriched fluids in direct contact with the dead organism, where the elements in the fluid successively replaces the organic material, or minerals are precipitated within or between the cells in the organism, leaving the organic matter largely intact.

Several studies have showed that there is a connection between clay minerals and the polymerization of biomolecules, as well as complex bio-polymers (Bernal, 1951; Cains-Smith, 1982; Hashizume, 2012; Gadd, 2007). The studies show that biomolecules can adhere to

vacant sites in clay minerals and that there is a molecular structure between the both that favours this coupling. Ivarsson et al. (2013) argues that the fossilization process could start while the organisms are still alive, based on the non-dehydrated morphology commonly found in dead fungi (Smith and Read, 1997). During fossilization of the microbes found in the samples from this study, as well as in previous studies (Ivarsson 2012, 2013), this coupling may be of importance in describing how organic molecules in fact can recrystallize into clays. Organic molecules, can in a simple way be characterized as hydrocarbons, containing simple bonds that are easy to break. The element rich fluids that enter the host rock, should be able to start recrystallize the organic molecules by breaking the simple bond between the carbon and hydrogen, opening a negative carbon site. Montmorillonite smectite was found as the more common fossilization mineral of the fungi. This is a 2:1 structured clay mineral that consists of 2 repetitive TOT layers (figure 26). Because of the layered structure in clays, elements are attracted by weak electrostatic bonds, making it easy to build the next layer. The TOT structure has an overall negative charge which is balanced by inter-layered cations between the TOT layers, usually by cations like K, Na, Ca and water molecules.

EDS and Raman of the fungi in cross section, shows that the clay ranges from Mg rich in the core to Fe and K rich in the outer wall. In between it is also found a Ti rich layer. Since K and Fe is thought to have been absorbed by the living organisms, these cations are readily available in situ, while Mg, Ti, Na and Ca most likely have been added by the hydrothermal fluids. All the elements, except Ti, are probably enriched from the oceanic water, or by dissolution of surrounding minerals, though Mg could also have been dissolved during the breakdown of the diopside and the olivine in the original host rock. Ti is probably delivered with the primordial water, and precipitated when pH and temperature changes. Beside clay, goethite is also found in the central strand in some fossilized microbes, as well as rutile crystals in vacant sites of the montmorillonite. Some bacteria obtain energy by oxidizing ferrous Fe, resulting in the precipitation of oxidized Fe-rich minerals such as goethite (Ghiorse, 1984; Ehrlich, 1996). It is found in this study that the microbes prefer colonization around Fe oxides, where Fe enrichment is also seen in the clays. Goethite in the fungi might therefore have been due to a high Fe content and fossilization into an oxide was preferred prior to clays, or the fungi might have already deposited the oxide during the time it was alive. Similar oxide rich strands have been found in studies by Ivarsson et al. (2008) and Bengtson et al. (2014). Looking at the hydrothermal history, fossilization in these samples might have occurred in the following way:

Microbes are introduced into the system with the early low hydrothermal fluids, respon-

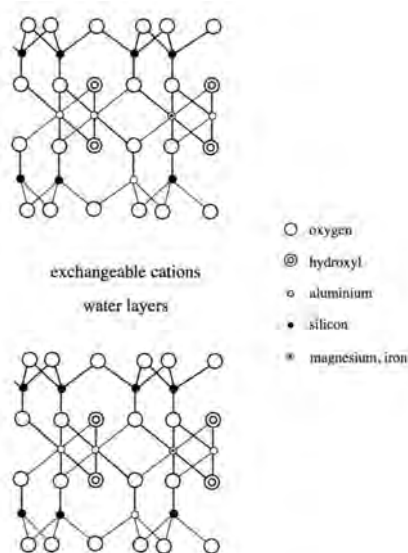


Figure 26: 2:1 structure of montmorillonite showing both TOT layers as well as the cation and water layer. (Modified from Ferris, 2006)

sible for the celadonite and saponite alteration, and colonization of the rock is initiated. This is followed by a second hydrothermal event with Na and Si rich fluids precipitating zeolites, lowering the general pH in the system as well as increasing the temperatures and thus stressing the microbes to start precipitate clay and oxide minerals as a defence mechanism. A last stage of hydrothermal fluids precipitates Ca carbonates, killing the microbes still alive due to too high temperature and pH. Total fossilization probably occurred before total encapsulation, based on fossilised, partly or non-encapsulated microbes found in the samples. In the handsample from the Skouriotissa mine, hyphae have zeolite precipitated at the tip of the hyphae, which could indicate that the charged surface of these microbes might have been a favourable nucleation site. Because the hyphae in the handsample shows the inner strand in the zeolite encapsulation, this indicates that these microbes were encapsulated first after fossilization occurred since the filament is broken off, showing the inner strand. The process of fossilization could also have continued after encapsulation, if enough access for the fluids is given into the minerals. Fossilization thus seems to be highly dependent on both fluid composition as well as rate and time of secondary precipitation.

Implications for life on Mars

Science is already today working towards several interesting aspects when it comes to potential life on other planets in our own solar system. Several missions are planned for to find biosignatures on Mars, where most work is aimed towards isotope signals, biomolecules or possible fossil deposits in lake and lacustrine environments. One of the bigger challenges with biosignatures that have been discussed is the possibility of contamination. How can we ensure that the possible life we find is not a direct contamination from Earth send space crafts now or in the past? How can we be sure that the biosignature we see is a biosignature and not carbon residues from other abiotic events? Fossils should, in contrast to chemical signals, thus be a more valid evidence, if we can find such on Mars. Further research and a comprehensive understanding of microfossils in extreme environments should therefore be of importance. Together with the upcoming missions to search for possible life, such as the European Space Agency's ExoMars rover, NASA's Mars 2020 and China Aerospace Science and Technology Corporation's 2020 Chinese Mars Mission, it is essential for us to evaluate possible landing sites from different aspects, with geology as one of those. In order to know where we should search for life, we also need to understand where life evolves, what it needs, and how it might be preserved.

This study has focused on the oceanic mafic crust, comparable to what is thought to have evolved during Mars early history, where plate tectonics were short lived giving rise to mafic and ultramafic rocks, and probably submerged in an early ocean (Baker et al. 1991; Yin, 2012; McSween Jr. 2015). In this study both prokaryotic and eukaryotic life is found as abundant and well preserved in this type of environment. Though these samples are much younger than possible volcanic terrain submerged in an early ocean on Mars (Bradenburg, 1987), Mars also lacks the extensive weathering that we have on Earth, giving us reason to believe that similar fossils might still be preserved even in older bedrock. This study is also of importance for possible living microbes on Mars. Ohja et al. (2015) found brines on the surface of Mars, indicating that Mars still has flowing surface waters. This means that with

increasing depth and geothermal gradient, flowing water could be readily available. Because Mars has a lower gravity, porous spaces as well as heat flows are different from what we have on Earth, and a deeper microbial community, >2 km, might be more probable (Sleep and Zahnle, 1998; Michalski et al. 2013).

Beside the ongoing missions to search for life on Mars, this area also opens questions on possible life on other terrestrial planetary bodies in our solar system that we know or suspect might have liquid water, such as Saturn’s moon Titan or Jupiter’s moon Europa. Other interesting aspects to further investigate is the connection between deep subsurface microbes and extreme climate changes. The study shows that there is a connection between microbial abundance and ion availability in the hydrothermal fluids. The composition of the hydrothermal fluids controls, and is preserved in the form of fossilization, as well as secondary mineralization, giving us additional information about the fluids temperature and pH for the period. Any change in the oceanic waters that arise during a climate change or impact event, could therefore be present in the fluids percolating down in the deep subsurface, and might be incorporated into the microbes during metabolism or during the fossilization process. Extreme climate changes or impacts, might therefore be recorded in these fossilized microbes, opening a new area for climate research, with igneous rocks as a climate archive, and fossilized microbes as a proxy.

Conclusions

It is found that the microbial abundance increases towards higher temperatures, more pervasive hydrothermal alteration, and that colonization is favoured in volcanic rocks that are in close association with ore deposits. Microbial colonization is found around K and Fe rich minerals, which they probably adhere to for elemental dissolution. Fossilization of the microbes has mainly been done into Fe and Mg rich clays, where some fungi have fossilized into, or preserved, goethite in the central strand, and rutile crystals in vacant sites of montmorillonite. Elements such as Mg, Ca, and Na seems to have come in with the oceanic water, and Ti with the primordial water. Fossilization seems to have been initiated during temperature and pH changes of later hydrothermal activity, where at least three hydrothermal events can be seen. An early first hydrothermal event was initiated with temperatures <50°C, precipitating celadonite and saponite in open vesicles and veins, as well as introduced microbial life into open pore spaces. A later second event with temperatures <100°C precipitated Na and Ca zeolites, increasing the pH from 4-5 to 7-8, stressing the microbes into starting to adhere clays as protection. Fossilization was finalized with a last hydrothermal event with temperatures >75°C, precipitating Ca carbonates, increasing pH to >8-9, as well as making the environment inhabitable for the microbes. It is thus believed that the hydrothermal fluids, temperature, as well as the rate and time of secondary precipitation in open vesicles and veins are the main factors controlling fossilization.

From this study, it is concluded that microbial colonization in basaltic pillow lavas favours open pore spaces that have had access to a high abundance of fluids, giving rise to more dissolved elements. These elements have come from both the oceanic and primordial water, as well as the host rock, and are essential for the microbes’ metabolism. The microbes seem to prefer temperatures <50°C and a pH below 7-8.

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Appendix

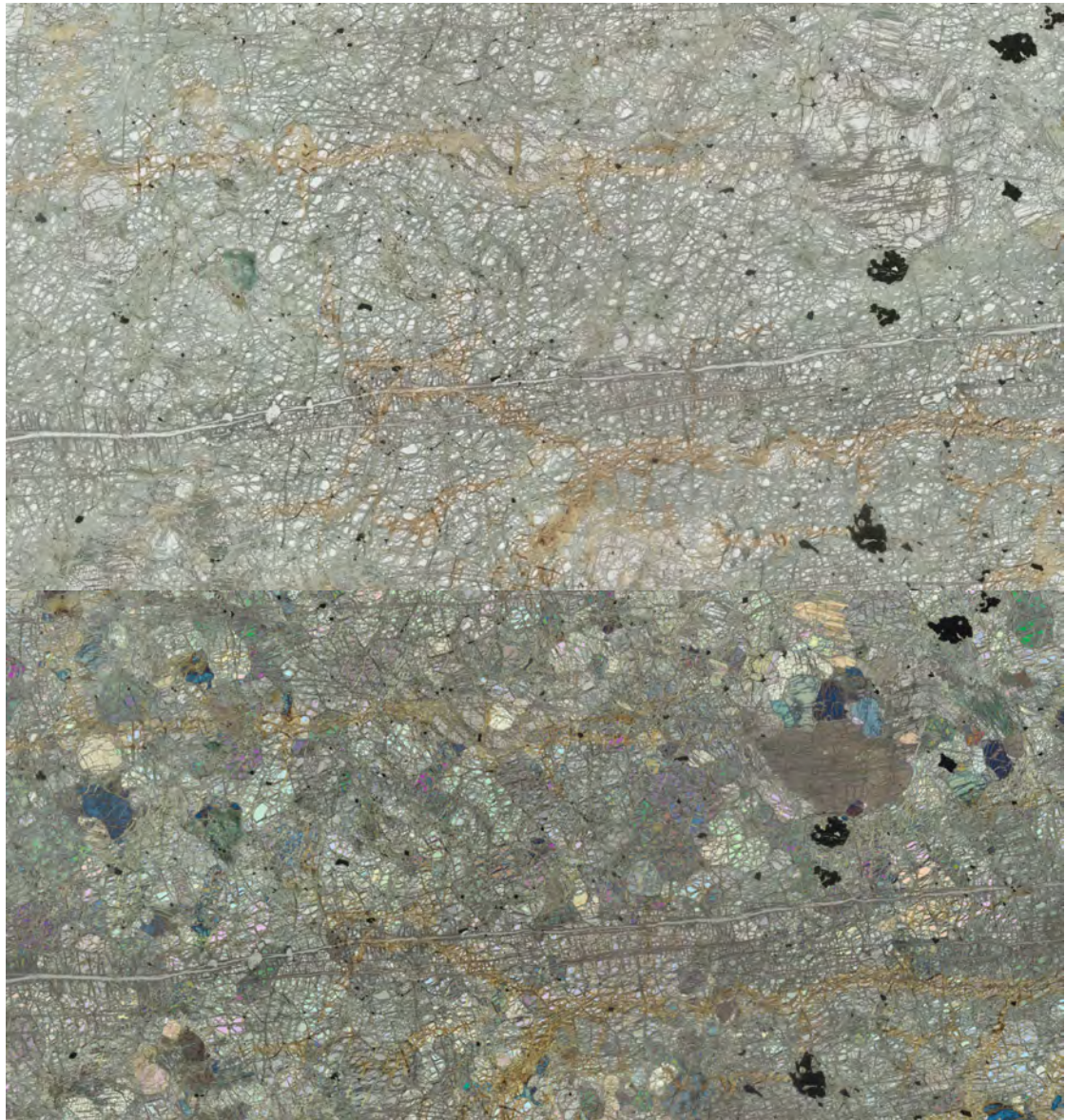
Appendix A: Macroscopic and Microscopic data



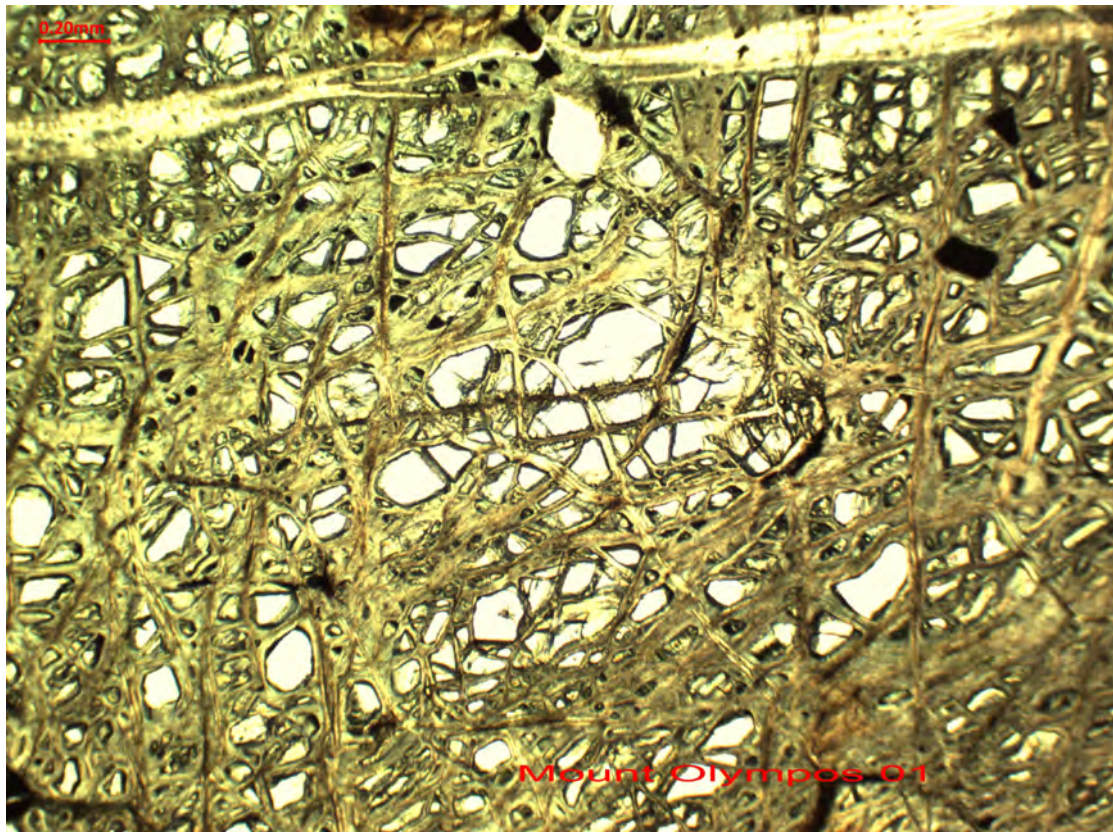
Mount Olympos, DTC151201, coordinates N34°56'52.7 / E32°51'43.9



Appendix A 1, hand sample of DTC151201, harzburgite



Appendix A 2, scanned thin section in PPL and XPL



Appendix A 3, olivine with a mesh texture of serpentine and clays, PPL and XPL

Chandria, DTC151202, coordinates N34°55'13.9 / E32°56'40.8



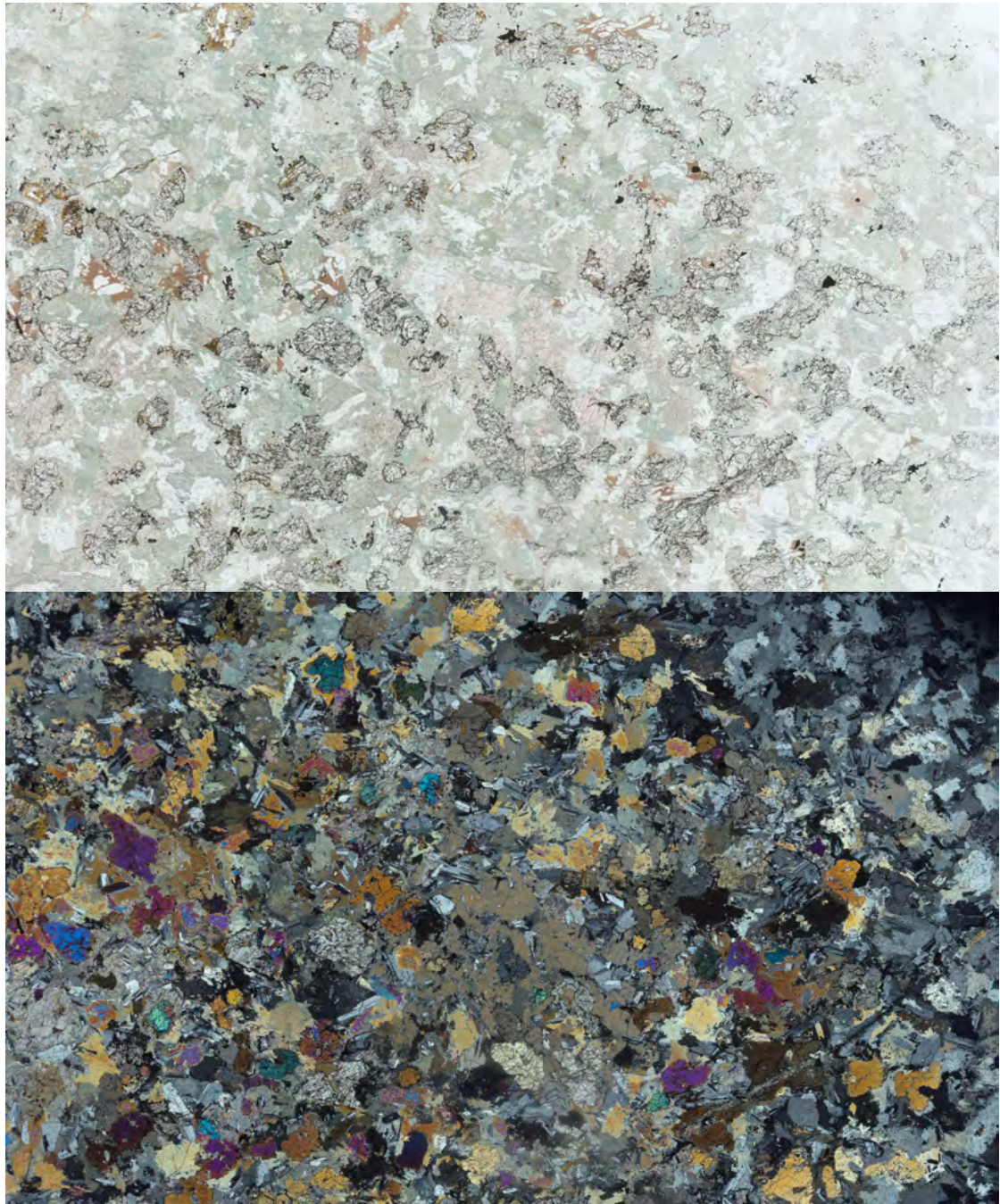
Appendix A 4, hand sample of DTC151202C, pyroxenite



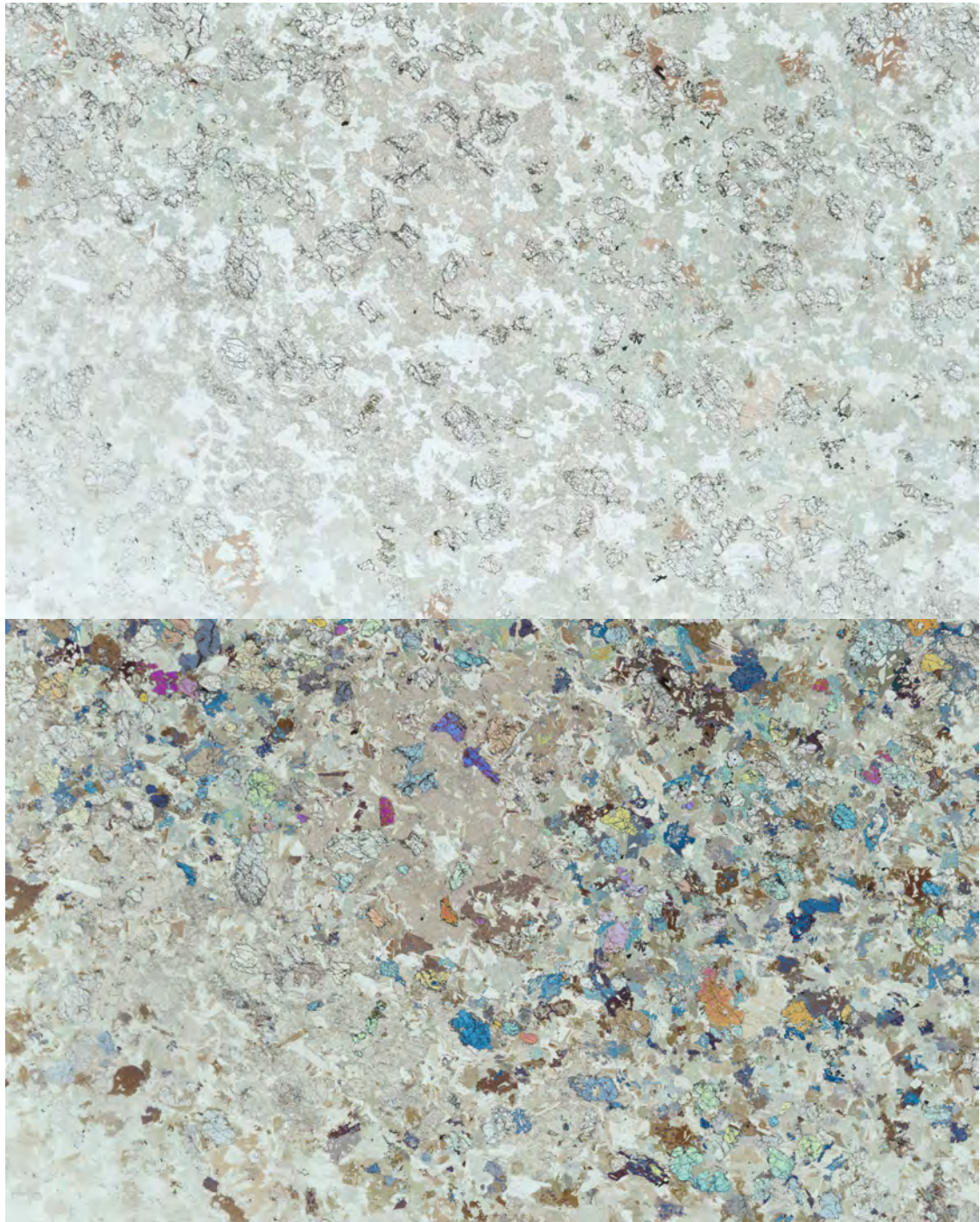
Appendix A 5, hand sample of DTC151202A, olivine gabbro



Appendix A 6, hand sample of DTC151202B, pale gabbro



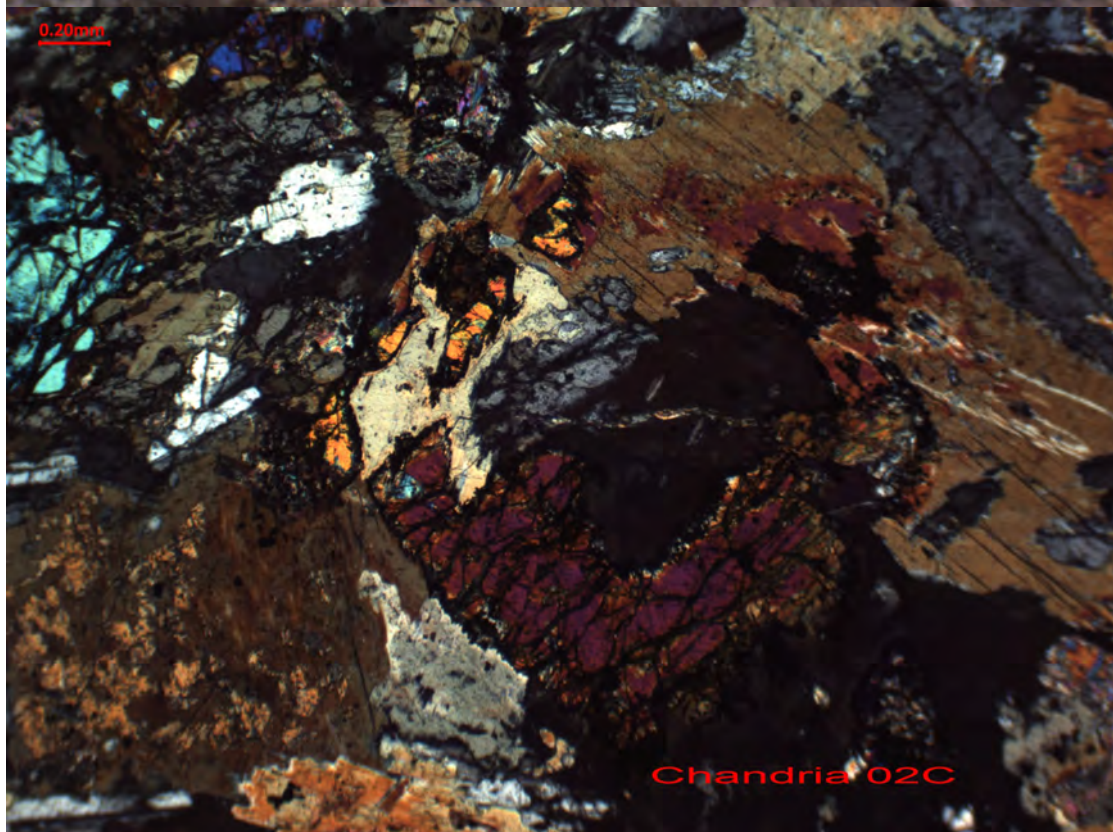
Appendix A 7, scanned thin section of pyroxenite (DTC151202C), PPL and XPL



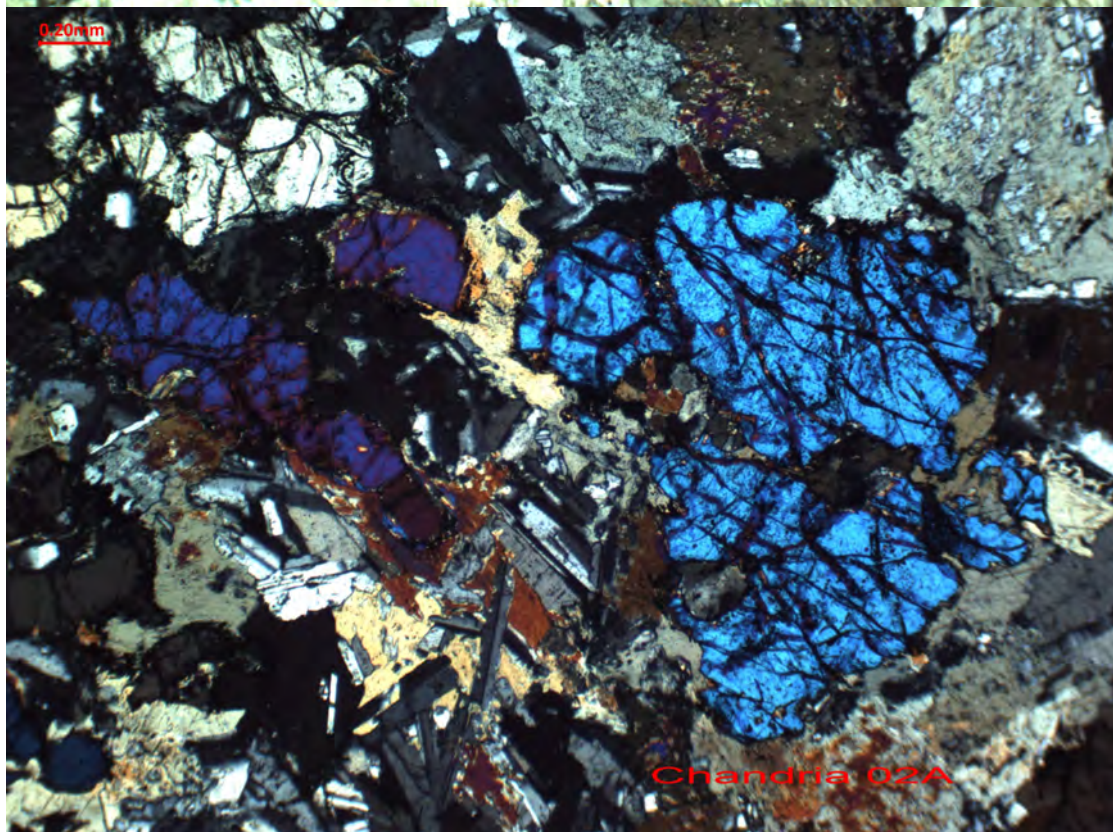
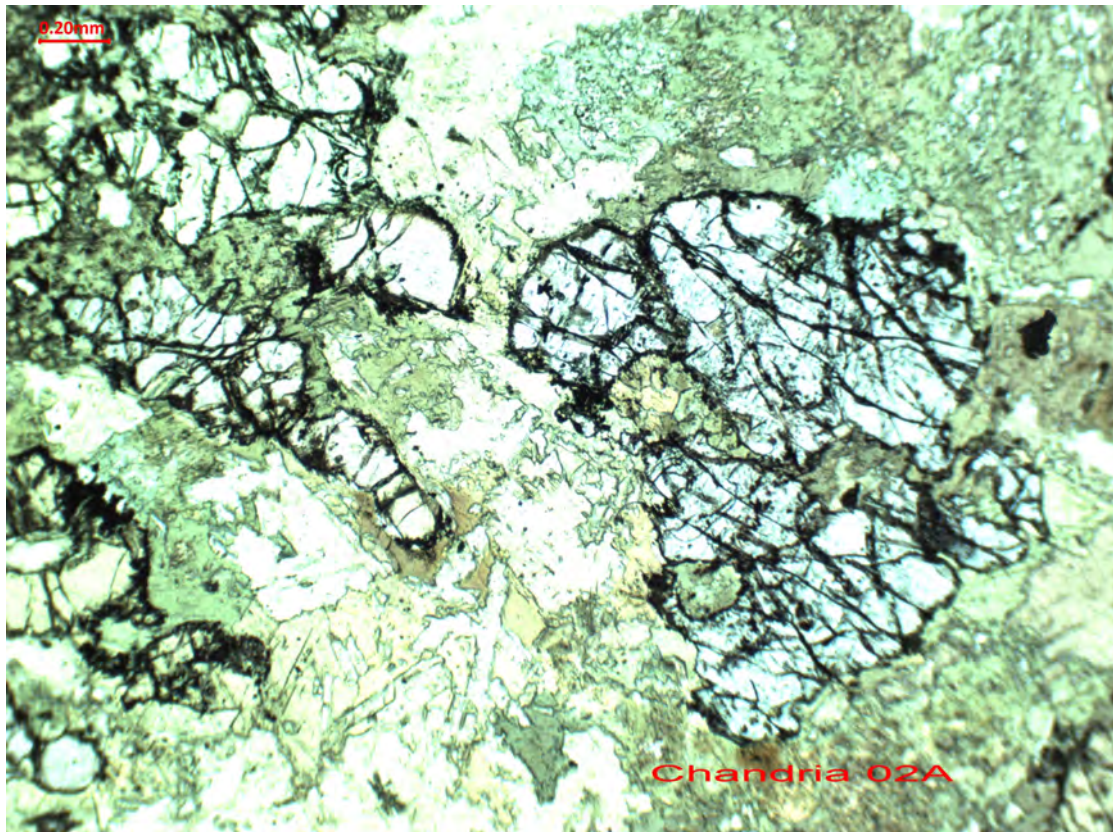
Appendix A 8, scanned thin section of the olivine gabbro (DTC151202A), PPL and XPL



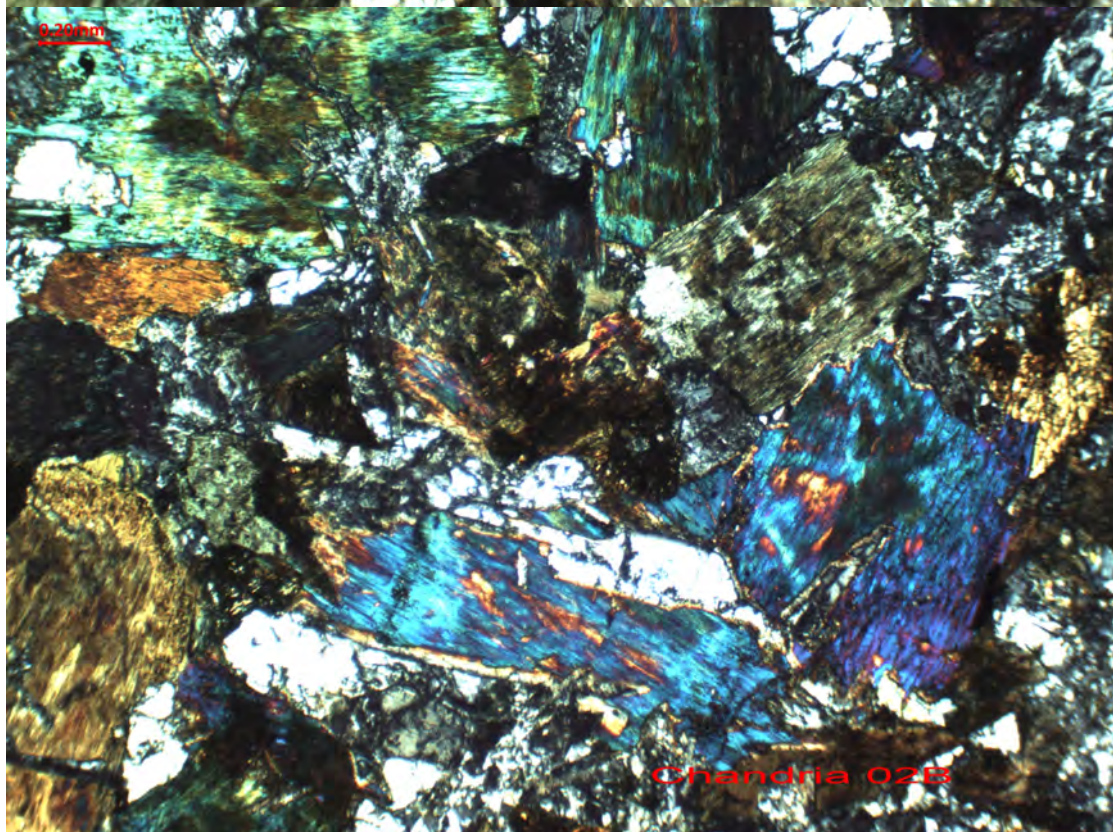
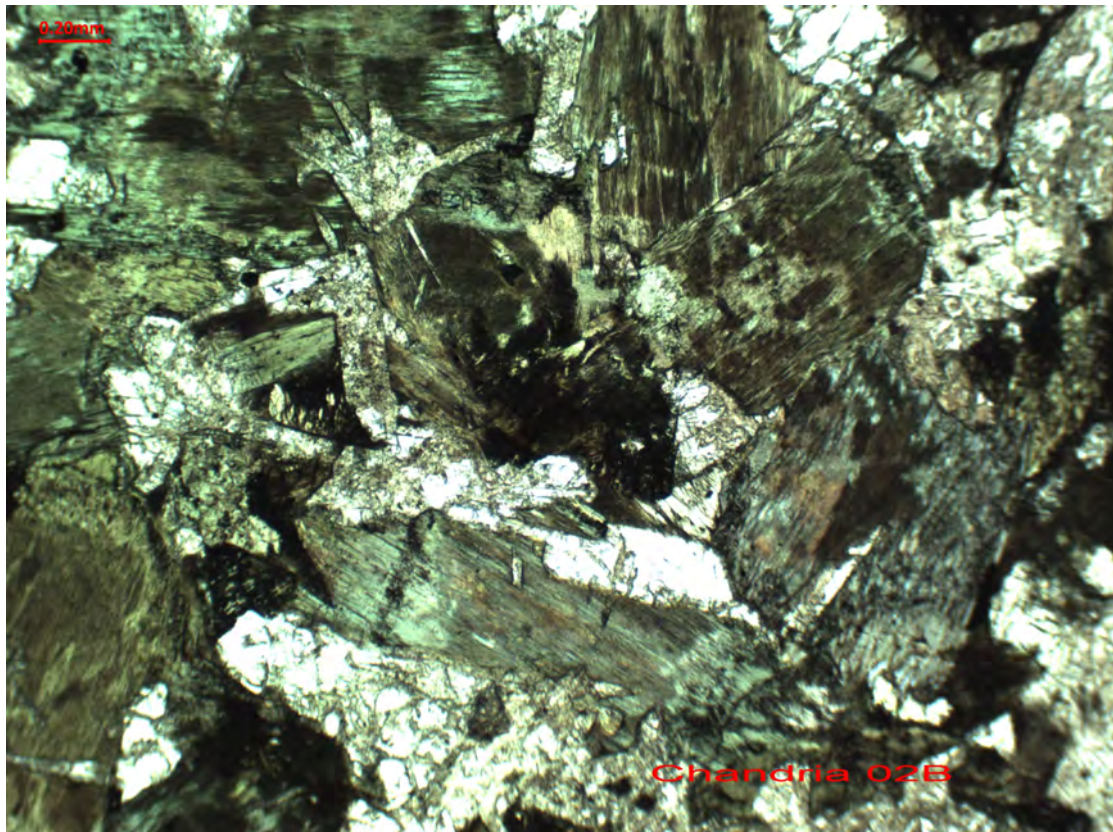
Appendix A 9, scanned thin section of the pale gabbro (DTC151202B), PPL and XPL



Appendix A 10, pyroxenite (DTC151202C), orthopyroxene partly recrystallized into hornblende



Appendix A 11, olivine gabbro (DTC151202A) with olivine crystals, plagioclase laths and hornblende



Appendix A 12, pale gabbro (DTC151202B), orthopyroxene, serpentine and hornblende

Palaichori, DTC151203, coordinates N34°54'58.6 / E33°05'32.0



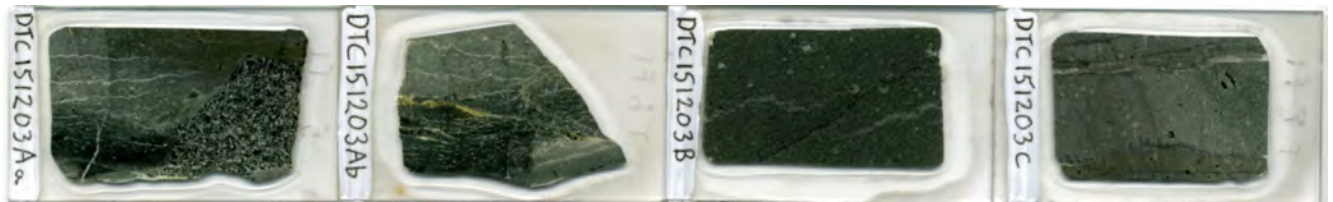
Appendix A 13, hand sample of basalt dyke (DTC151203A)



Appendix A 14, hand sample of basalt dyke (DTC151203B)



Appendix A 15, hand sample of basalt dyke (DTC151203C)

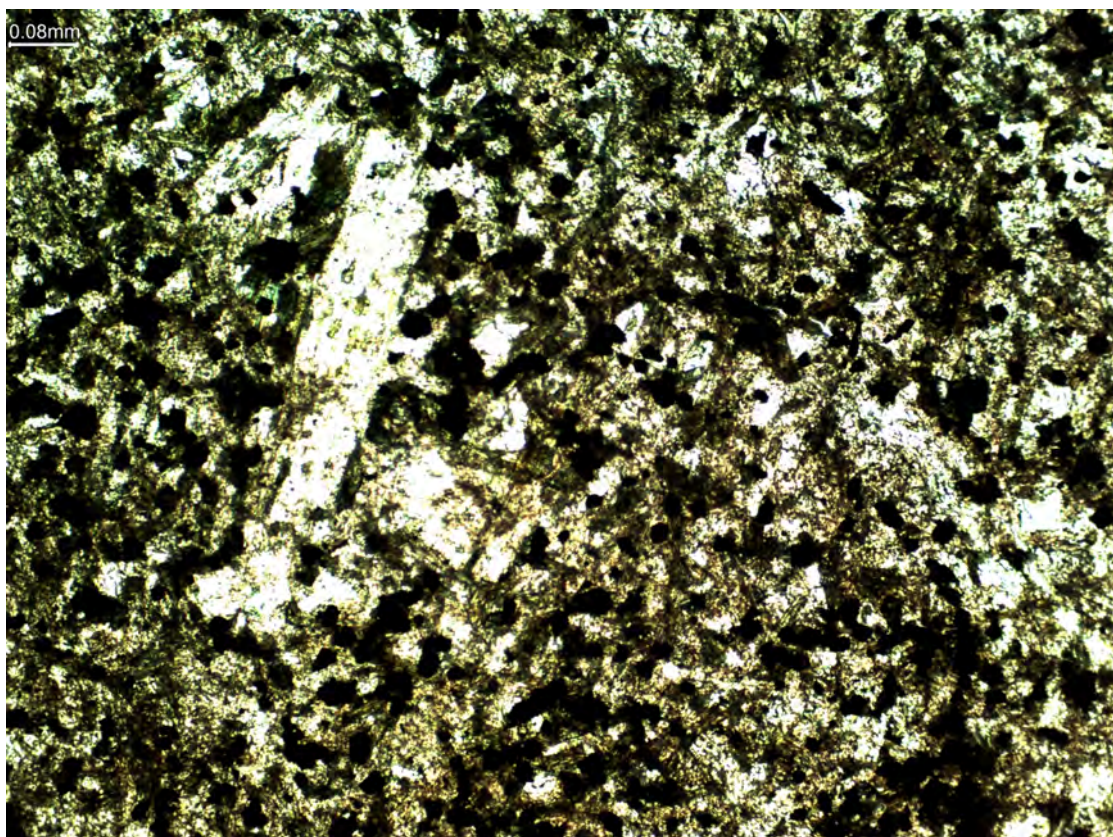


Appendix A 16, scanned thin sections

Infoga PP Loch XPL av tunnslip



Appendix A 17, scanned thin section (DTC151203AX), PPL and XPL



Appendix A 18, plagioclase lath in a mesostasi of oxides and clays (DTC151203A)

Akaki River, DTC151204, coordinates N35°00'41.2 / E33°09'18.1



Appendix A 19, hand sample of pillow lava (DTC151204A)



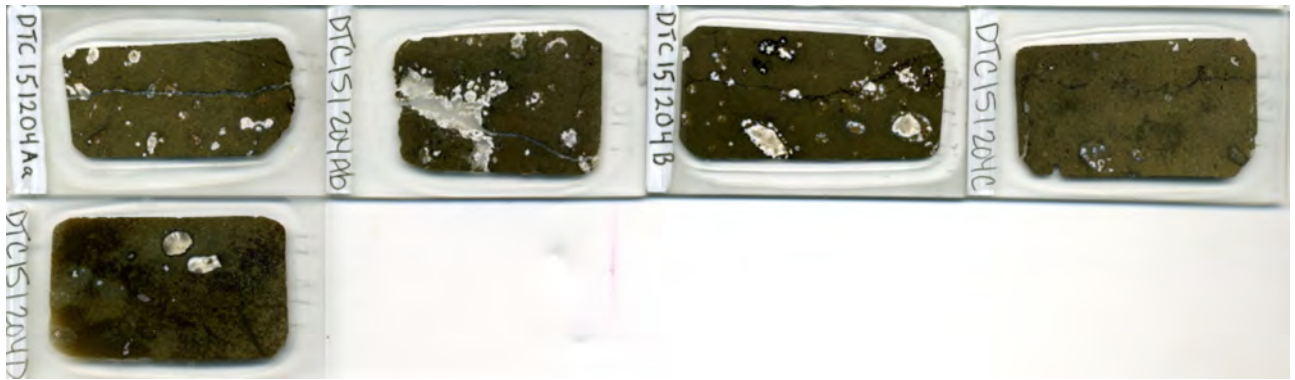
Appendix A 20, hand sample of pillow lava (DTC151204B)



Appendix A 21, hand sample of pillow lava (DTC151204C)



Appendix A 22, hand sample of pillow lava (DTC151204D)

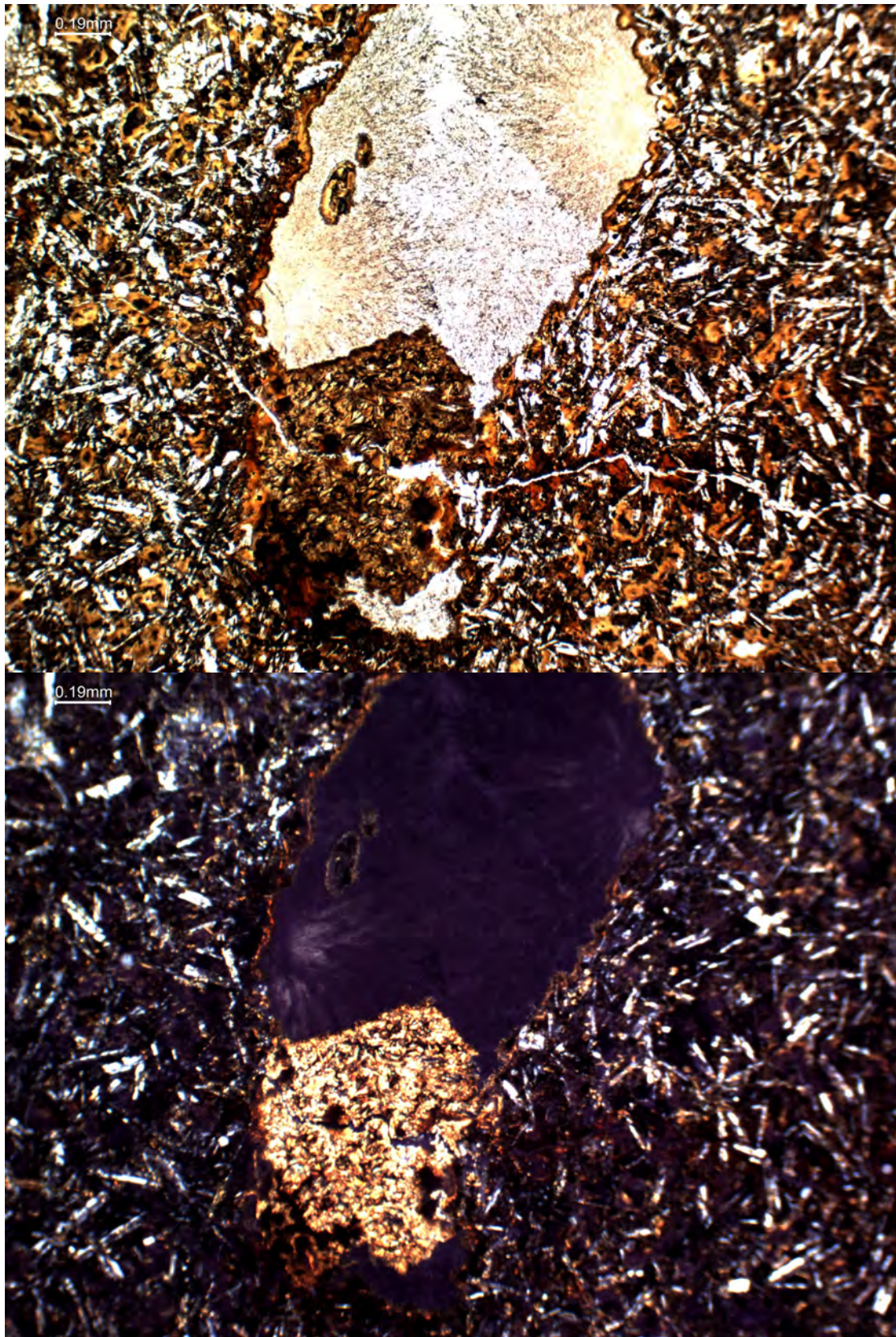


Appendix A 23, scanned thin sections

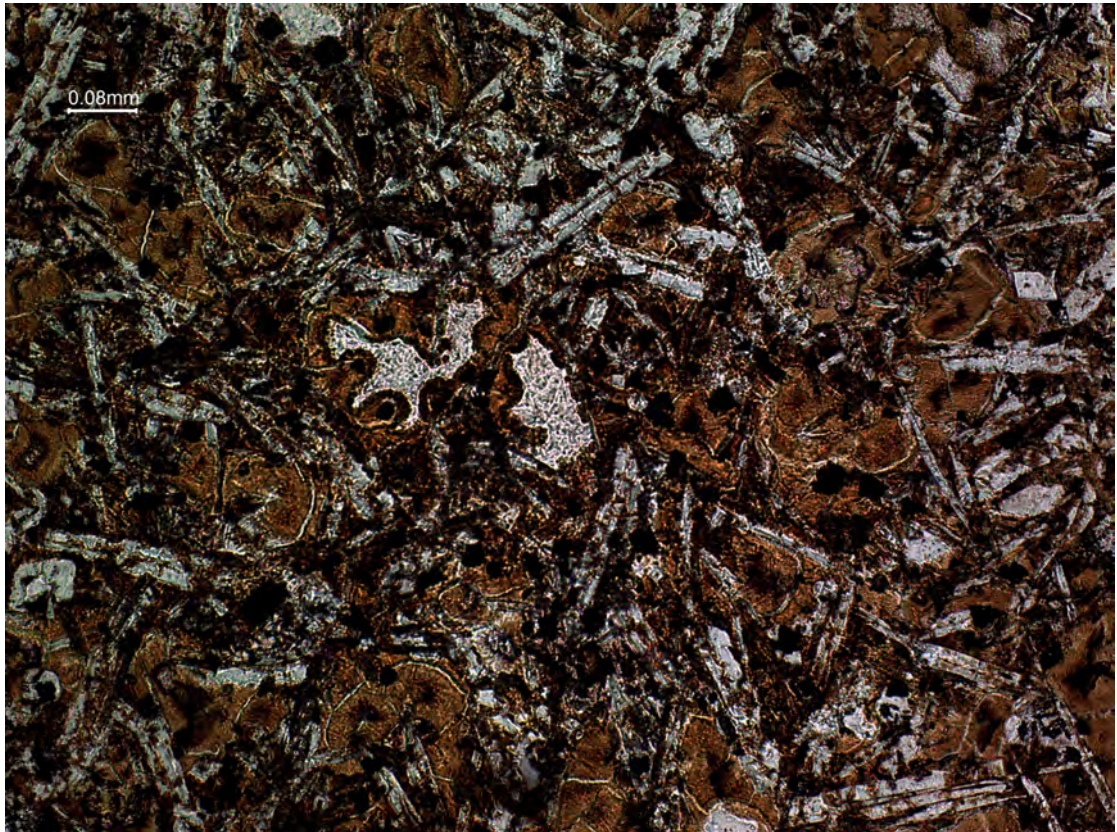
Infoga PP Loch XPL av tunnslip



Appendix A 24, scanned thin section (DTC151204DX), PPL and XPL



Appendix A 25, Zeolite and clay filled vesicle in pillow lava (DTC151204Da), PPL and XPL



Appendix A 26, clay and zeolite filled vesicles in pillow lava (DTC151204Da), PPL

Skouriotissa copper mine, DTC151205, coordinates N35°05'50.7 / E32°53'28.8



Appendix A 27, hand sample of pillow lava (DTC151205A)



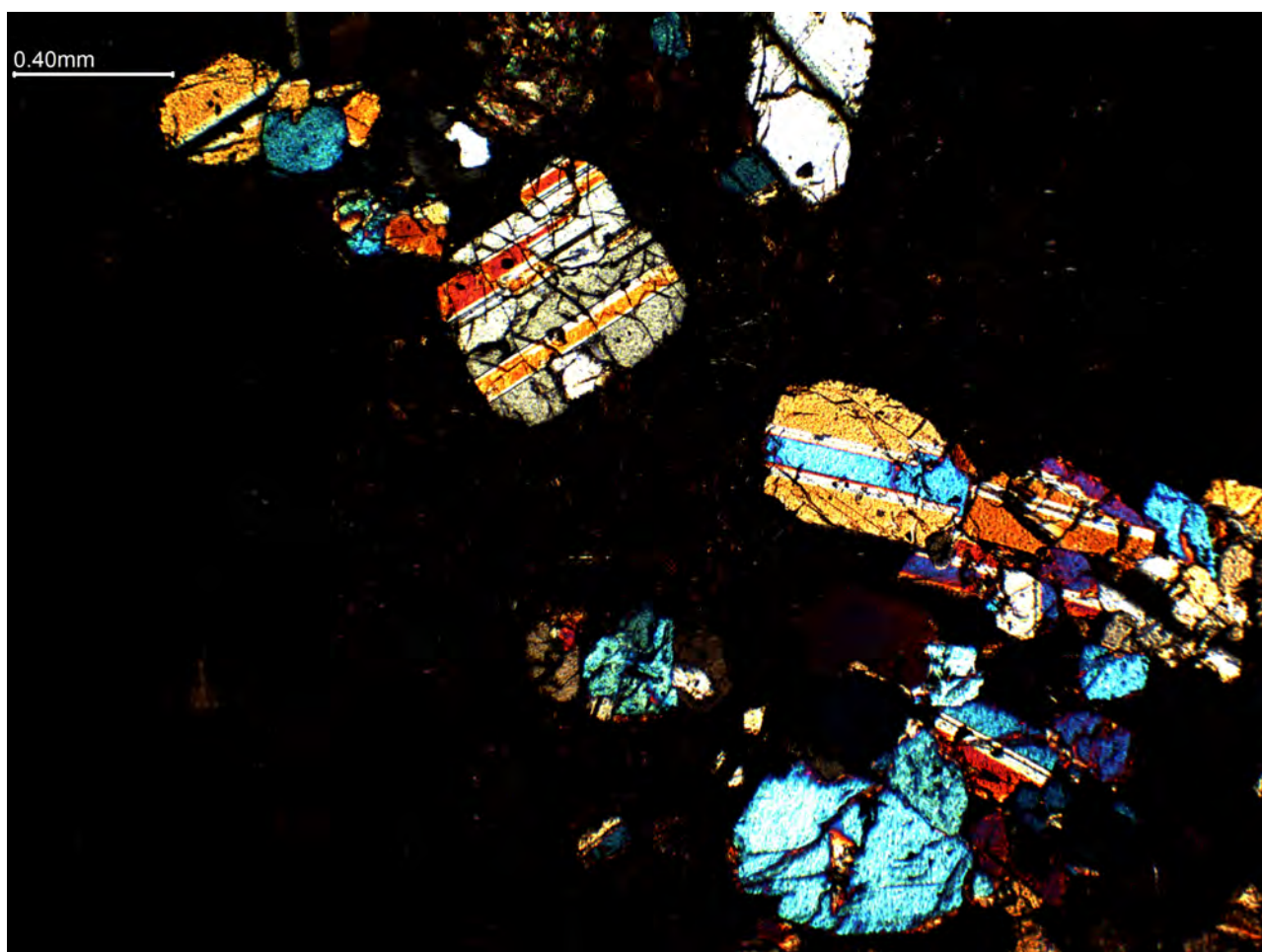
Appendix A 28, hand sample of pillow lava (DTC151205B)



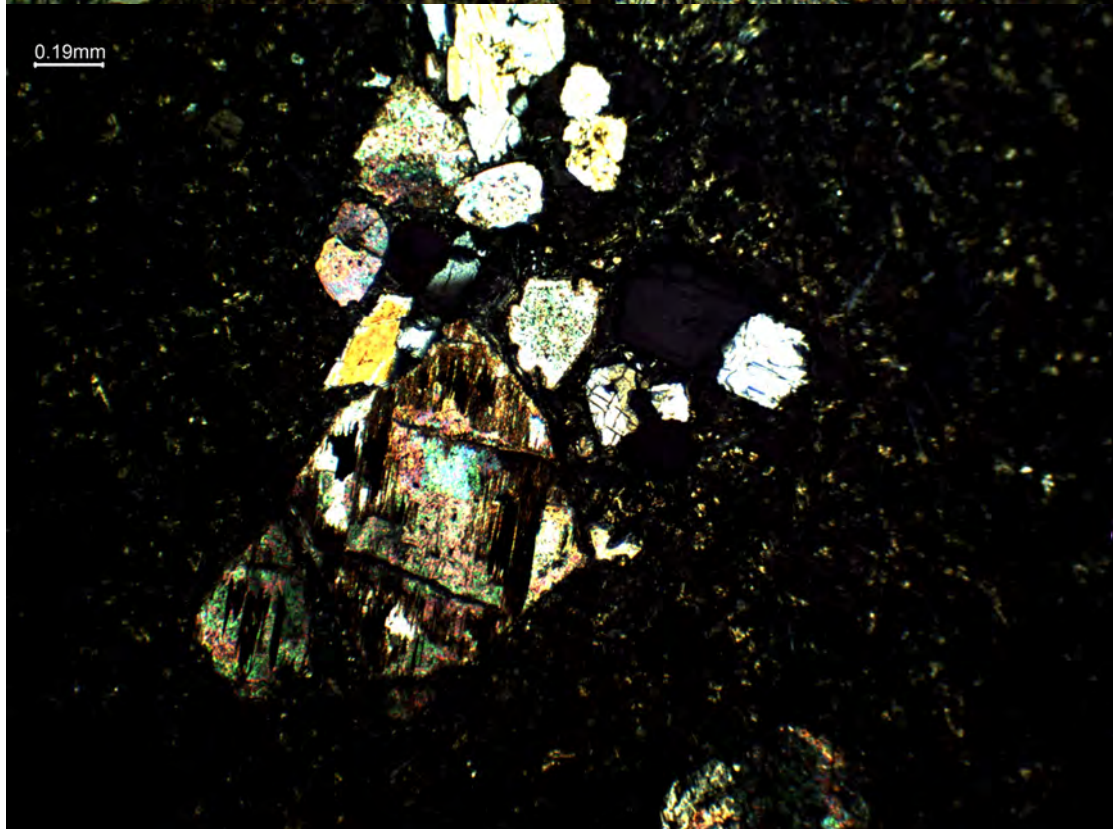
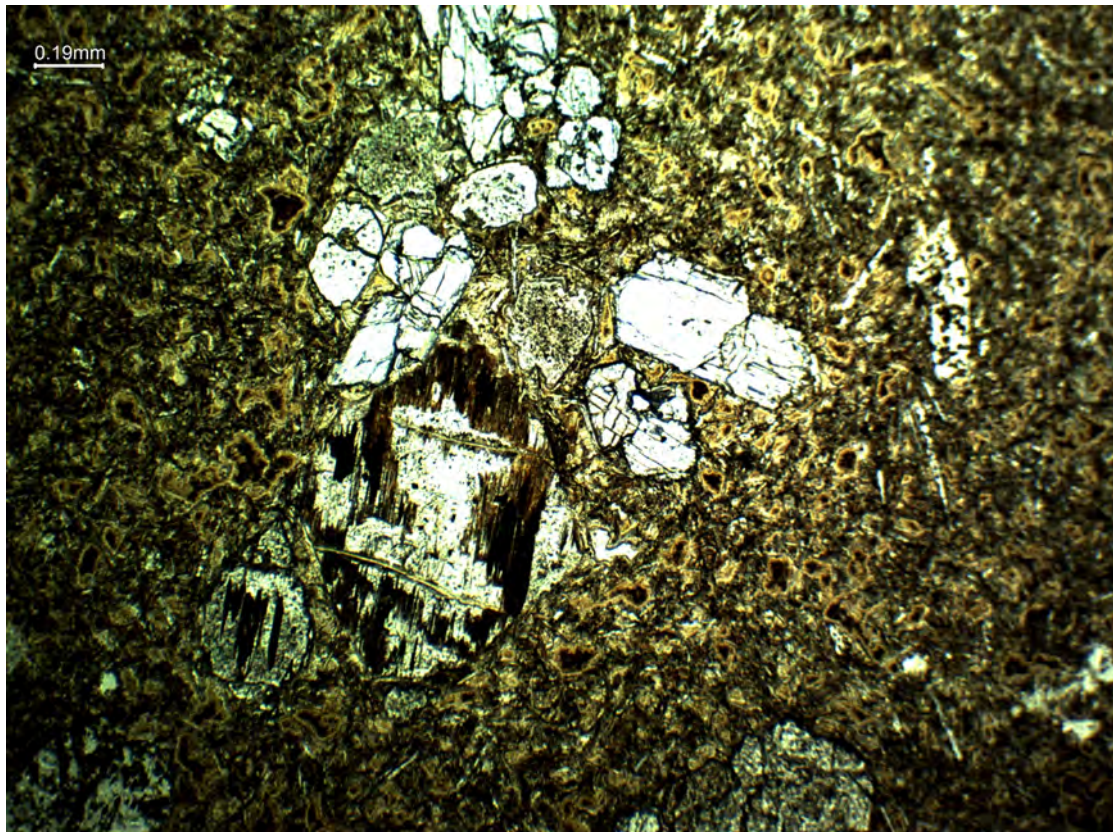
Appendix A 29, hand sample of pillow lava (DTC151205C)



Appendix A 30, scanned thin sections



Appendix A 31, twinning in diopside crystals (DTC151205BX), XPL



Appendix A 32, Diopside crystals and large relict olivine crystals recrystallized into clay and calcite, in a mesostasis of clay, plagioclase and oxides.

Kamara River, DTC151206, coordinates N35°00'42.2 / E33°09'13.6



Appendix A 33, sampled pillow lavas (DTC151206)



Appendix A 34, hand sample of pillow lava (DTC151206B)



Appendix A 35, scanned thin sections

Mathiatis mine, DTC151207, coordinates N34°58'33.8 / E33°20'53.0 to N34°58'35.1 / E33°20'43.8



Appendix A 36, scanned thin sections



Appendix A 37, hand sample of quartz and pyrite ore (DTC151207A)



Appendix A 38, hand sample of pillow lava (DTC151207B)



Appendix A 39, hand sample of pillow lava (DTC151207C)



Appendix A 40, hand sample of pillow lava (DTC151207D)

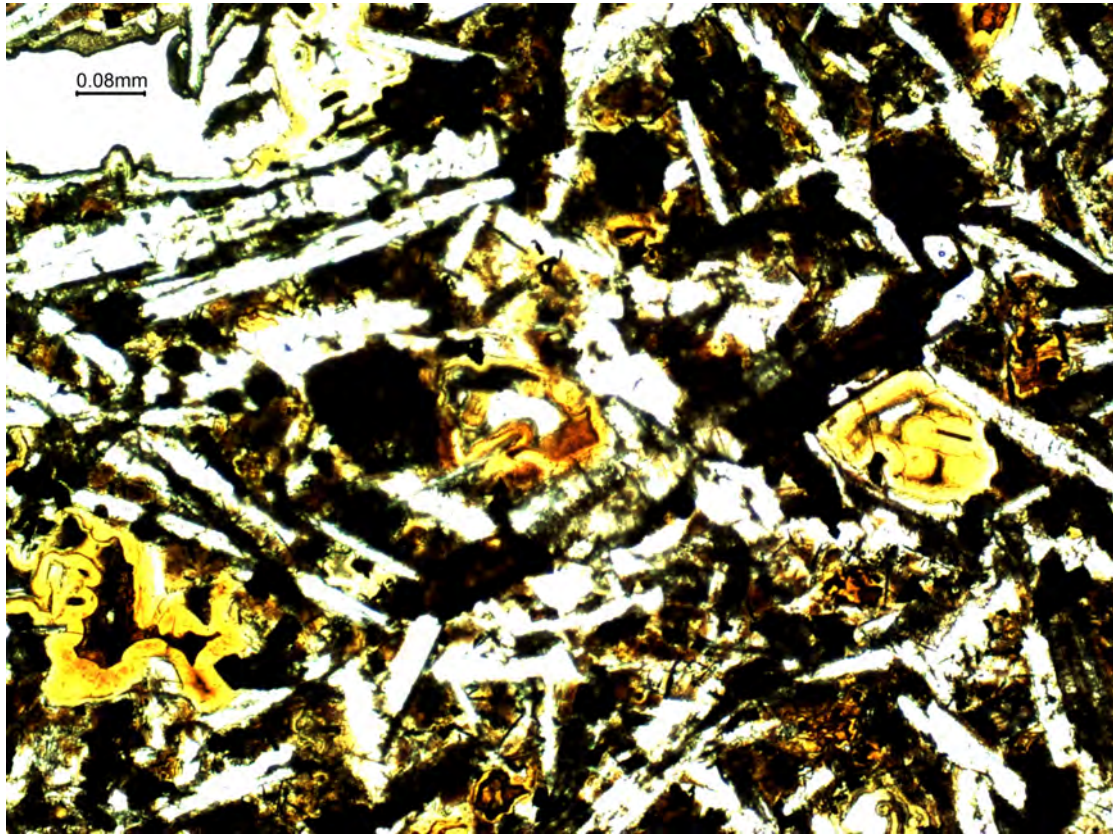


Appendix A 41, hand sample of pillow lava (DTC151207E)

Infoga PP Loch XPL av tunnslip



Appendix A 42, scanned thin section (DTC151207BX, DTC151207EX), PPL and XPL



Appendix A 43, clay and Fe-oxide filled vesicles surrounded by plagioclase laths and oxides, PPL



Appendix A 44, plagioclase laths in a mesostasis of clays and oxides

**Theotokos Monastery, DTC151208, coordinates N35°00'24.7 / E33°16'09.8 to
N35°00'27.5 / E33°16'11.5**

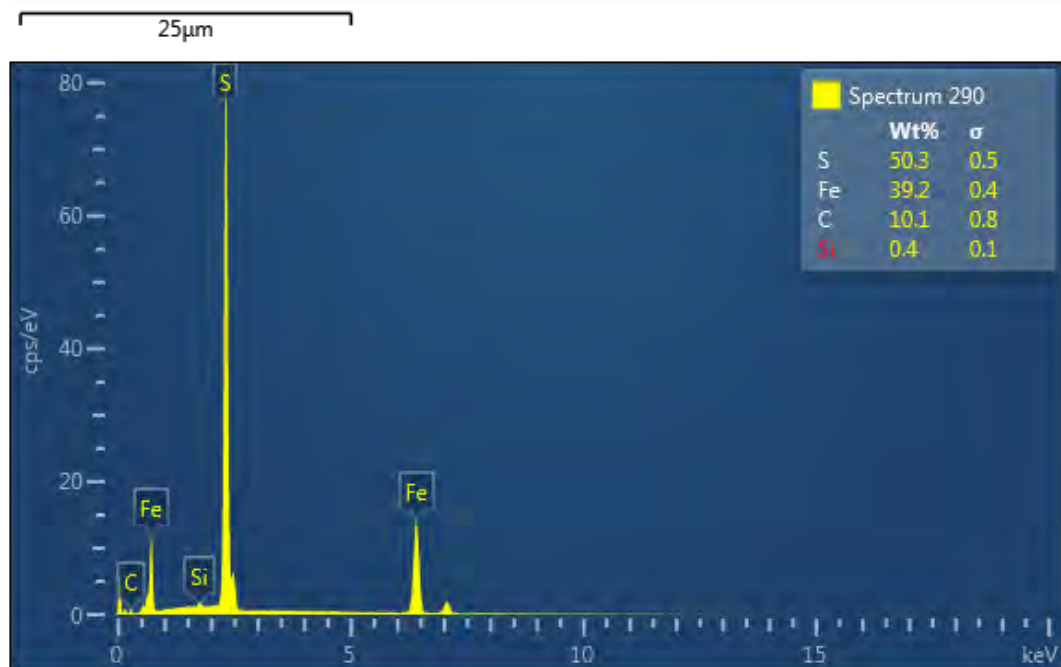
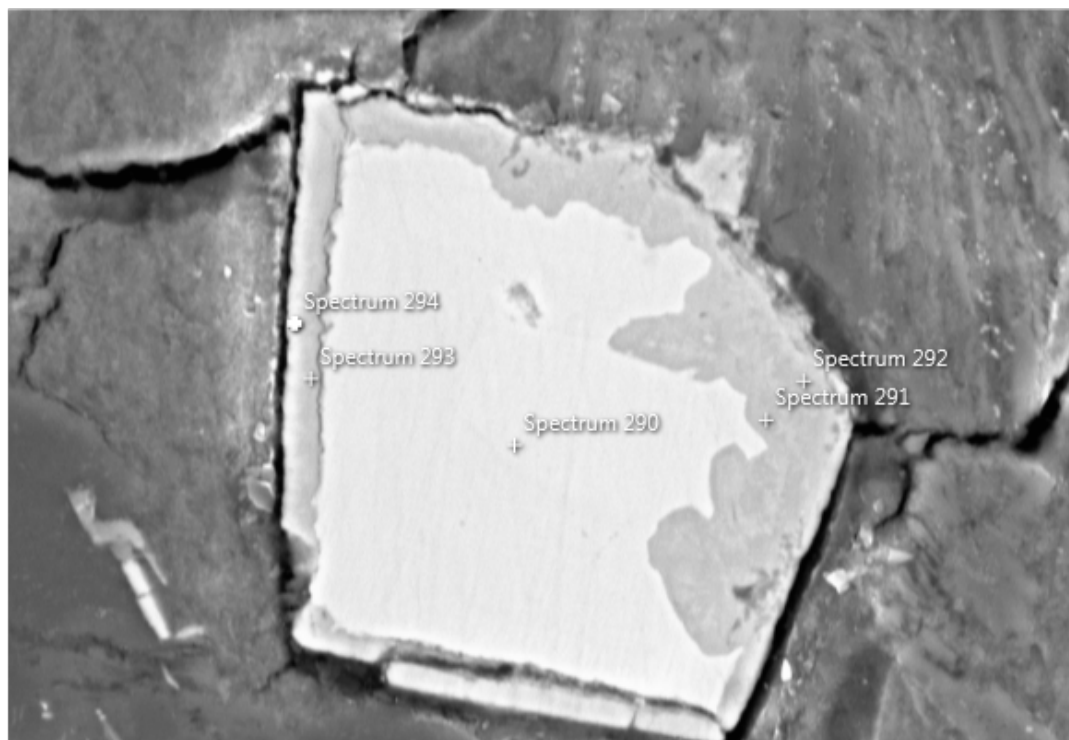


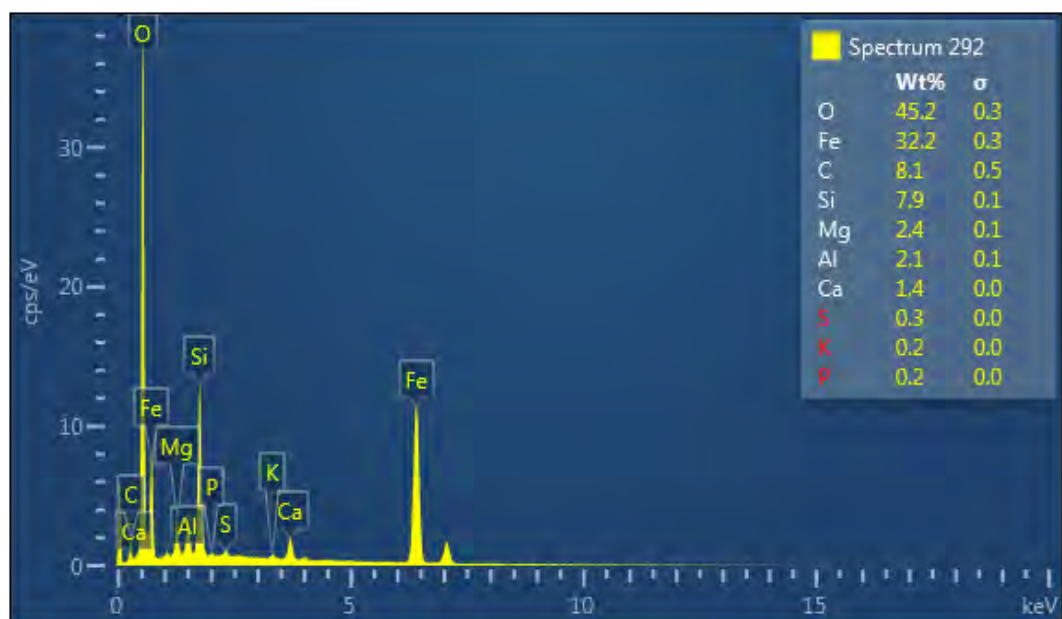
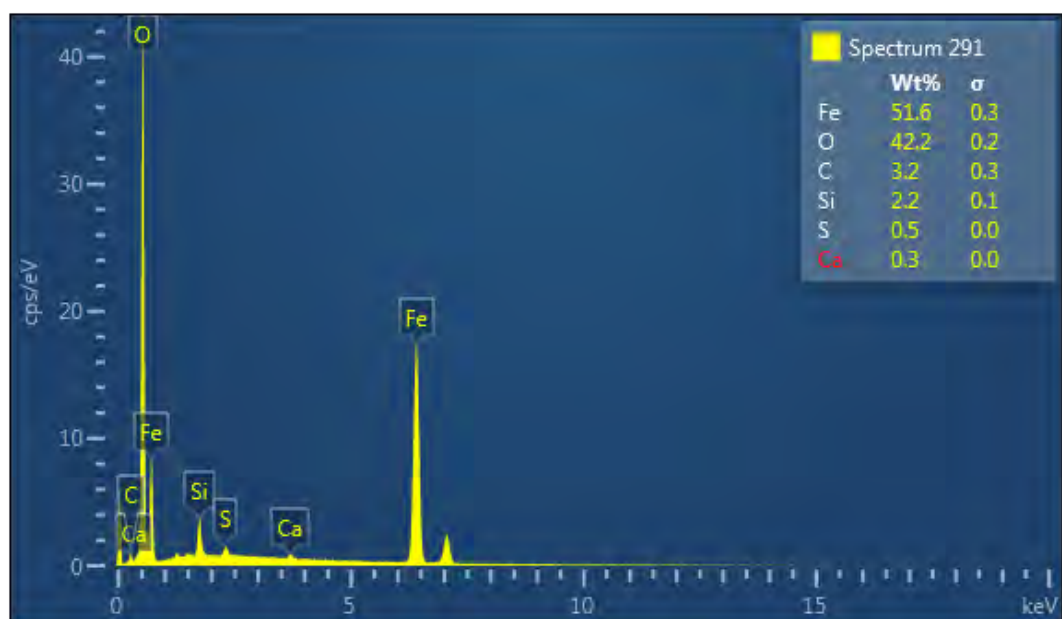
Appendix A 45, hand sample of umber (DTC151208A)

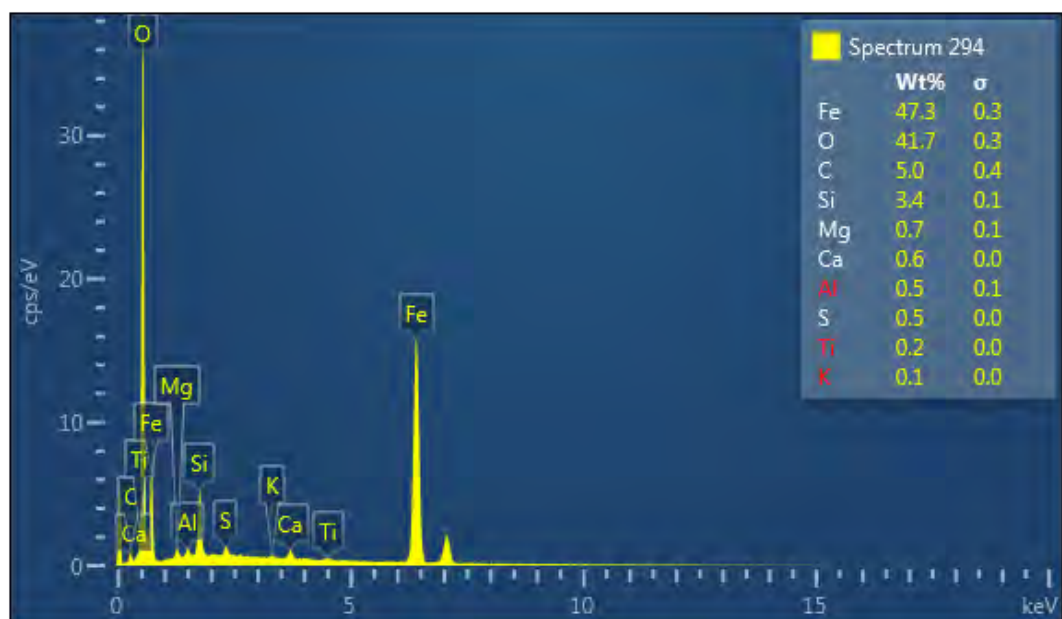
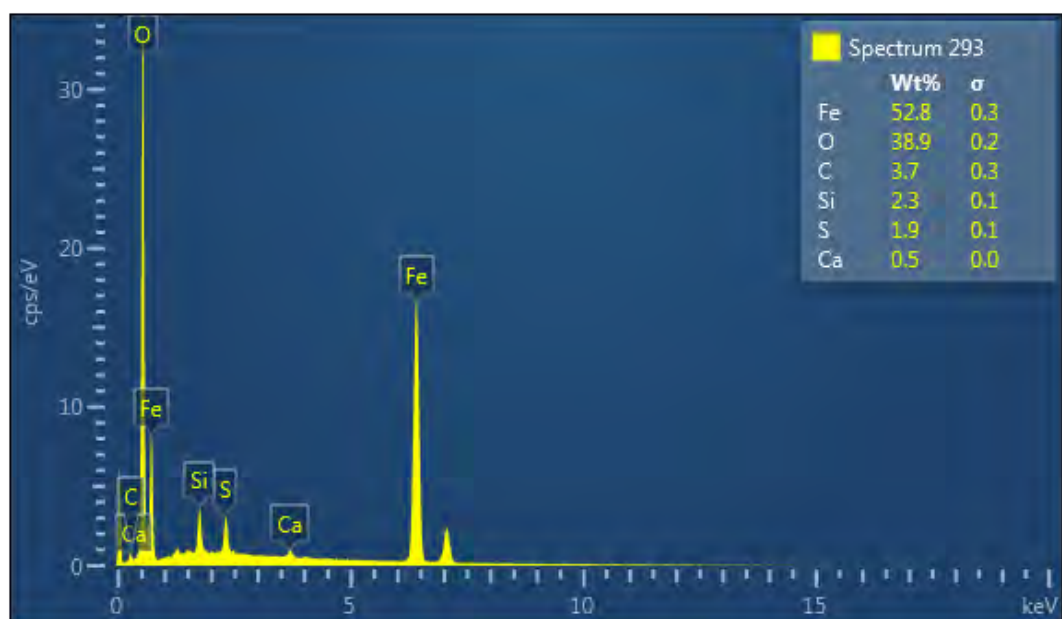
Appendix B: ESEM data

B1

Electron Image 60

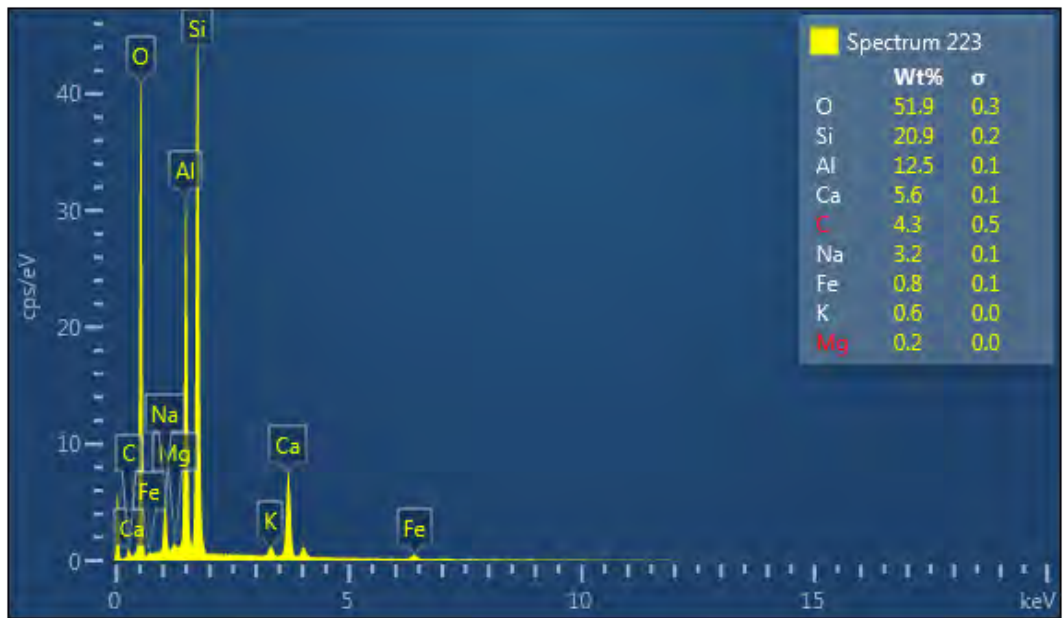
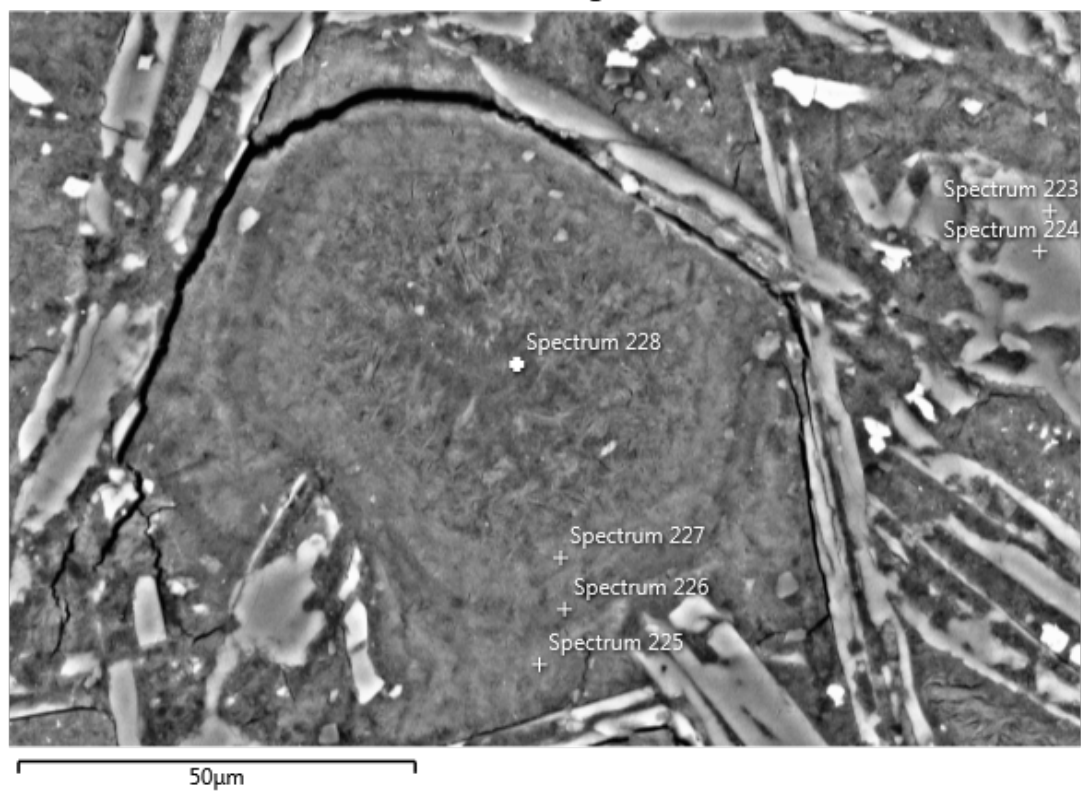


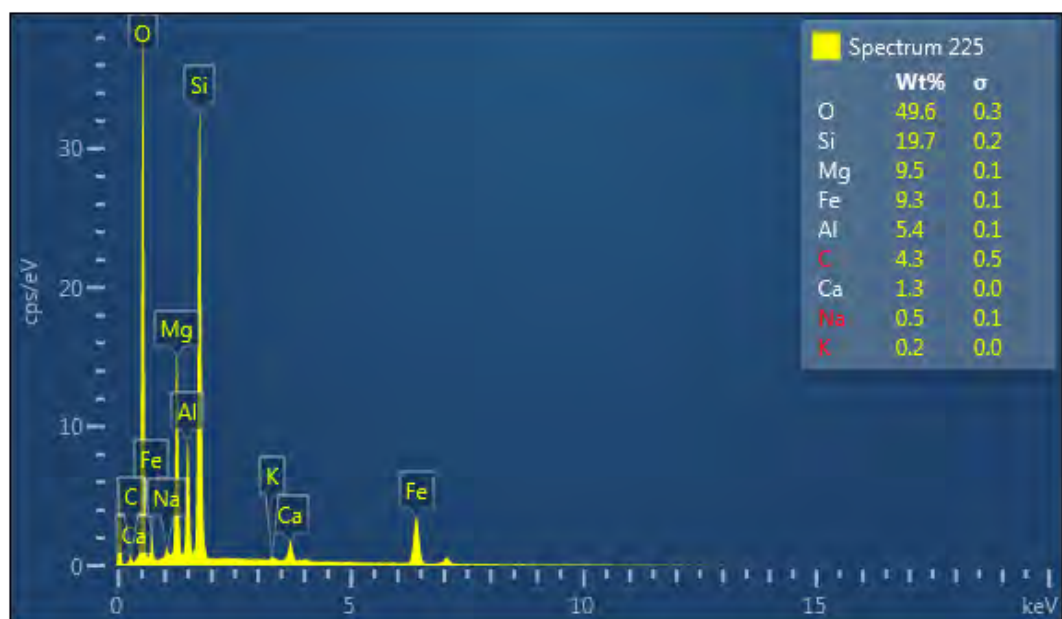
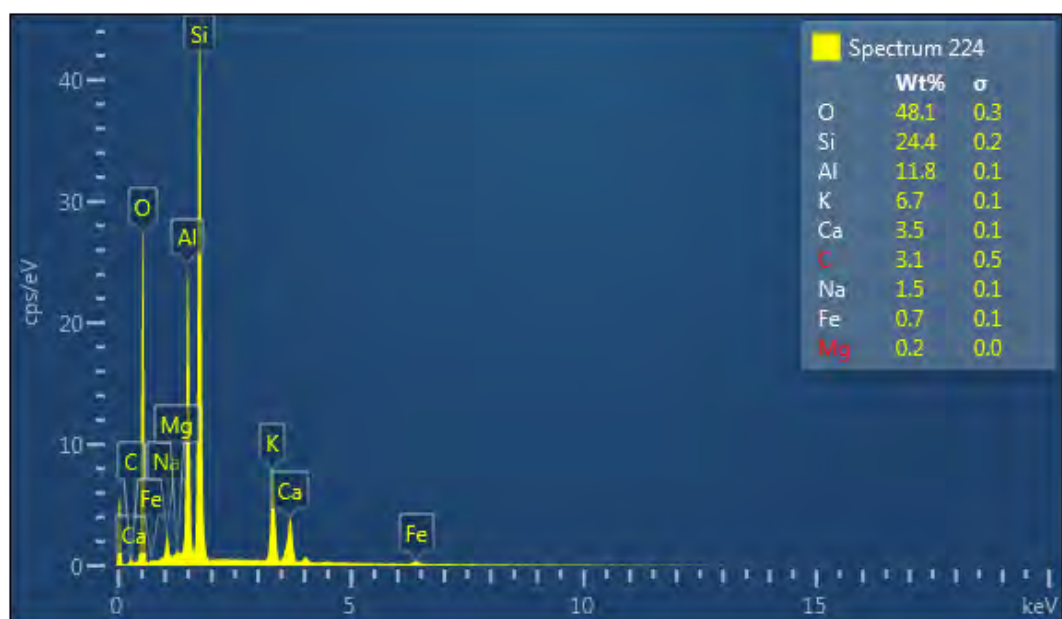


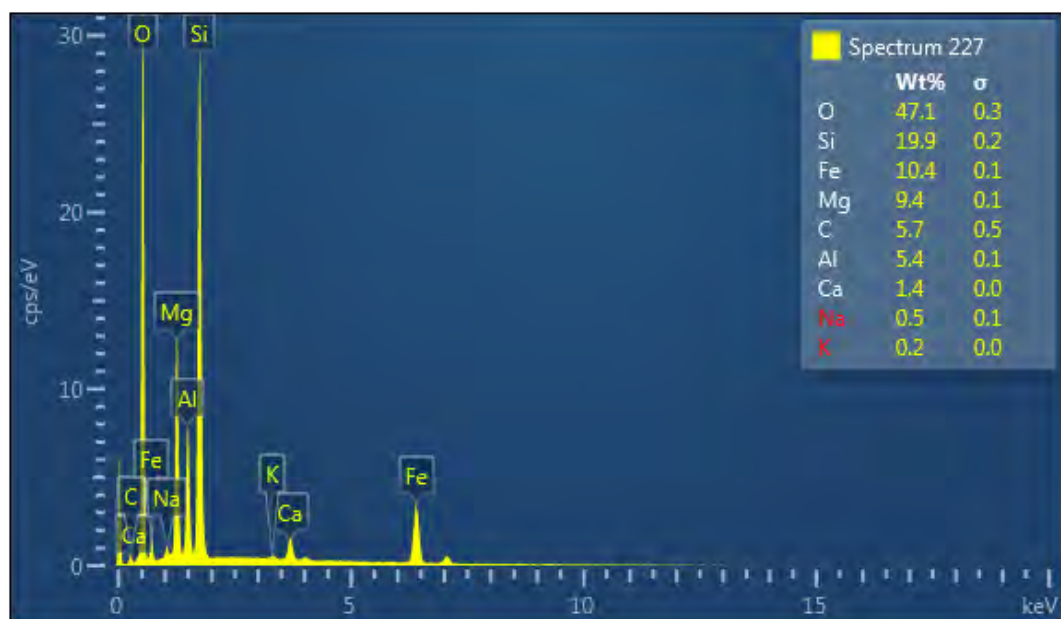
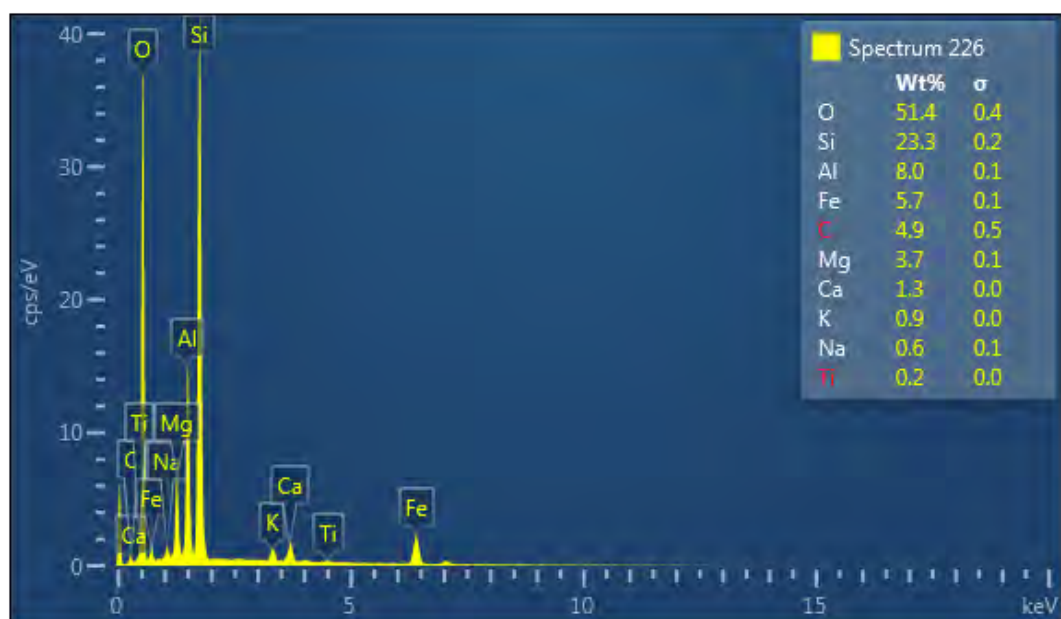


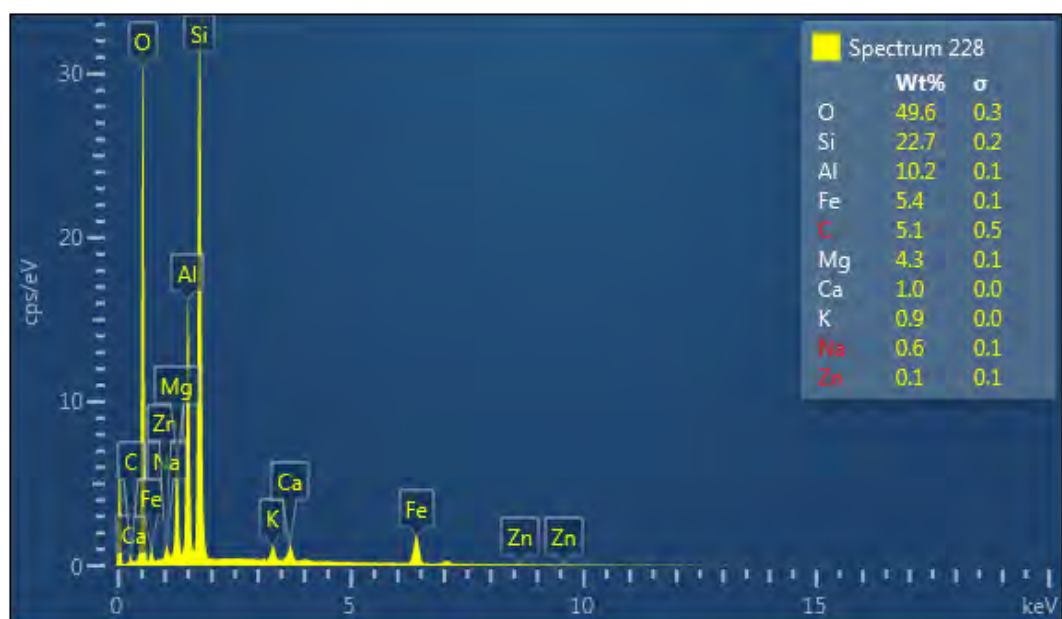
B2

Electron Image 49



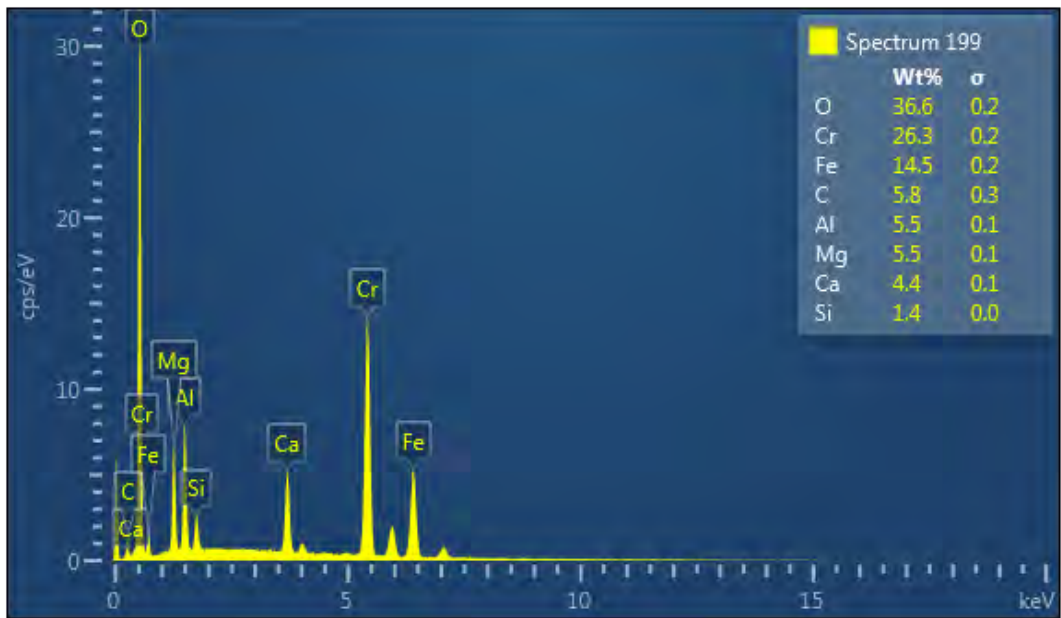
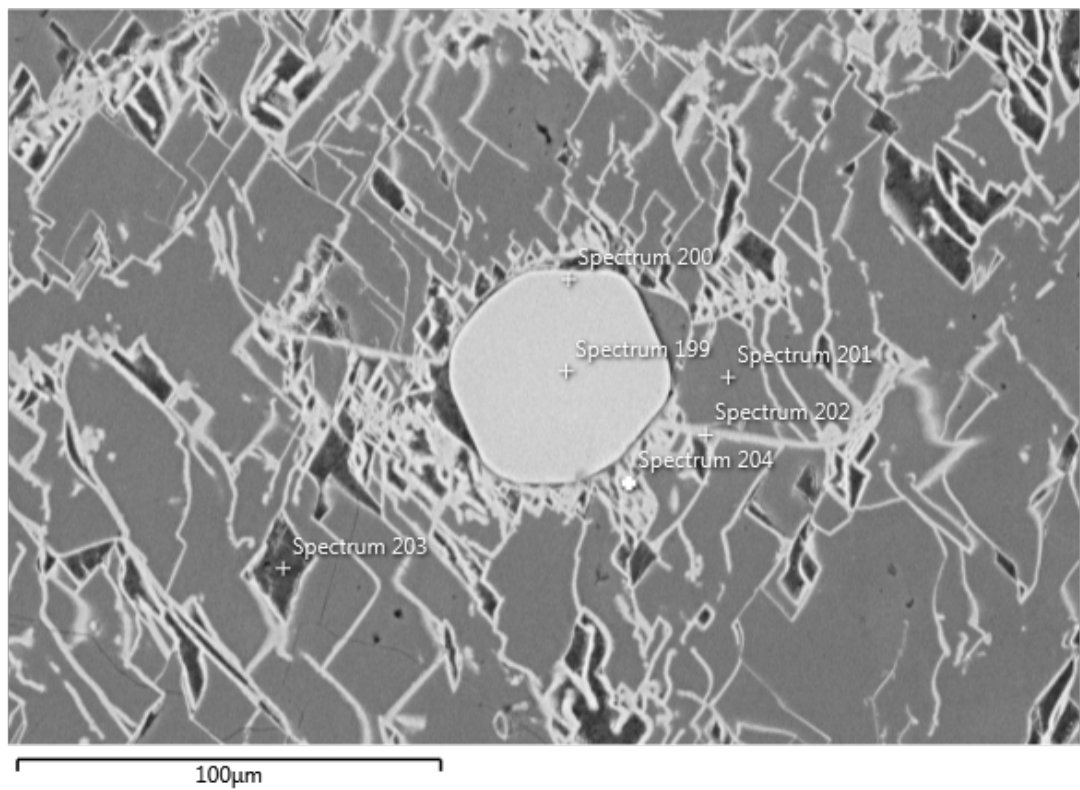


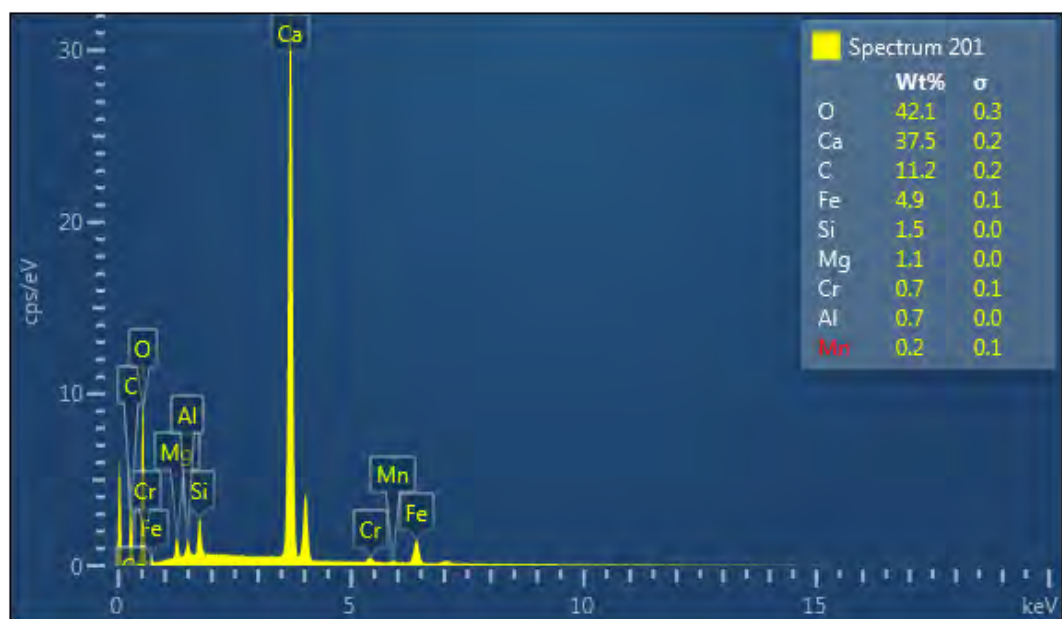
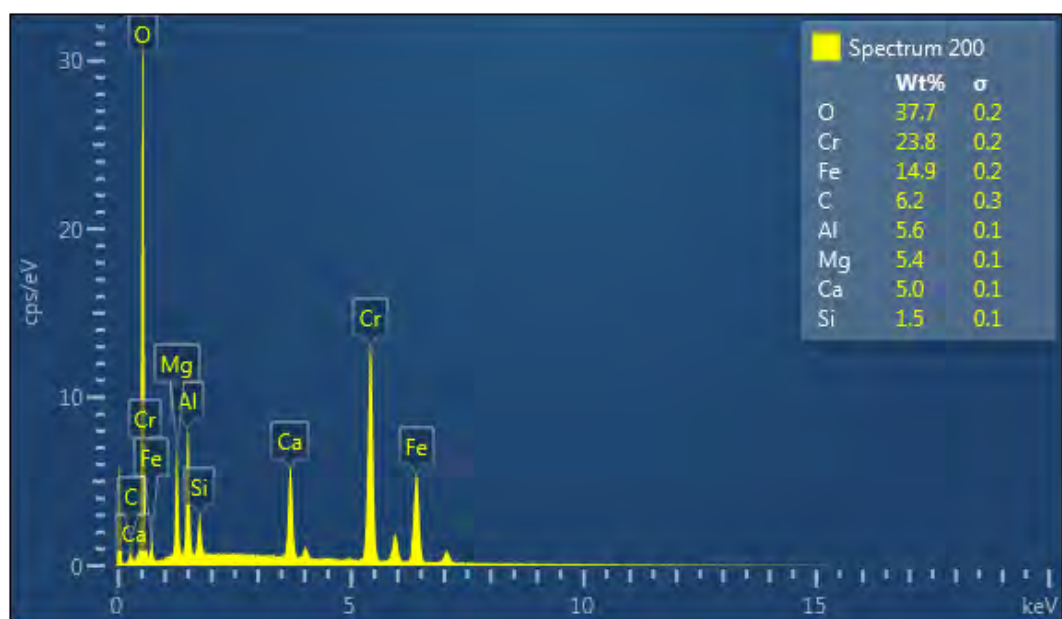


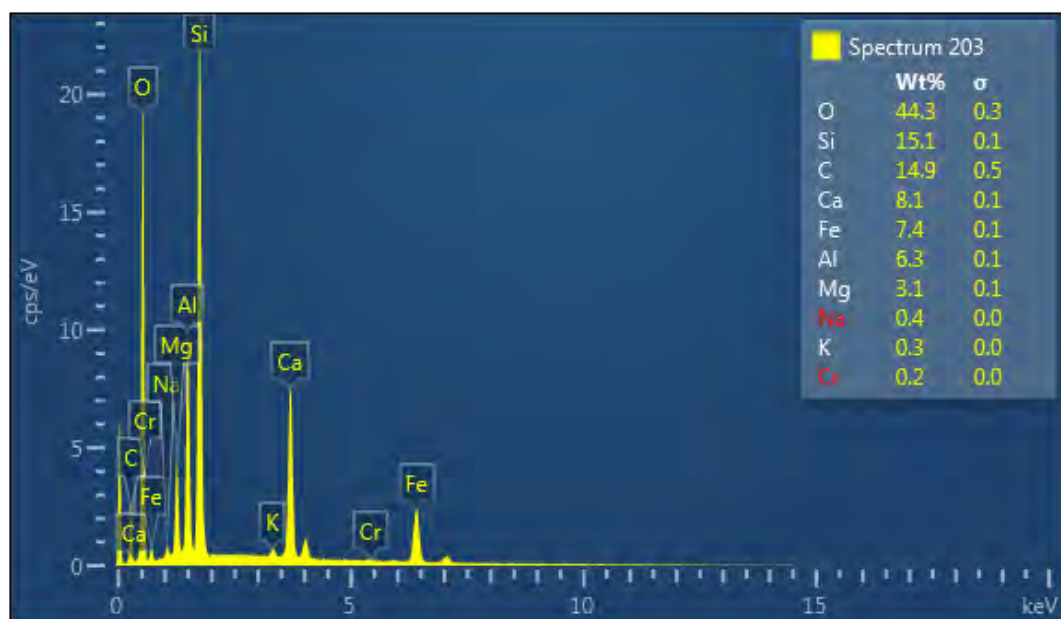
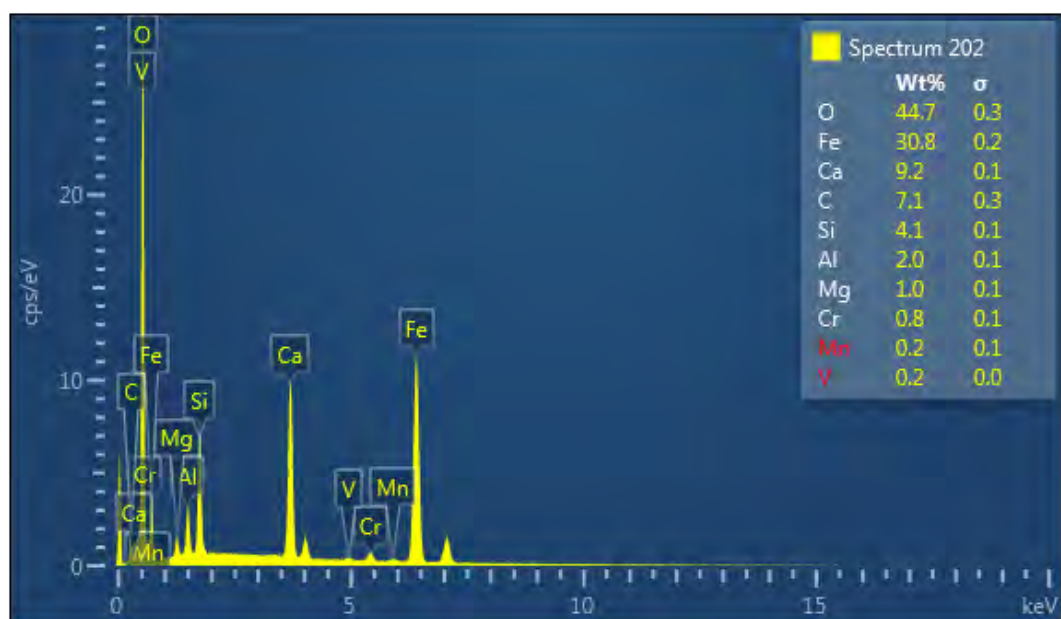


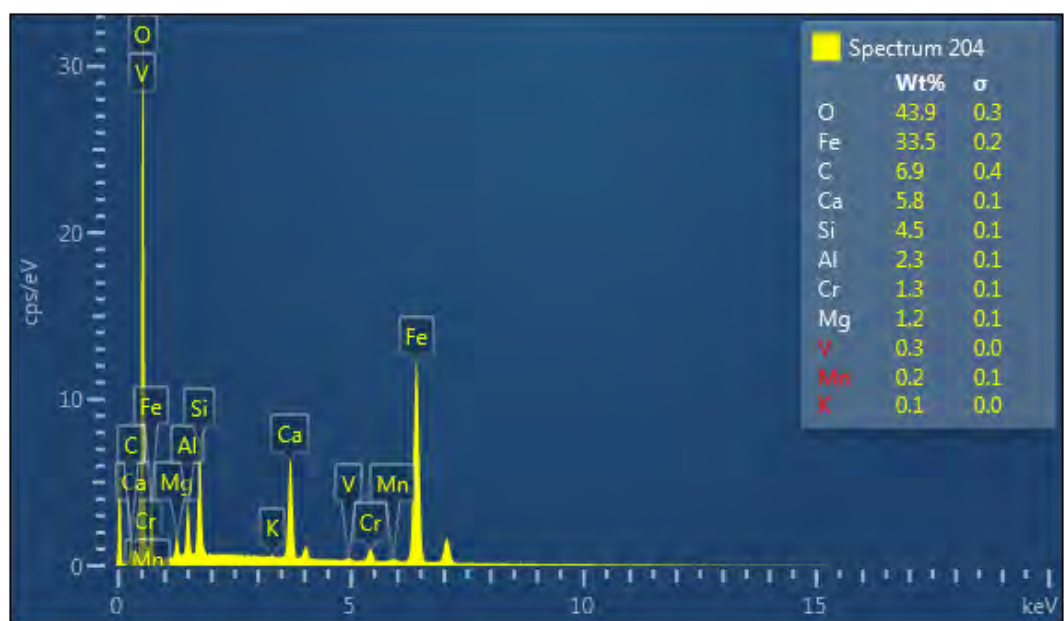
B3

Electron Image 45



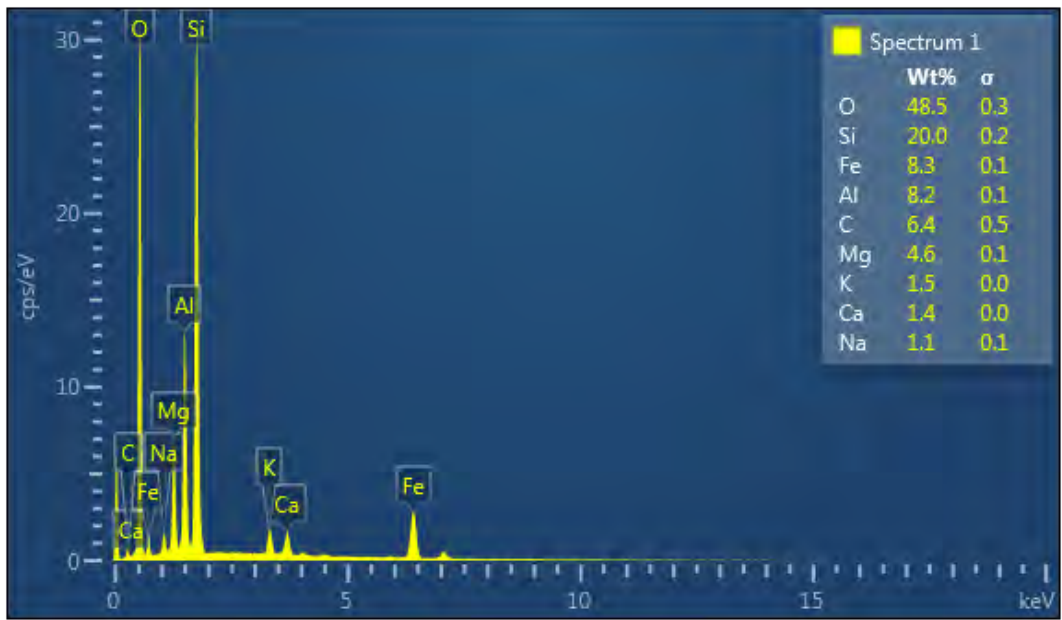


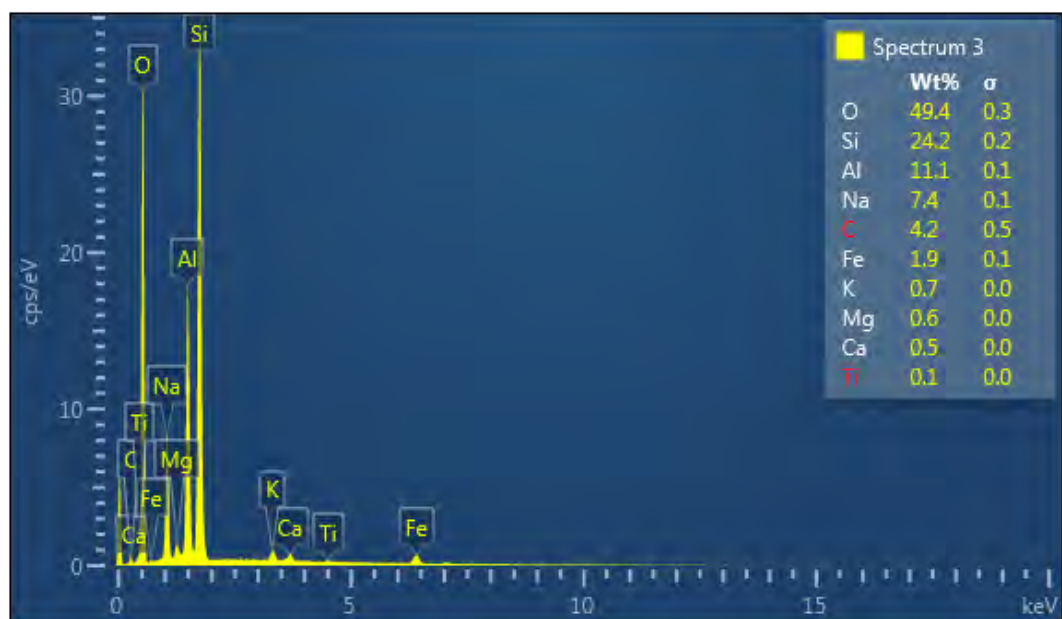
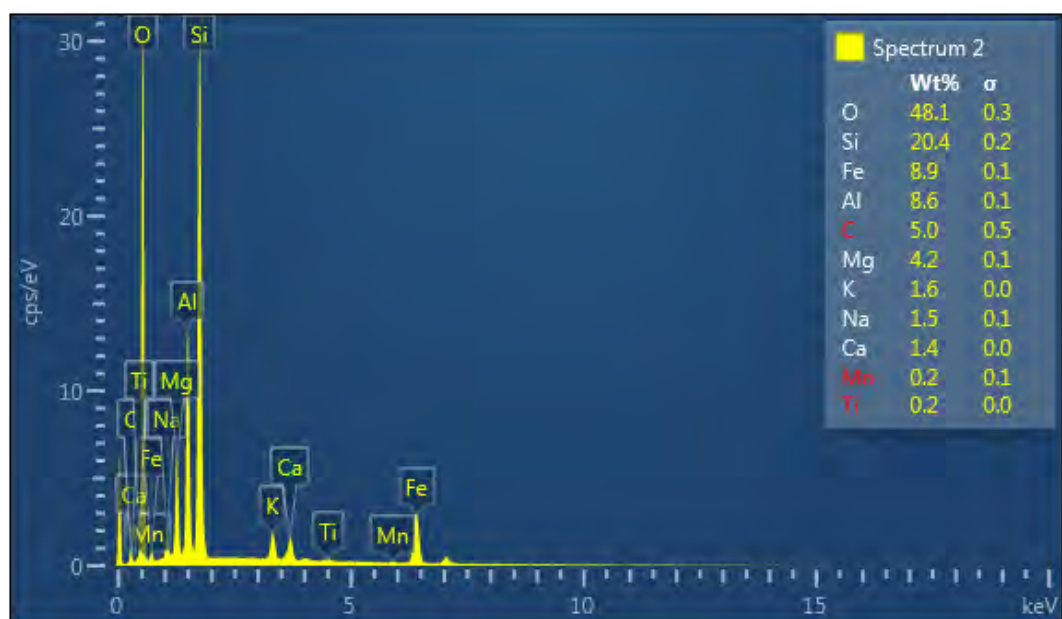


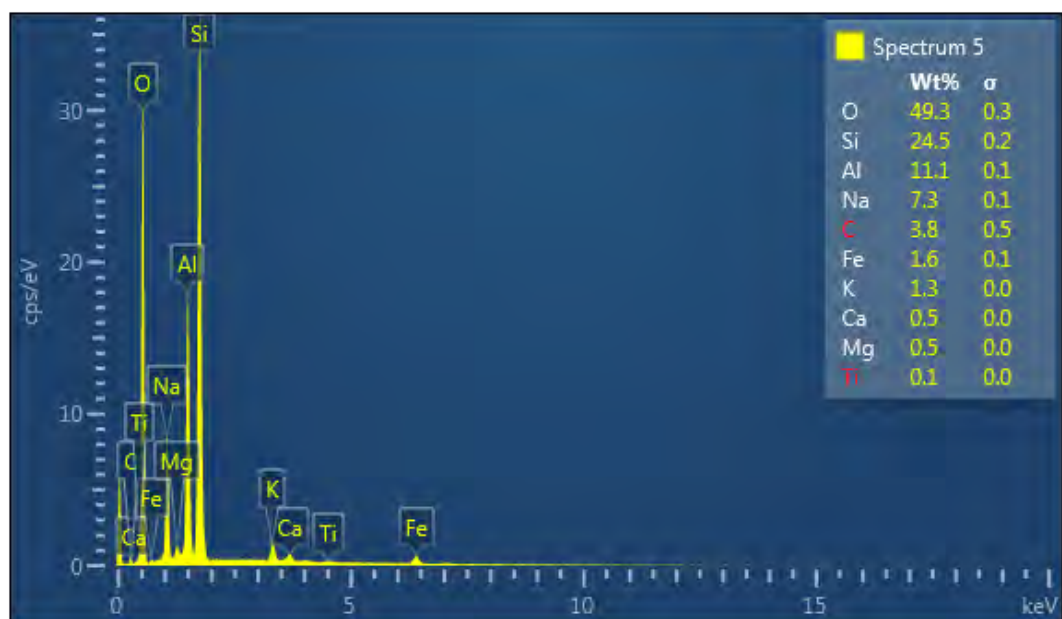
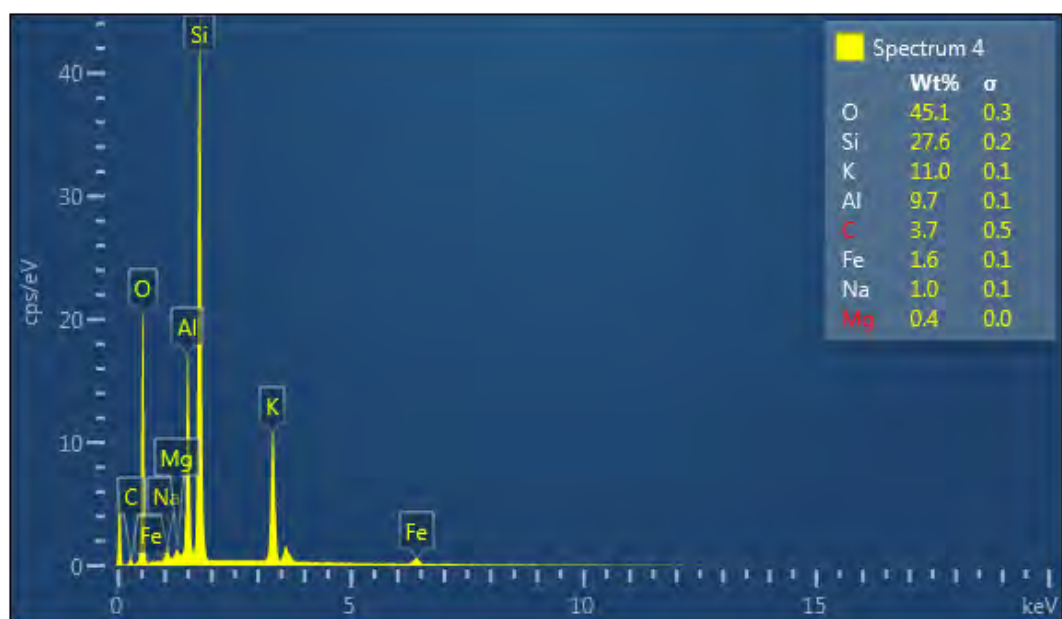


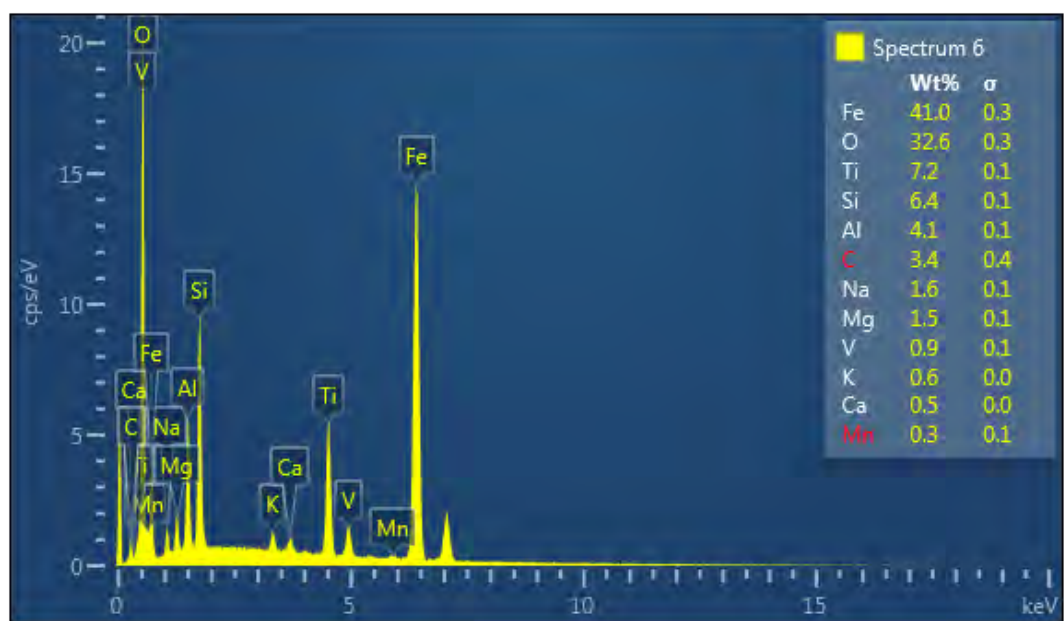
B4

DTC151207Ba

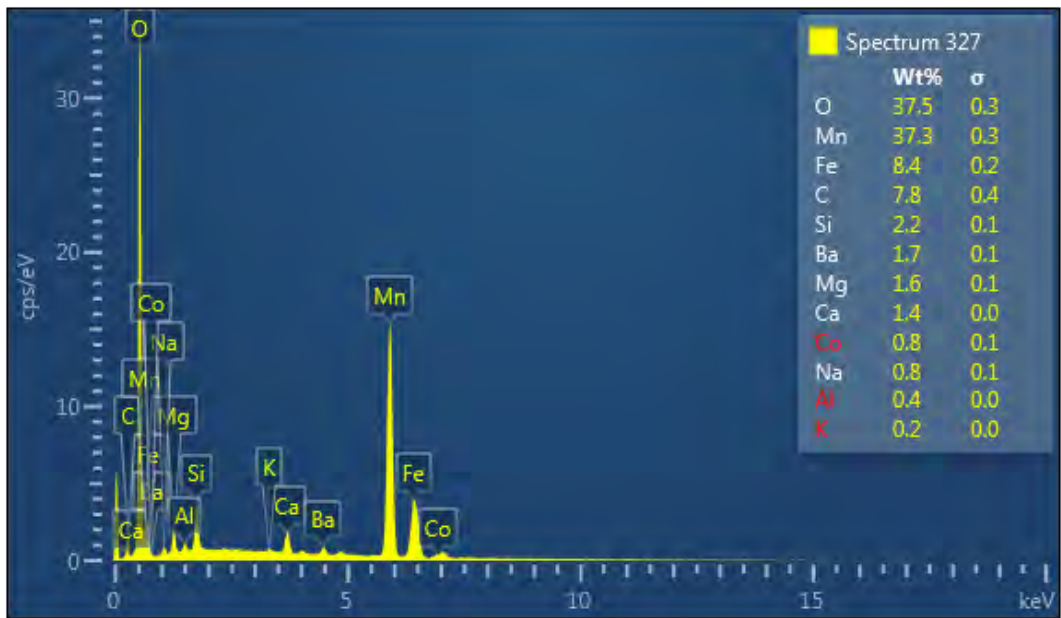
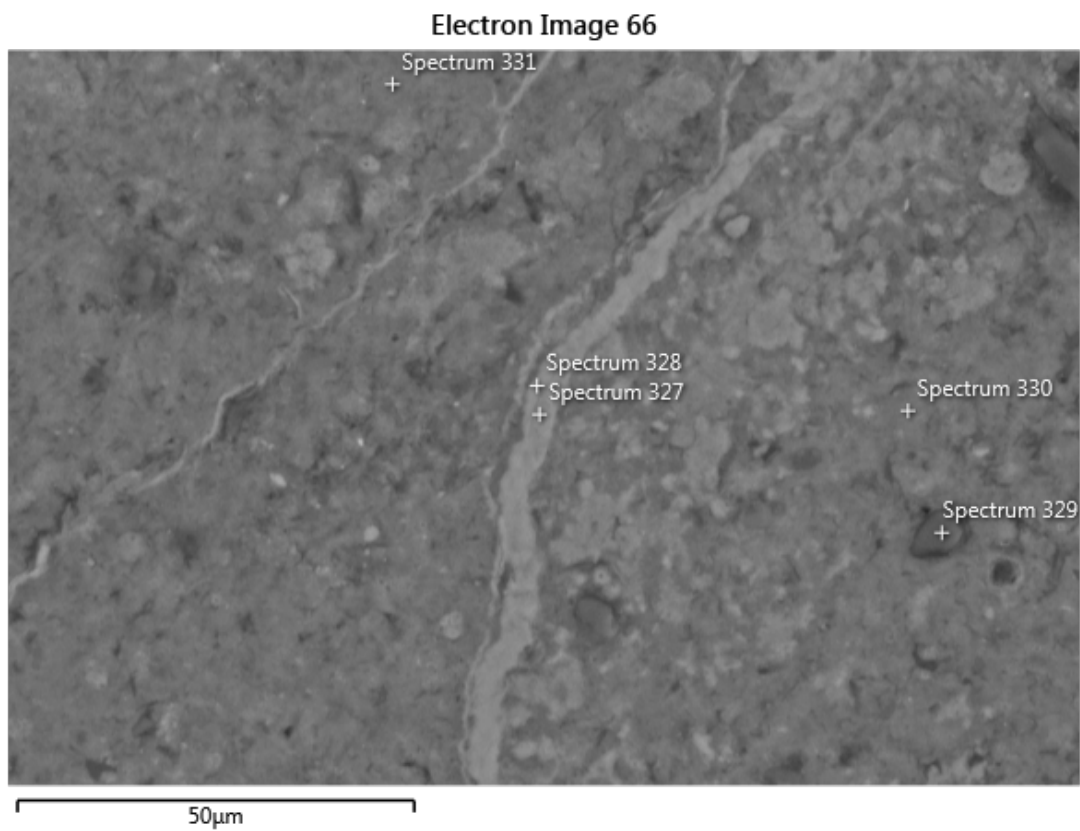


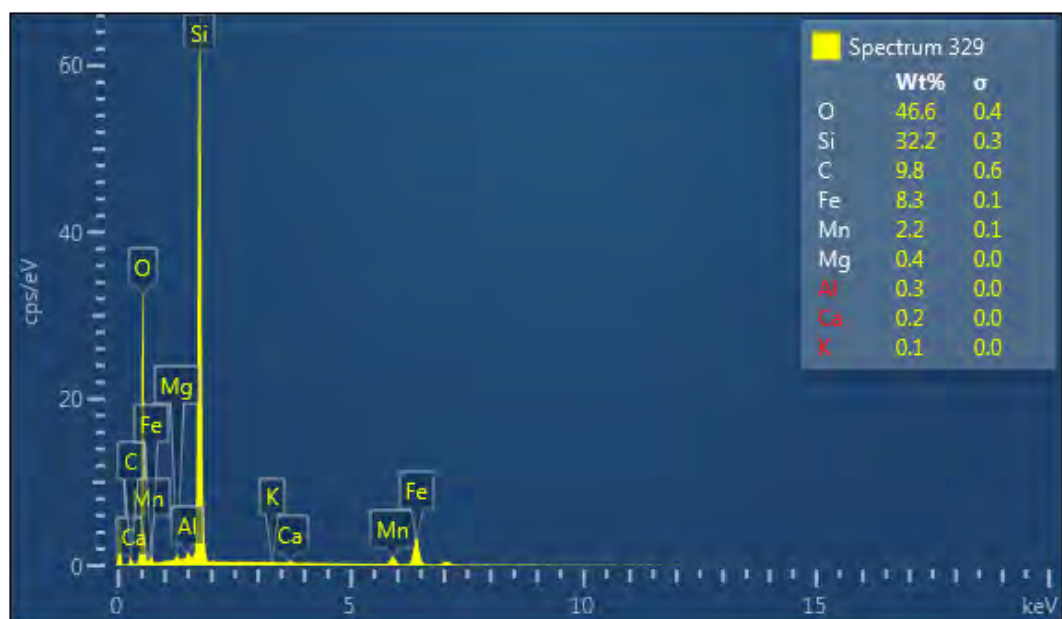
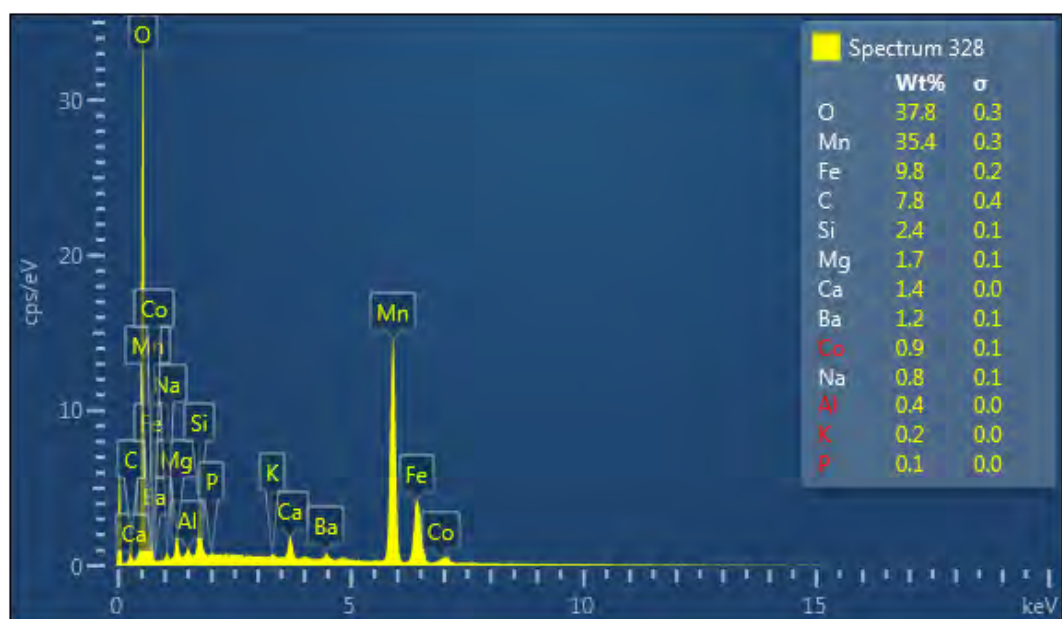


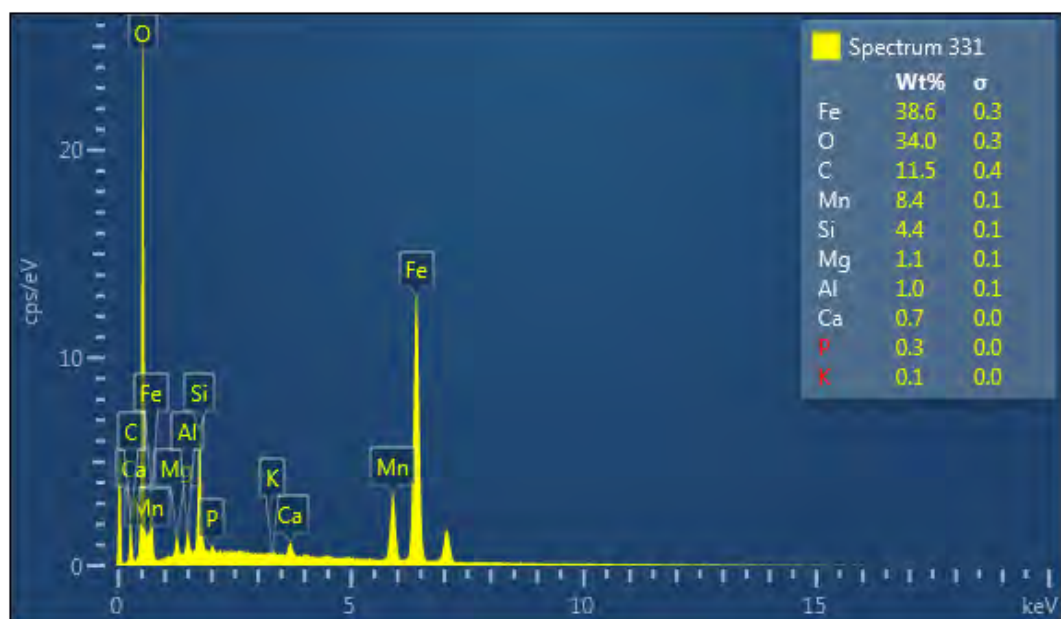
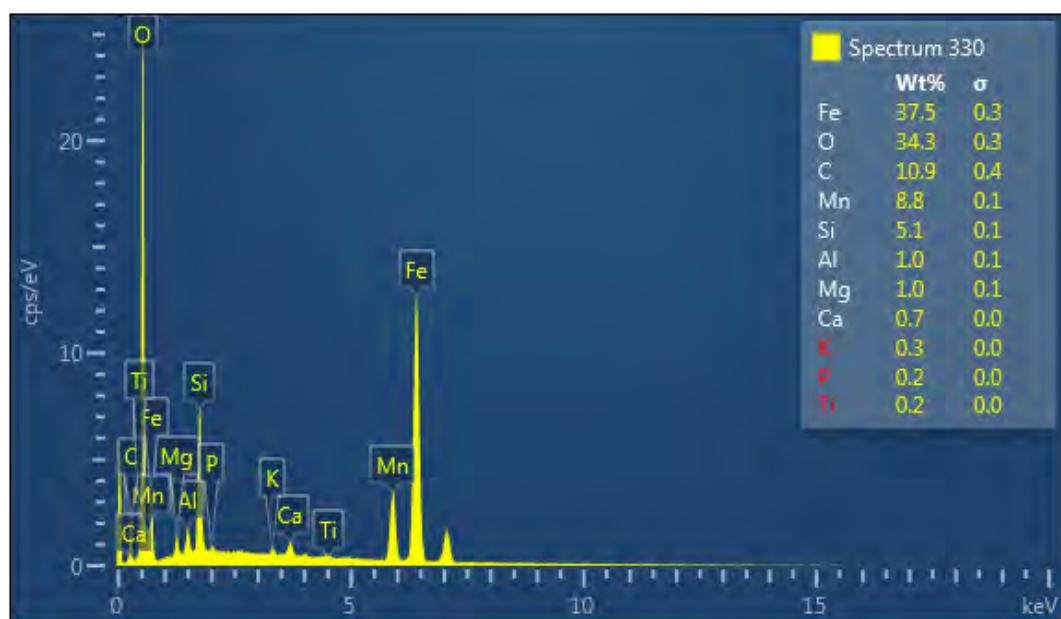




B5

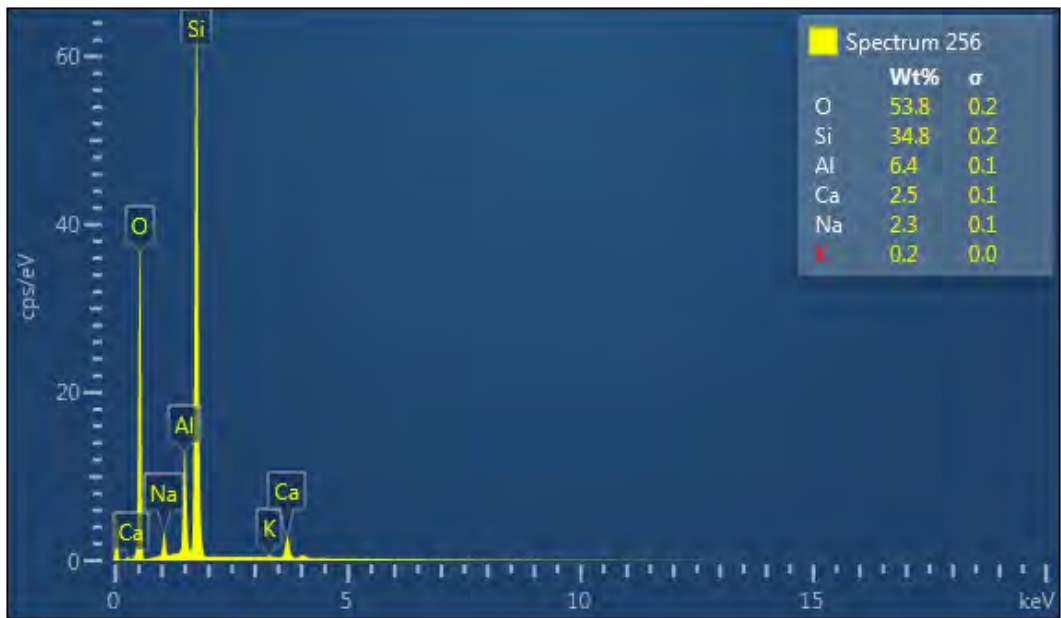
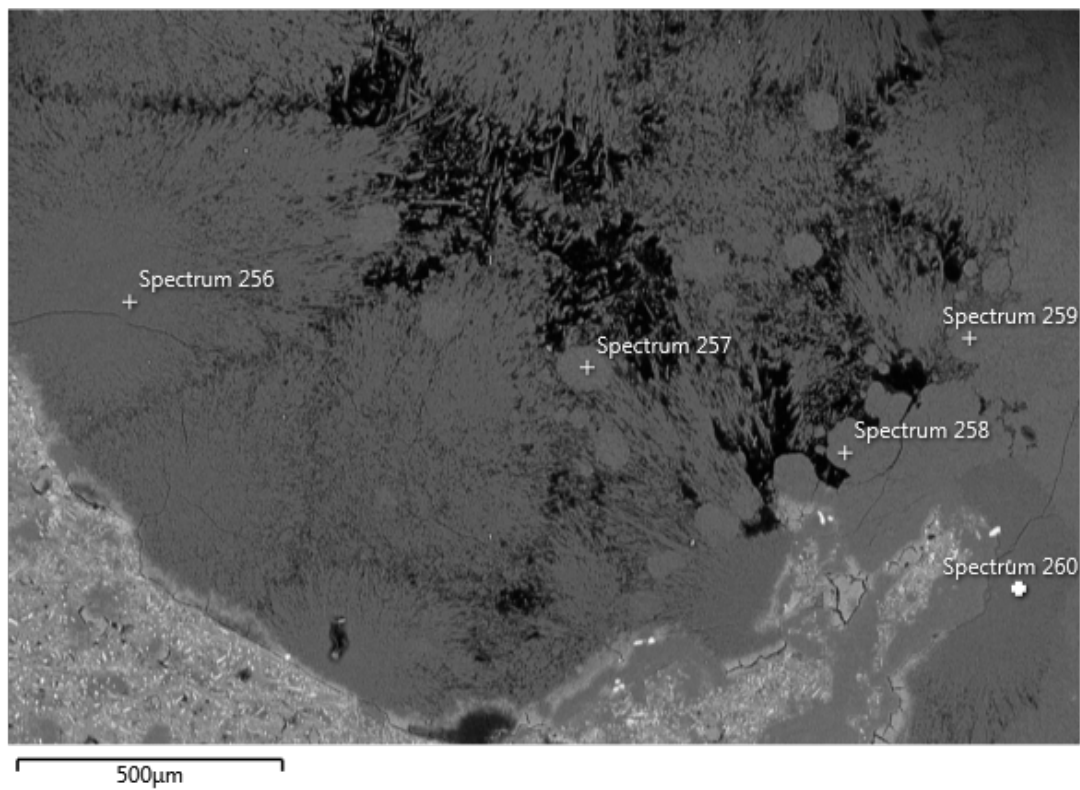


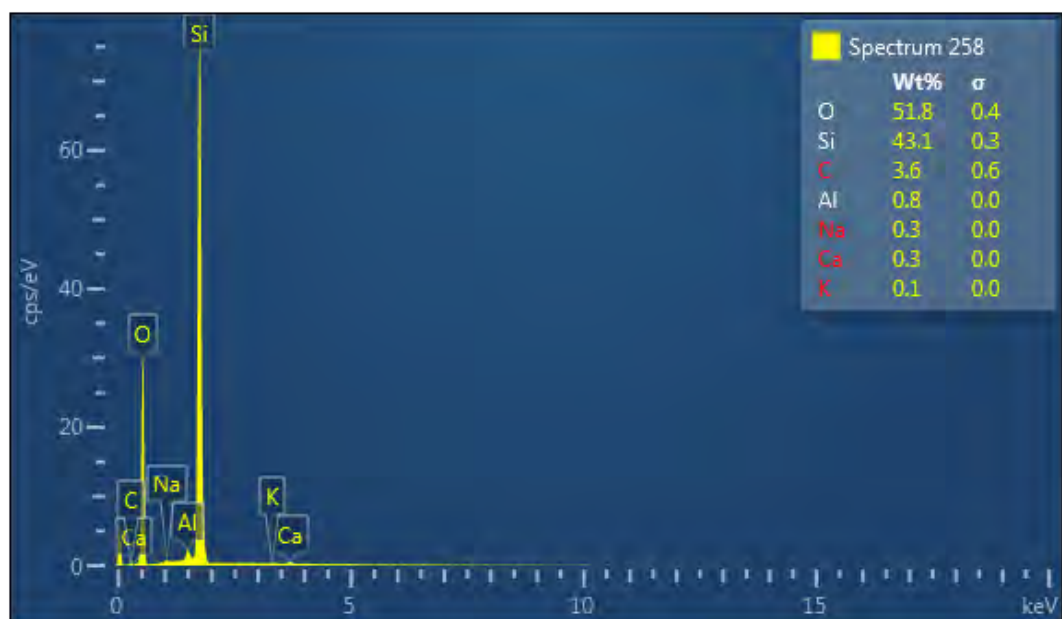
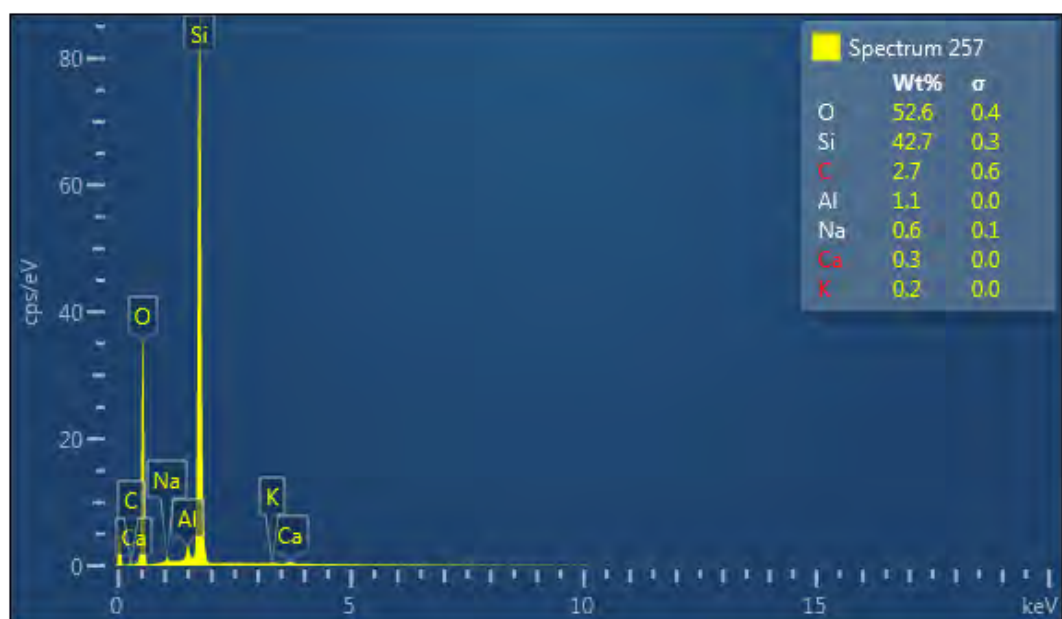


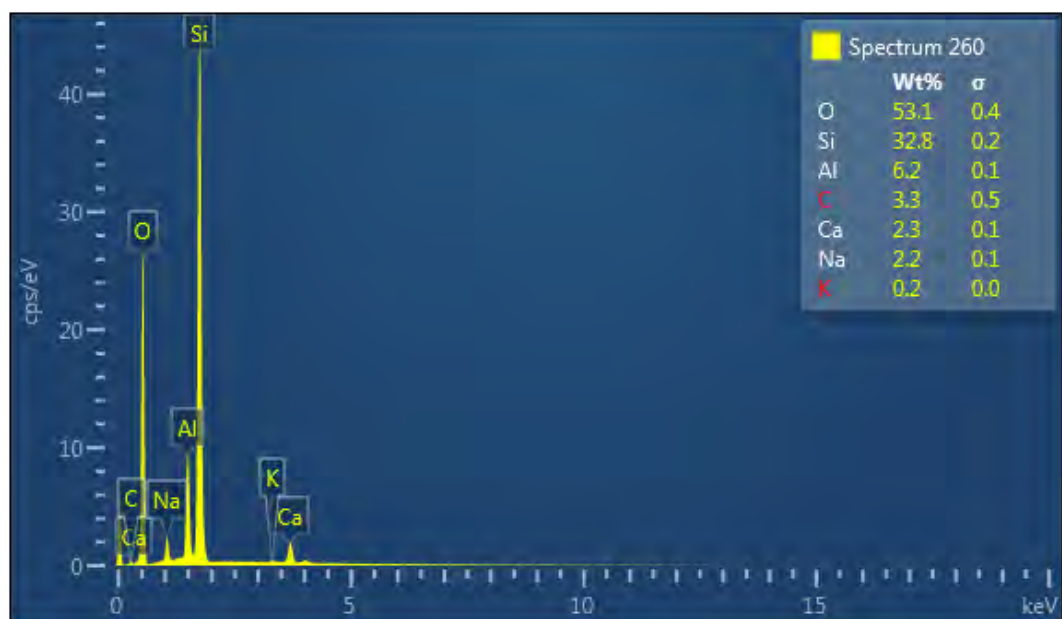
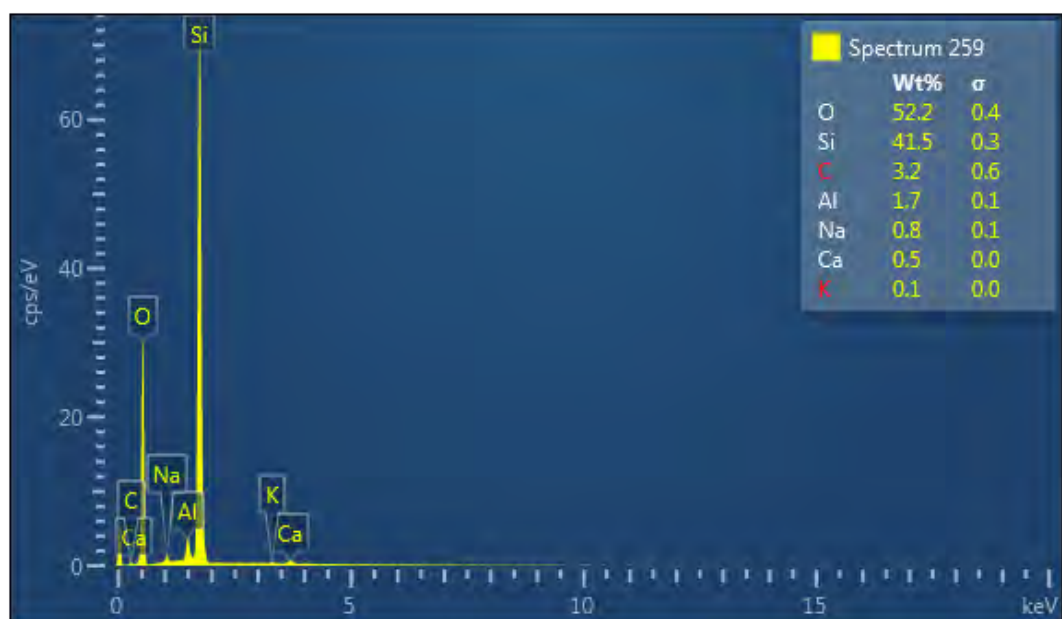


B6

Electron Image 53

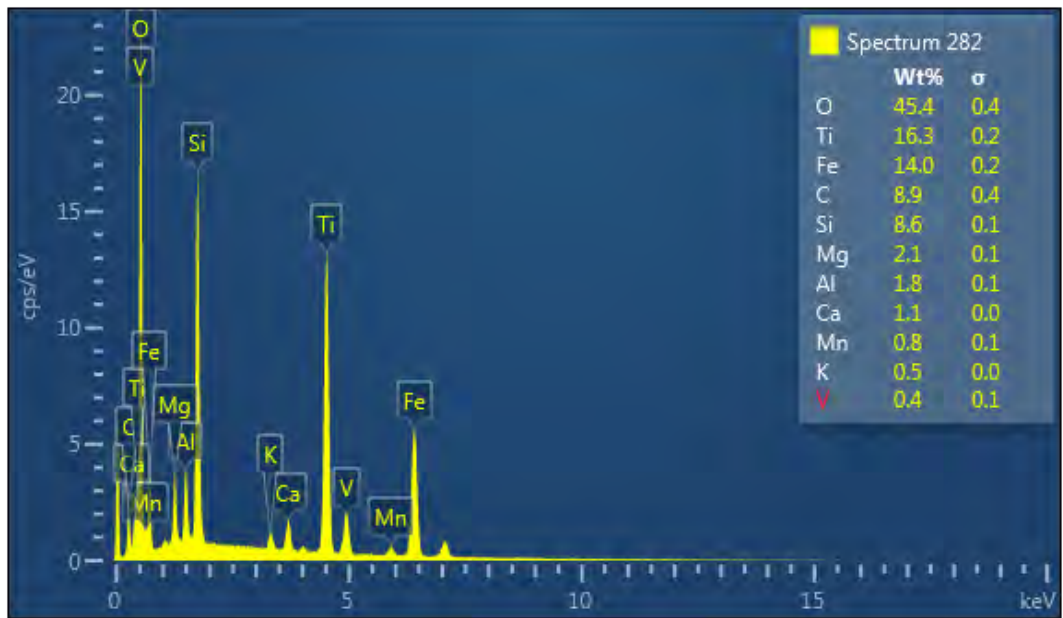
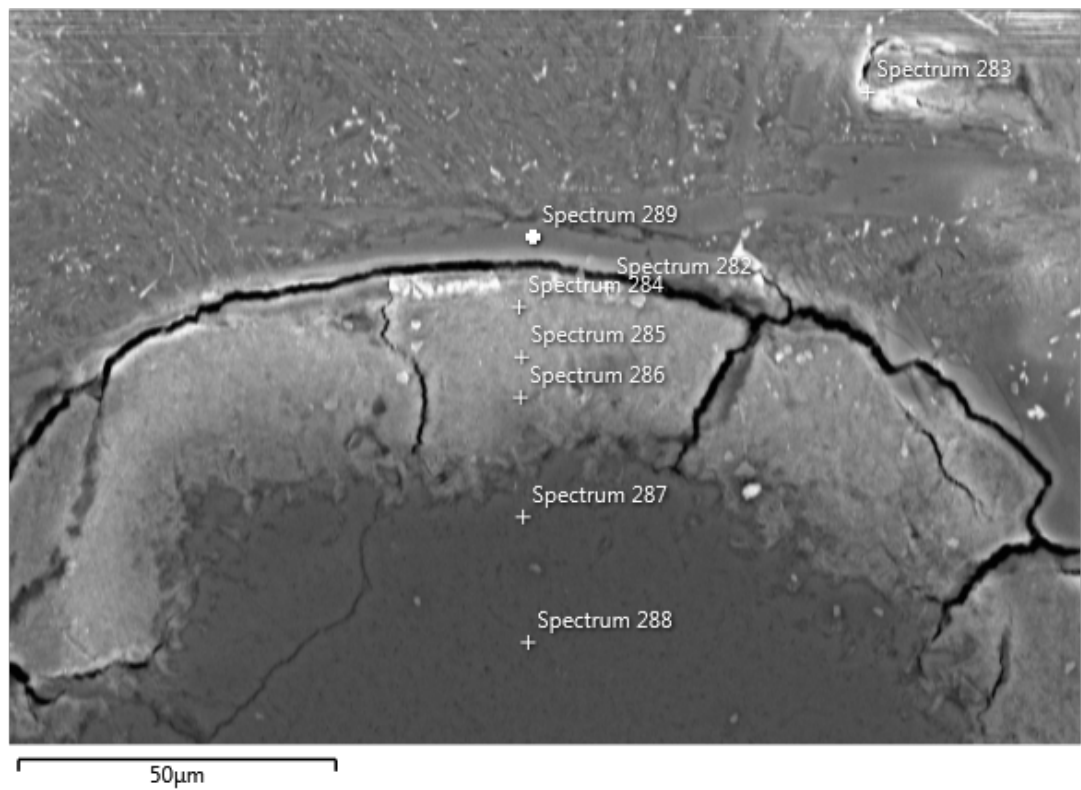


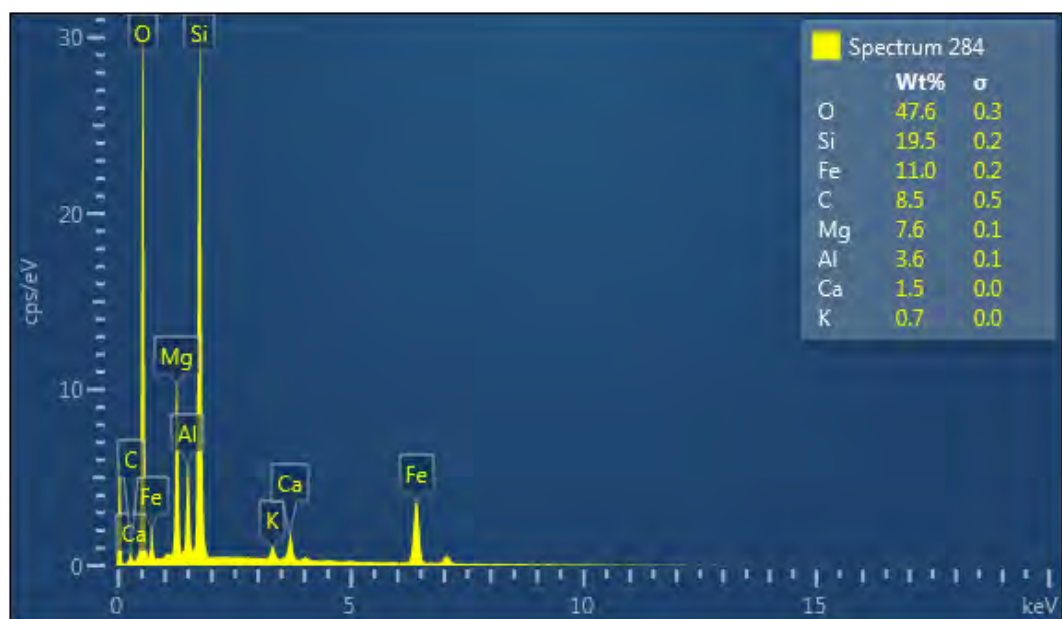
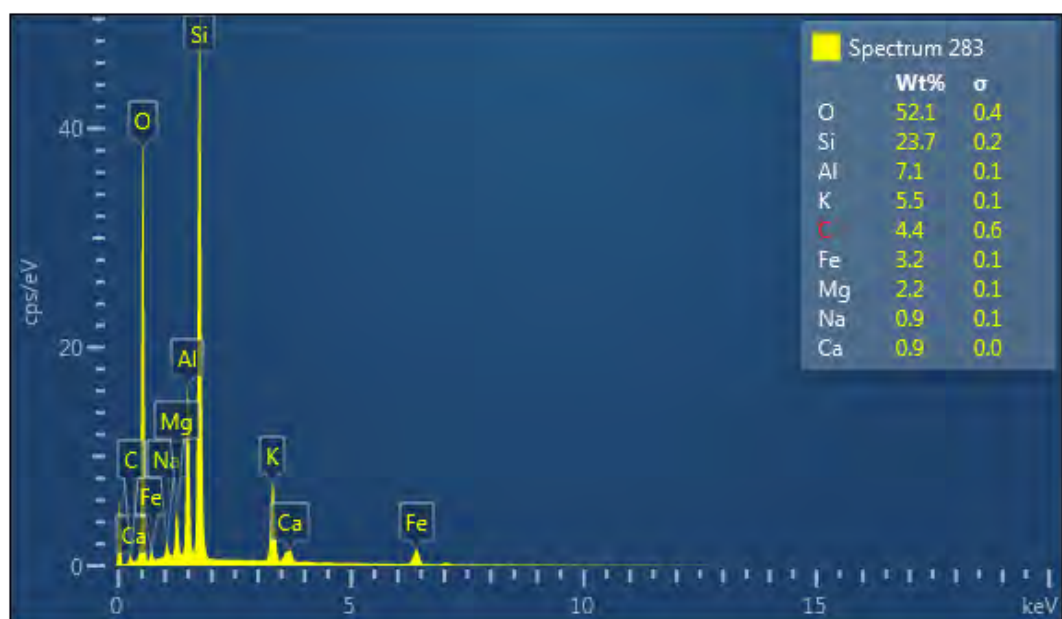


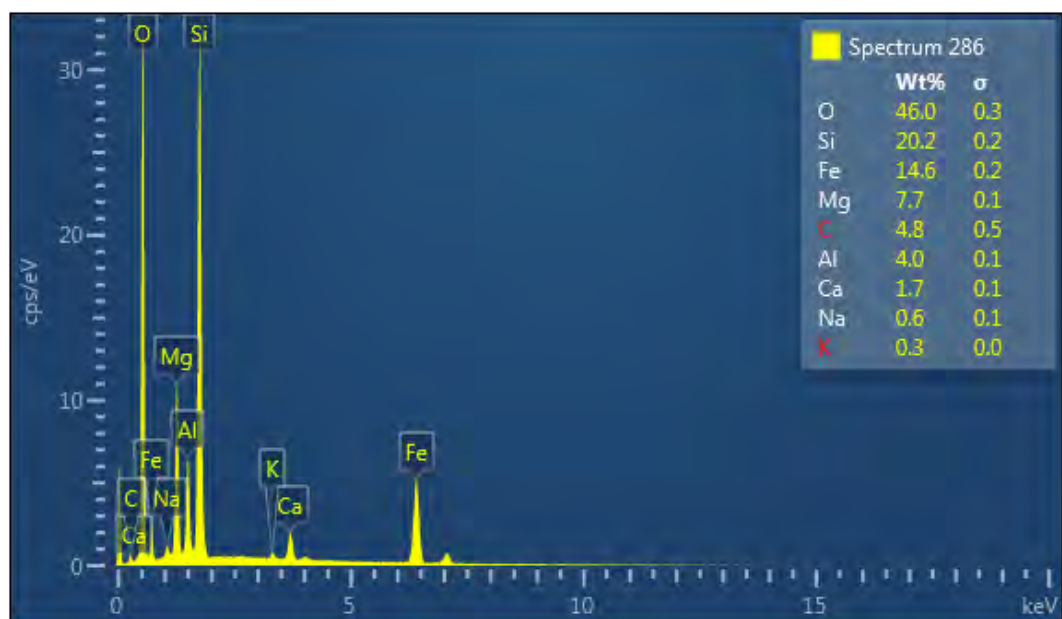
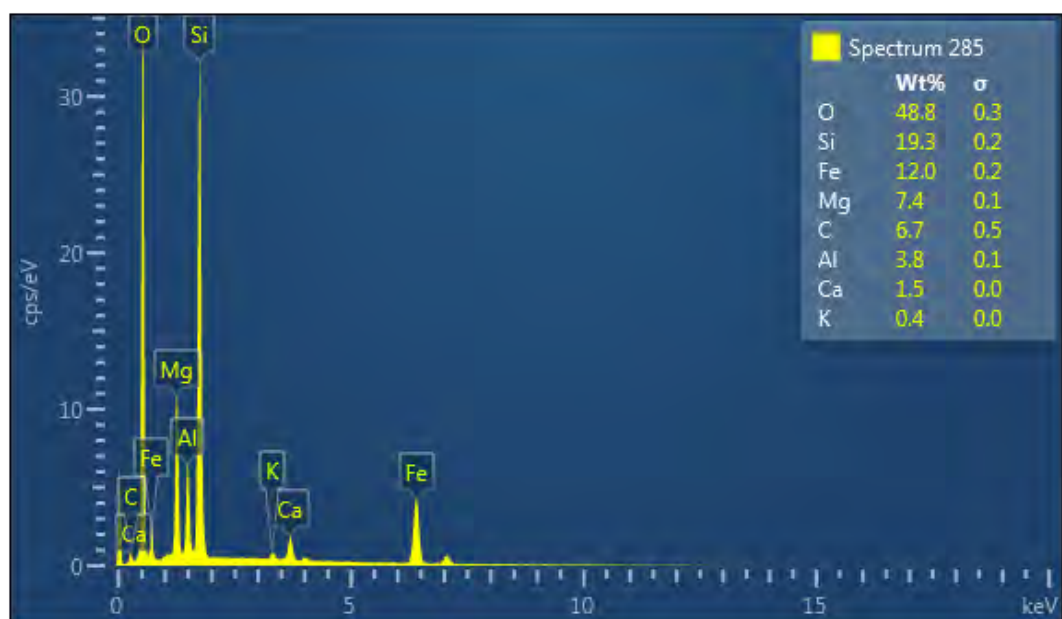


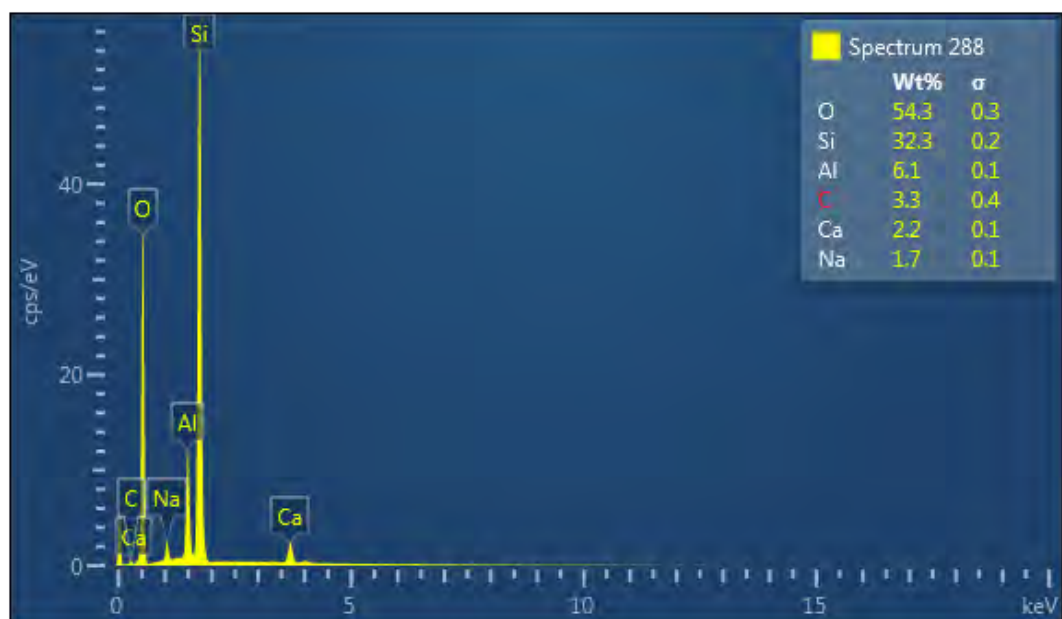
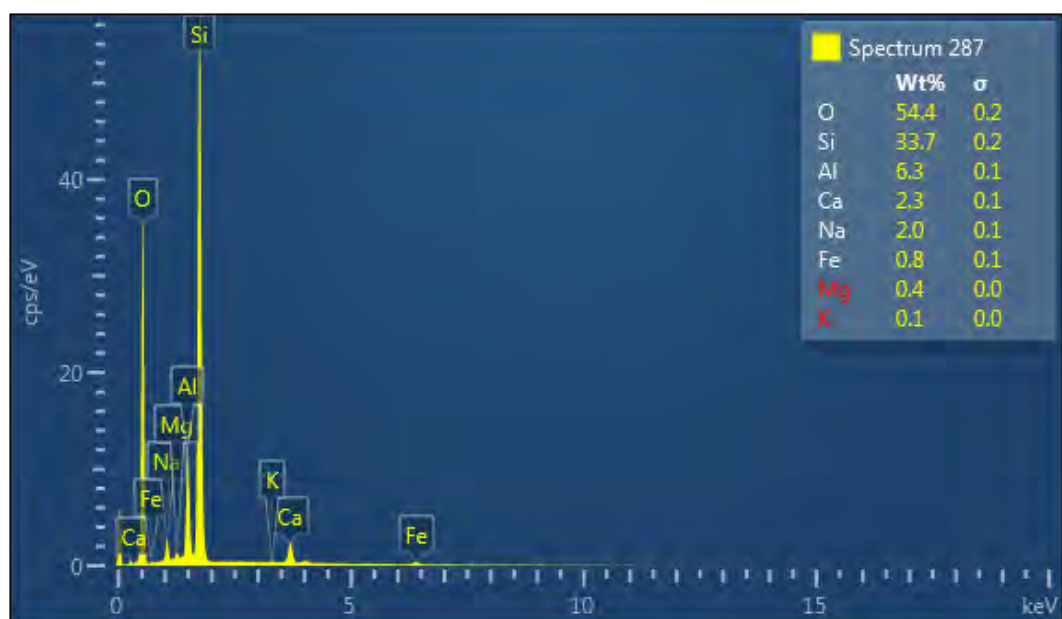
B7

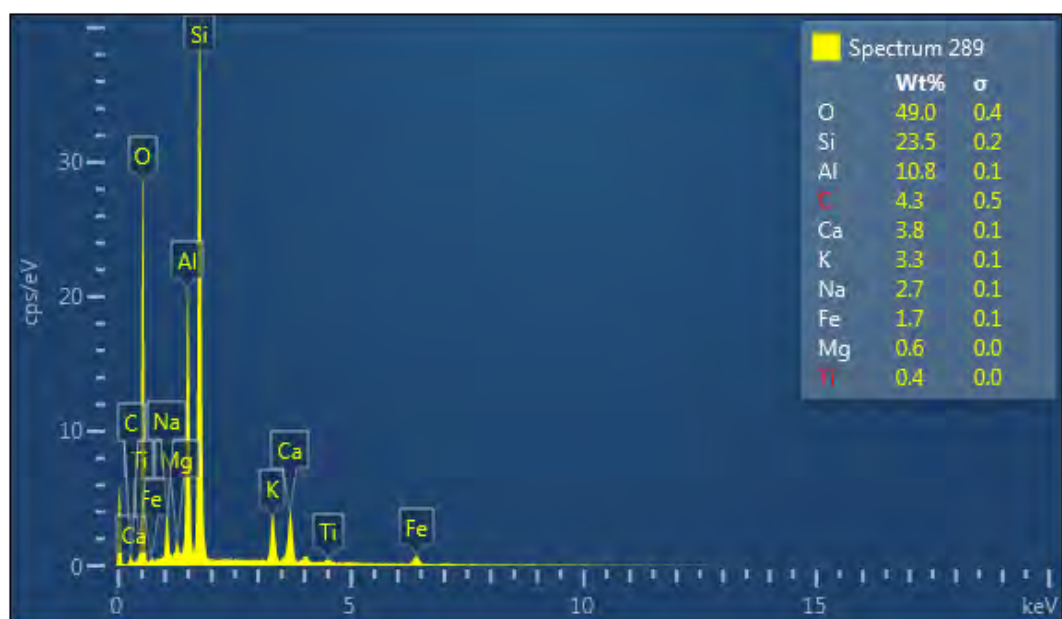
Electron Image 59





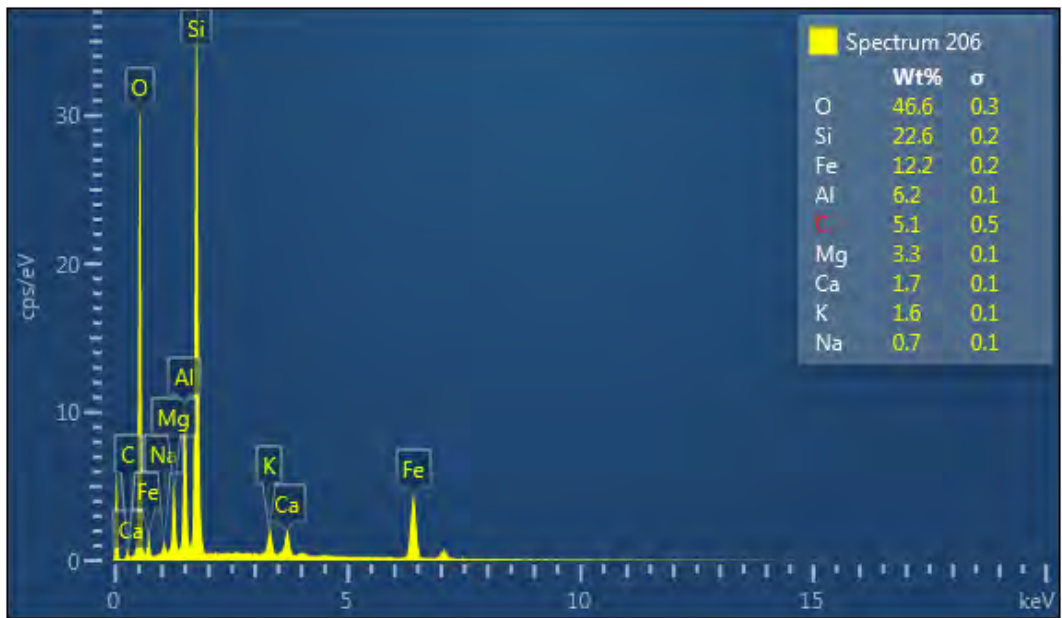
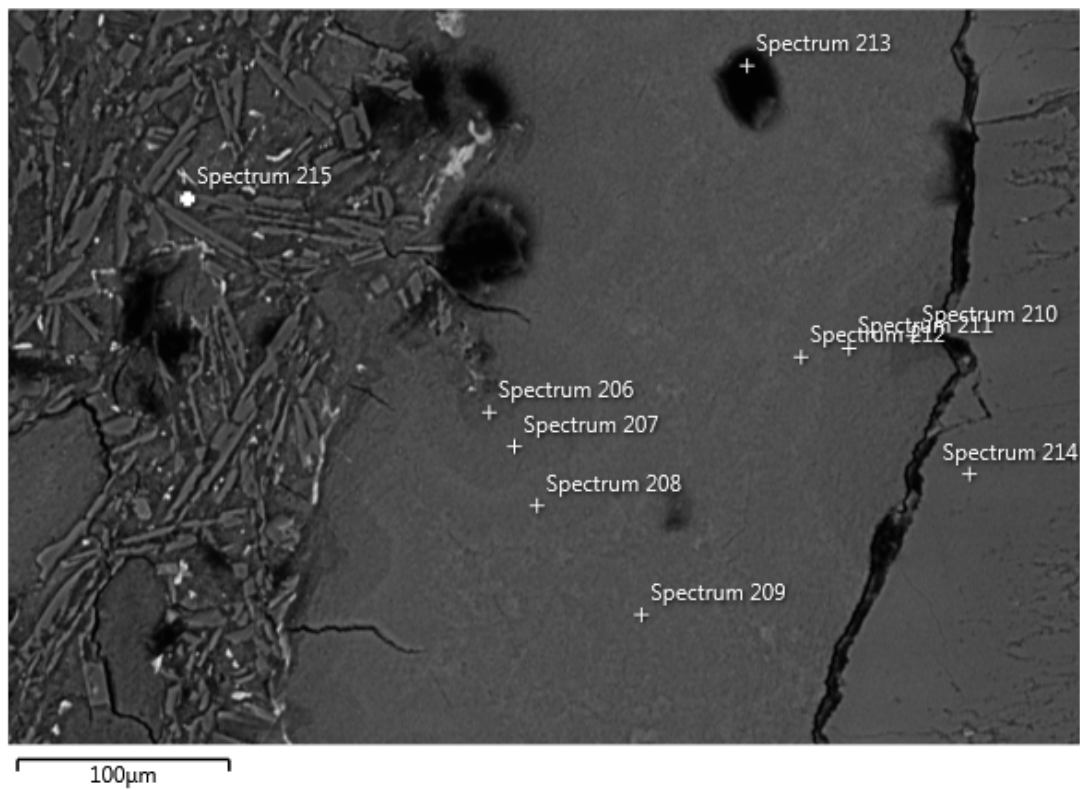


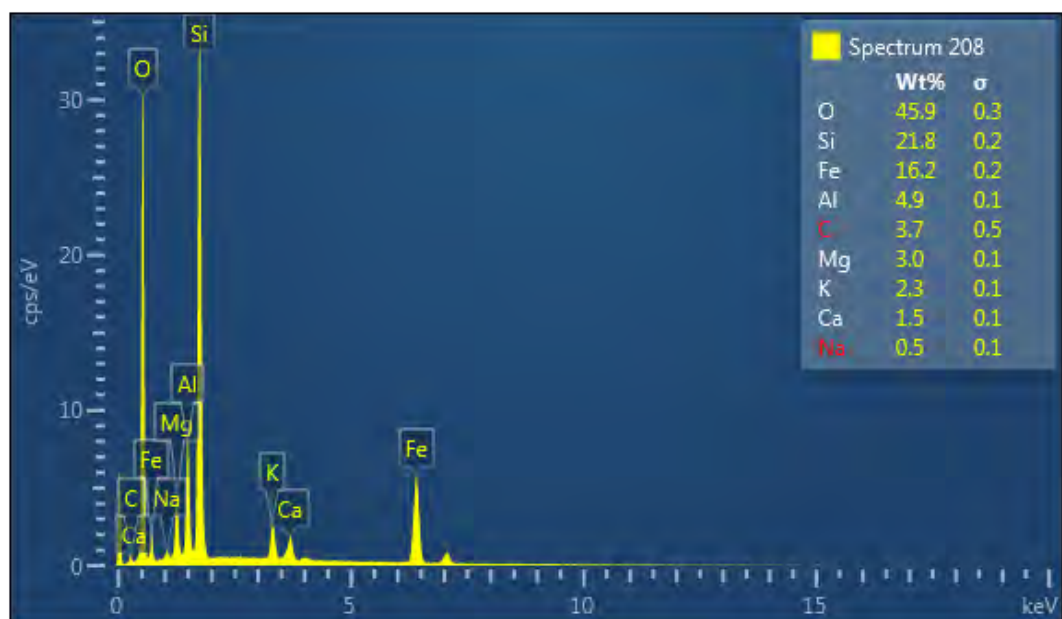
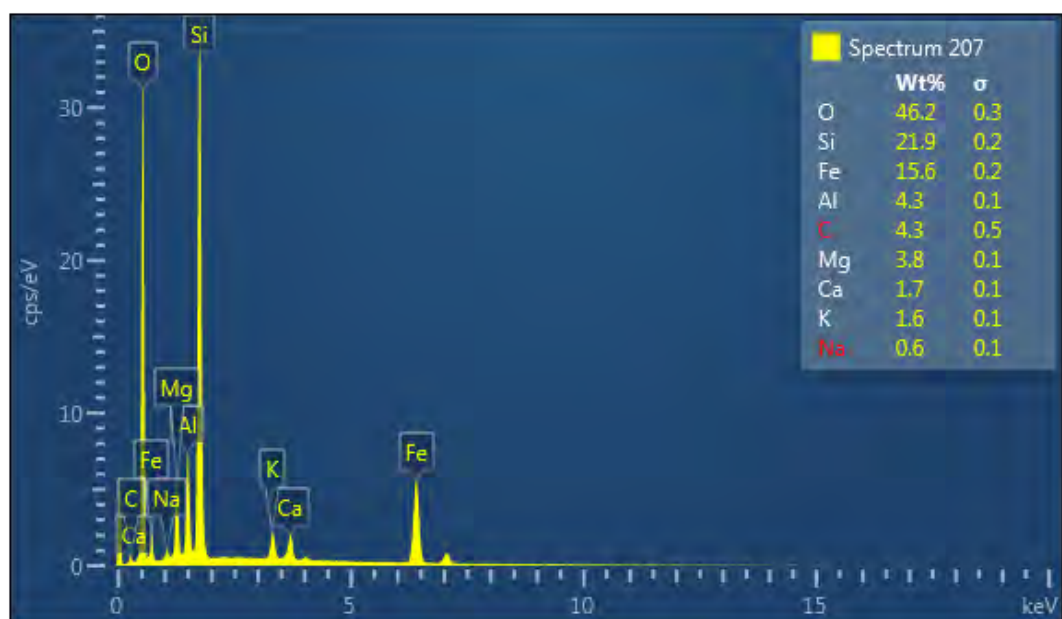


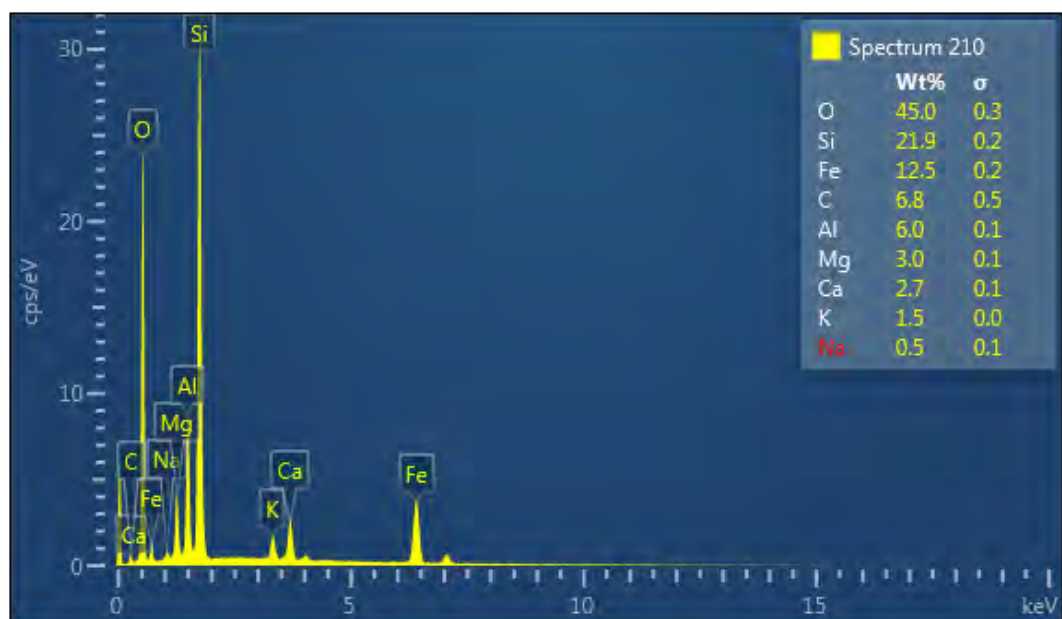
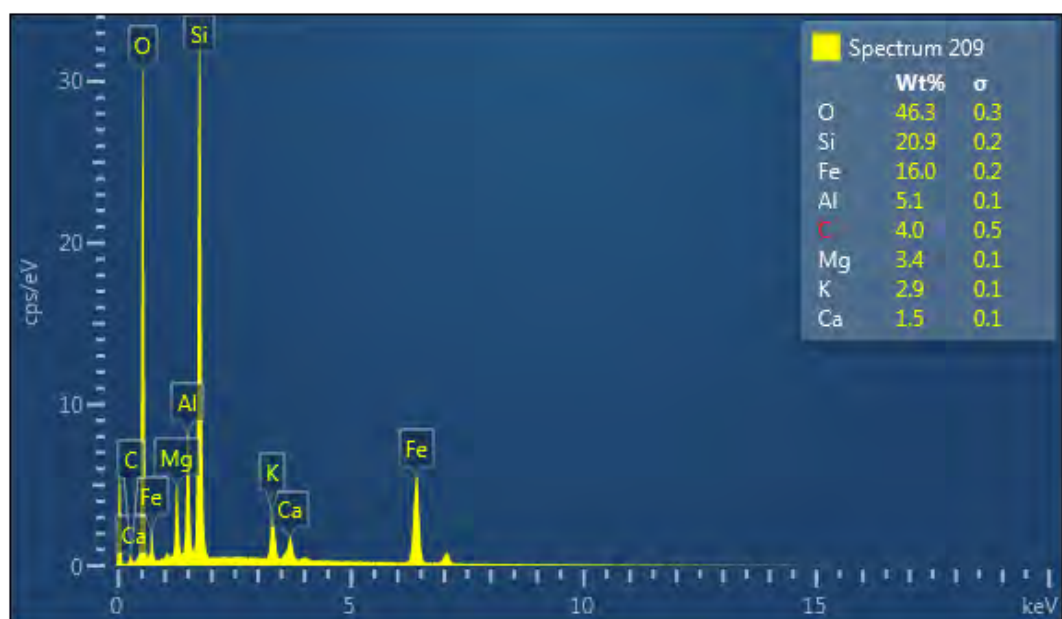


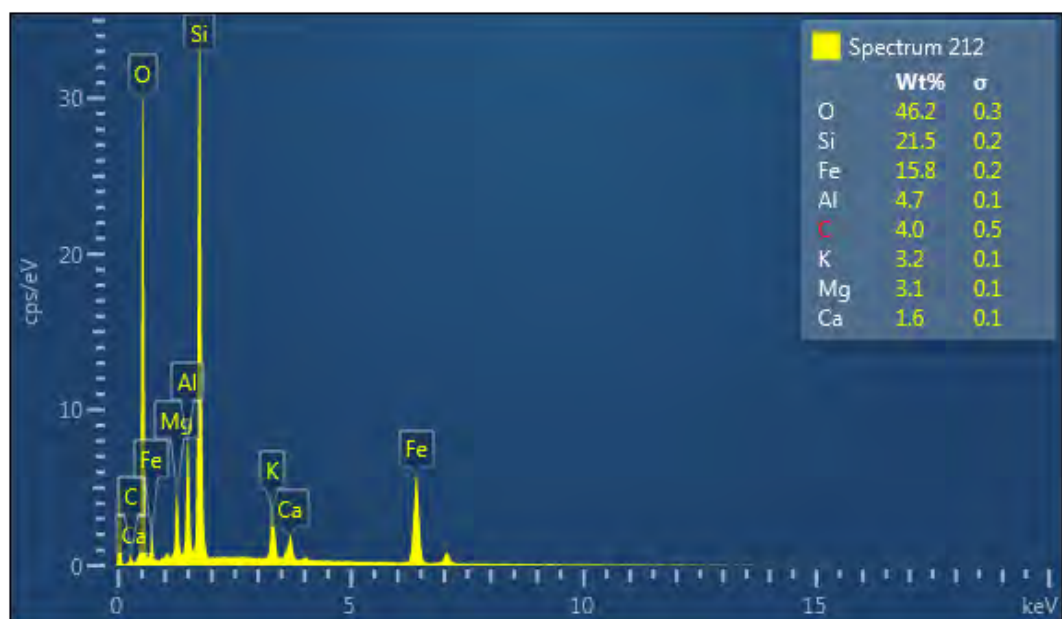
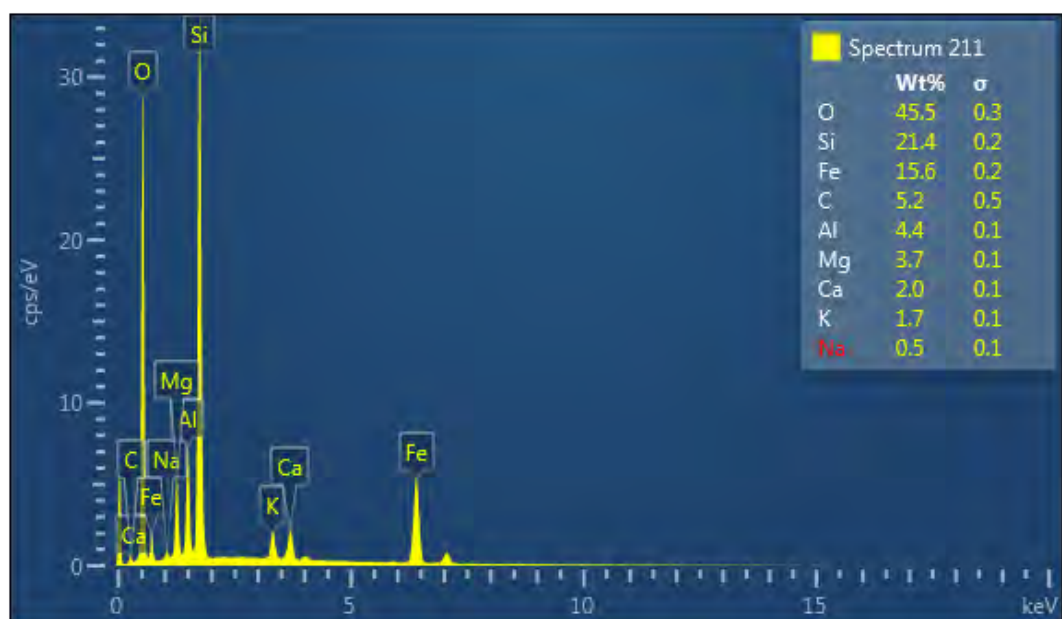
B8

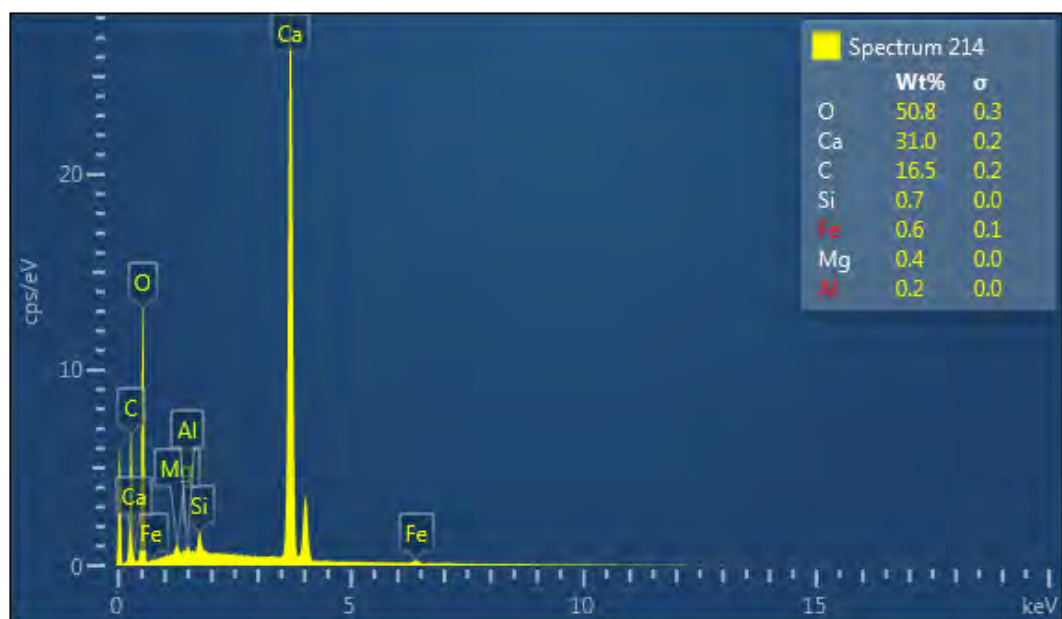
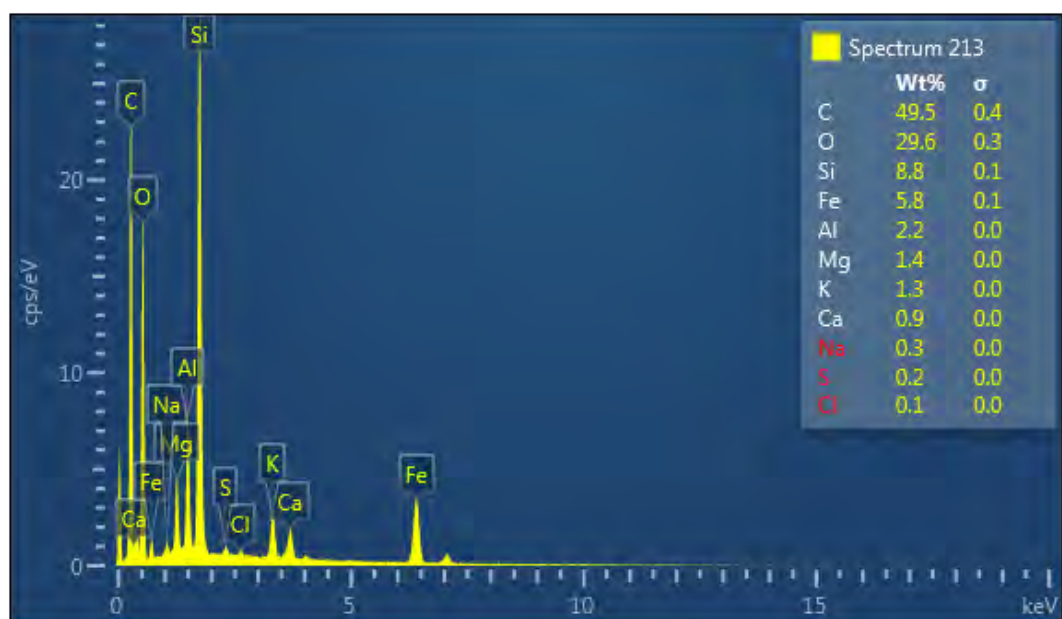
Electron Image 47

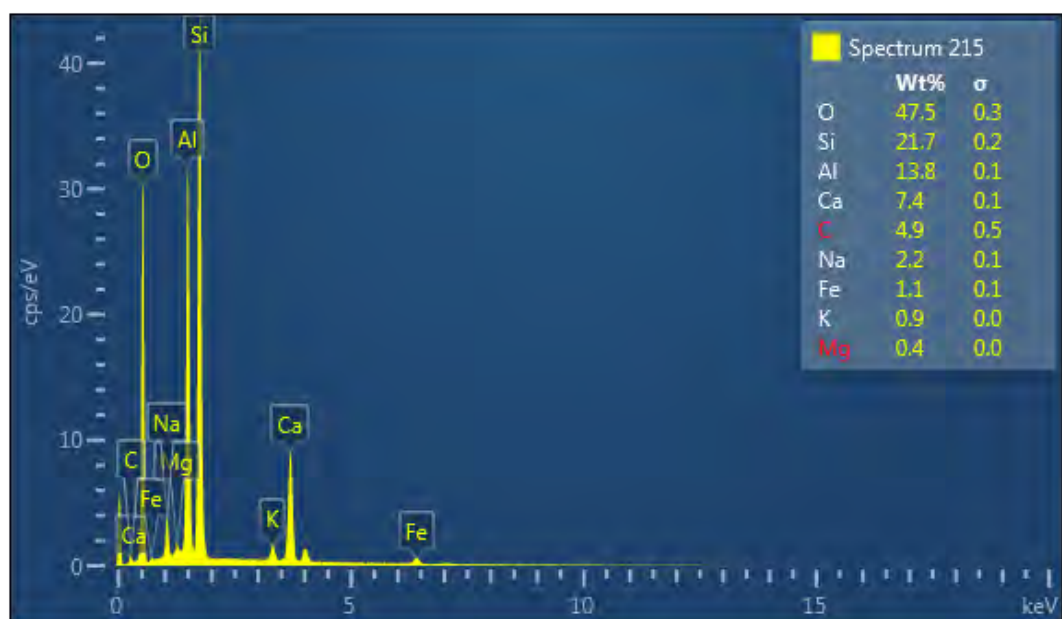






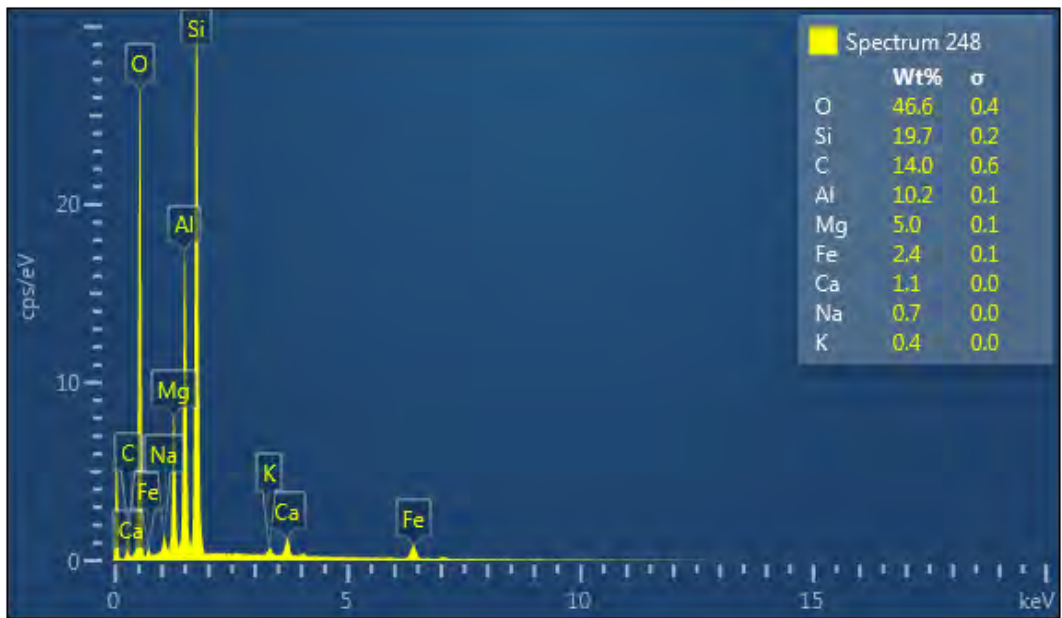
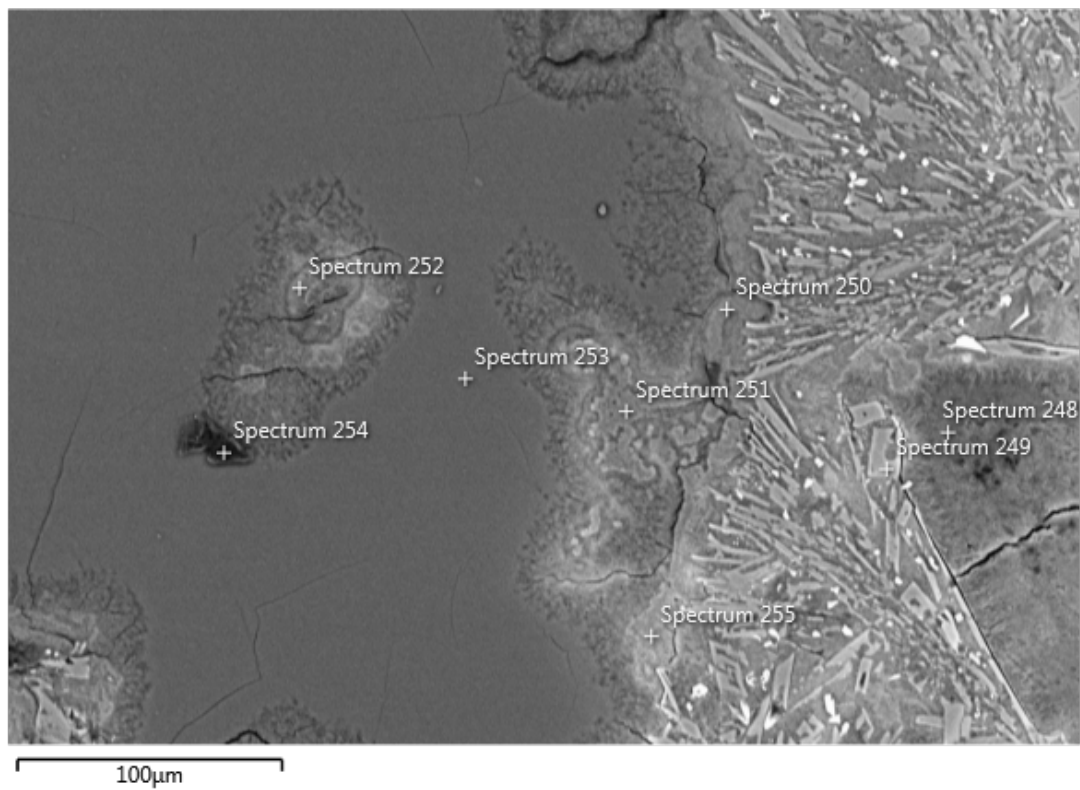


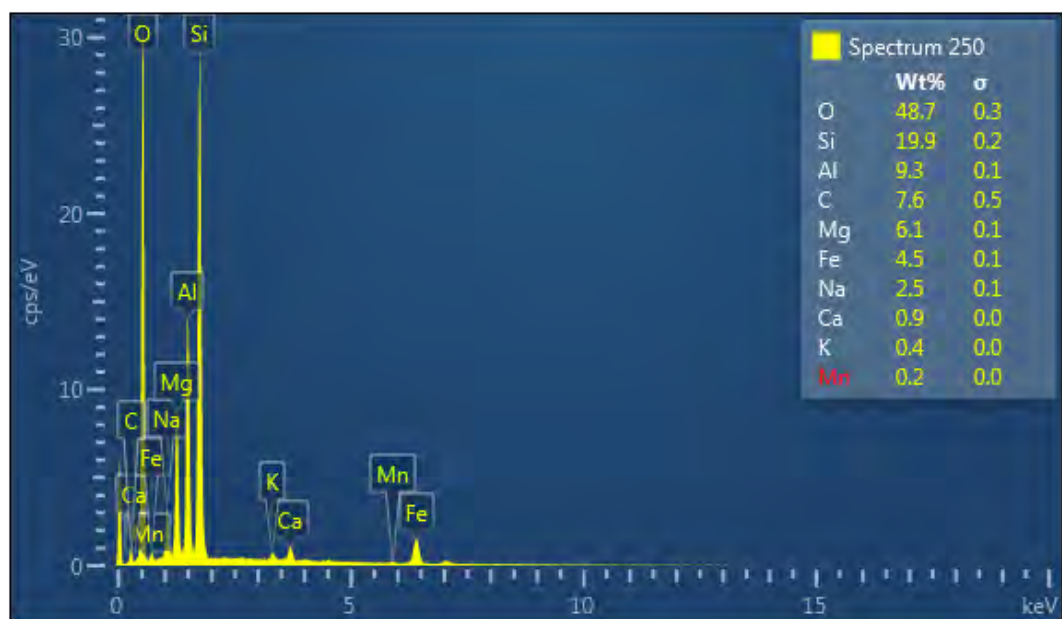
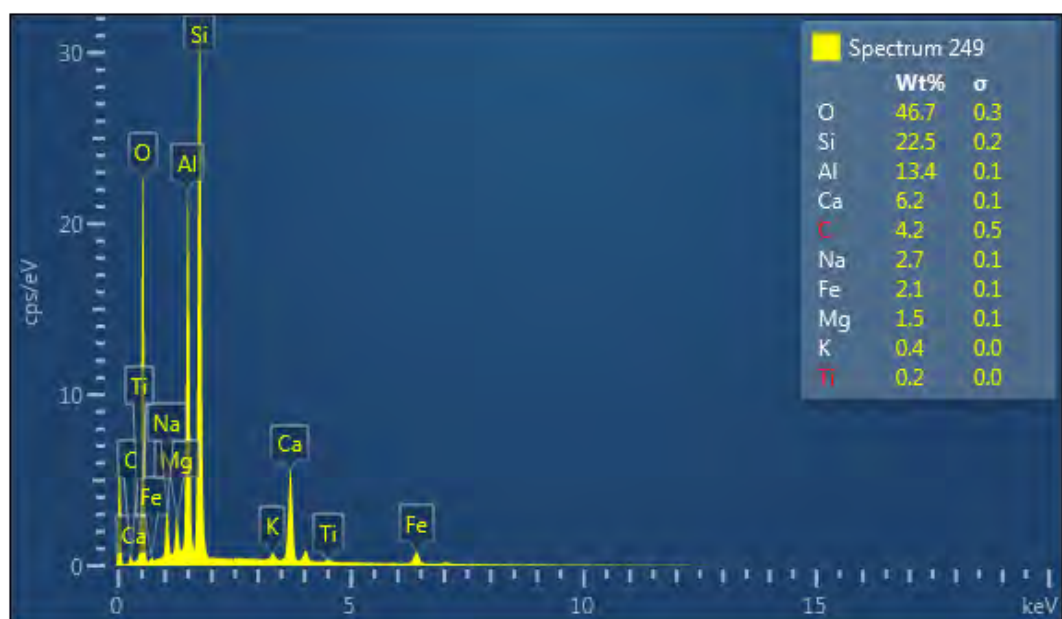


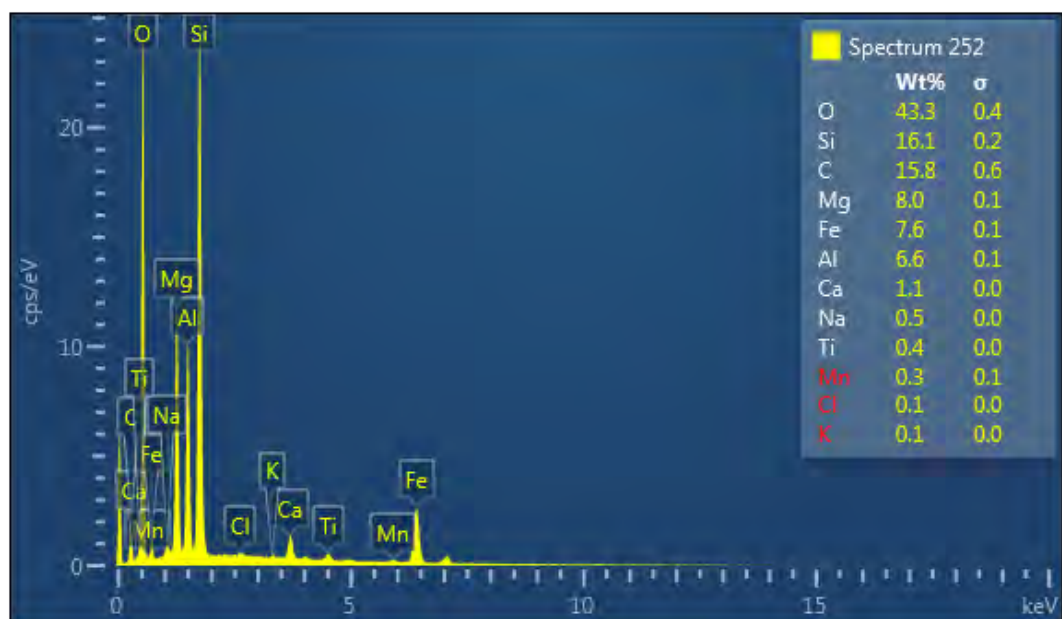
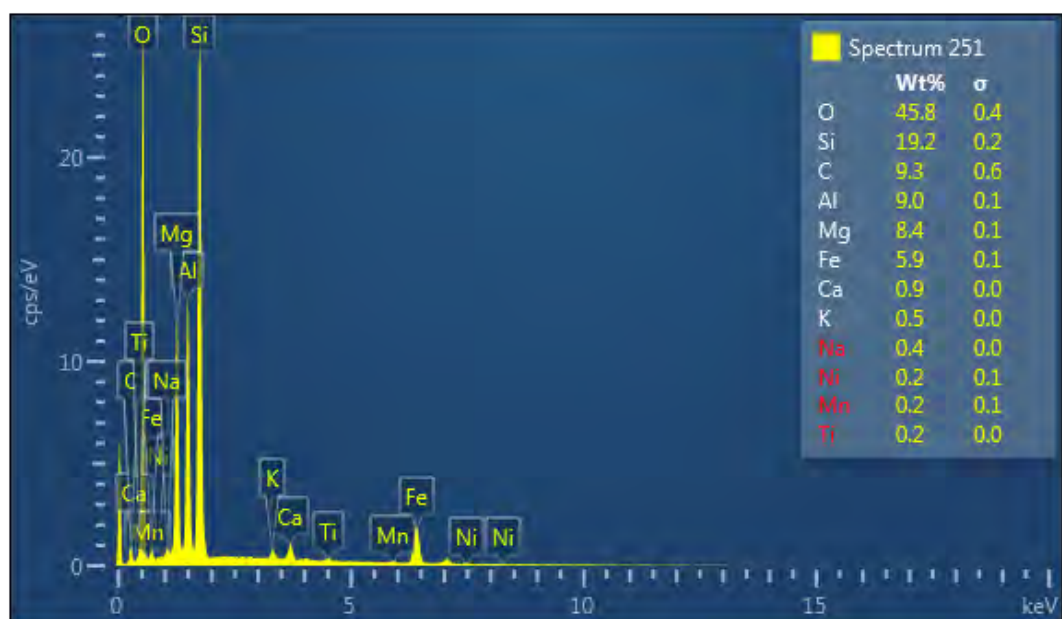


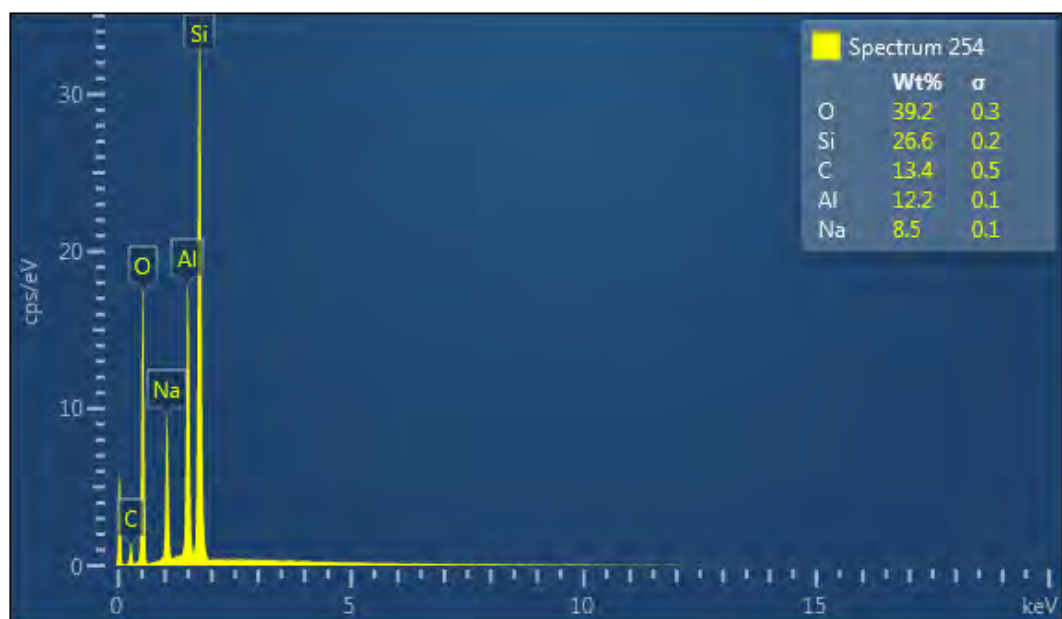
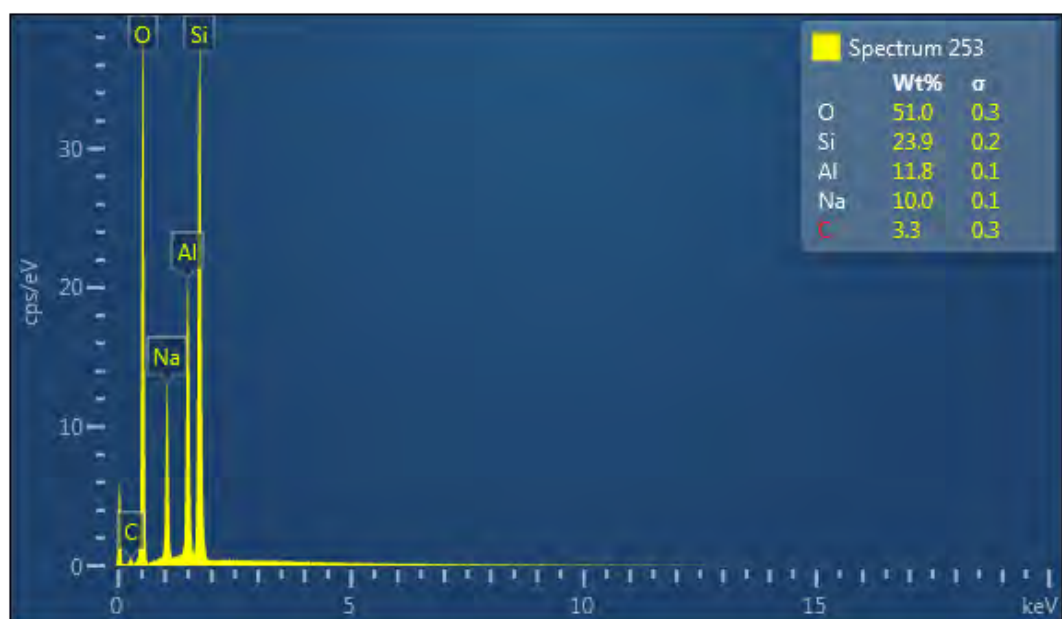
B9

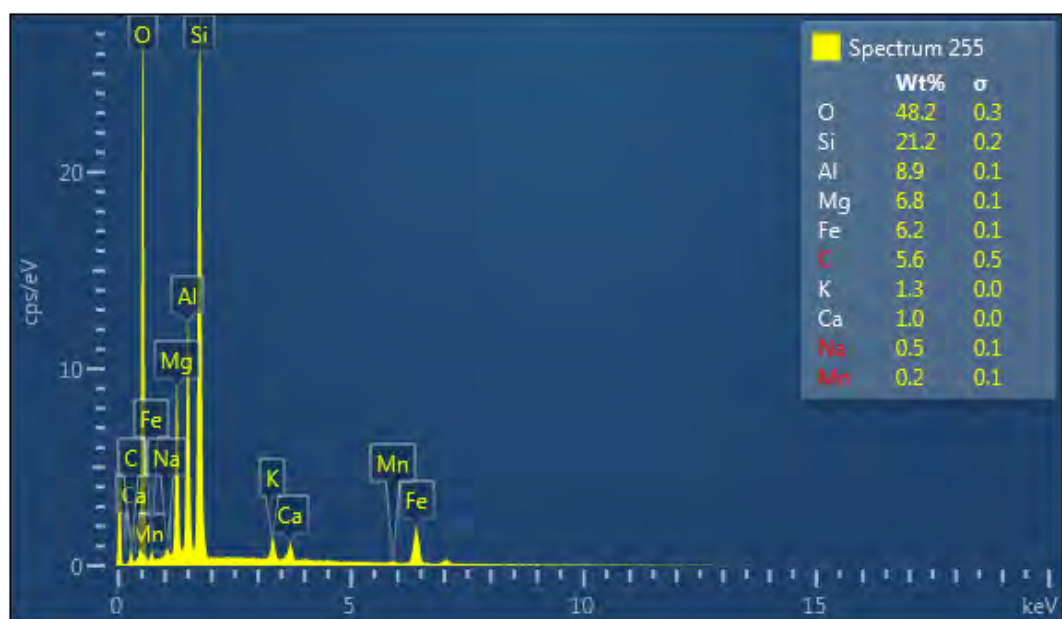
Electron Image 52





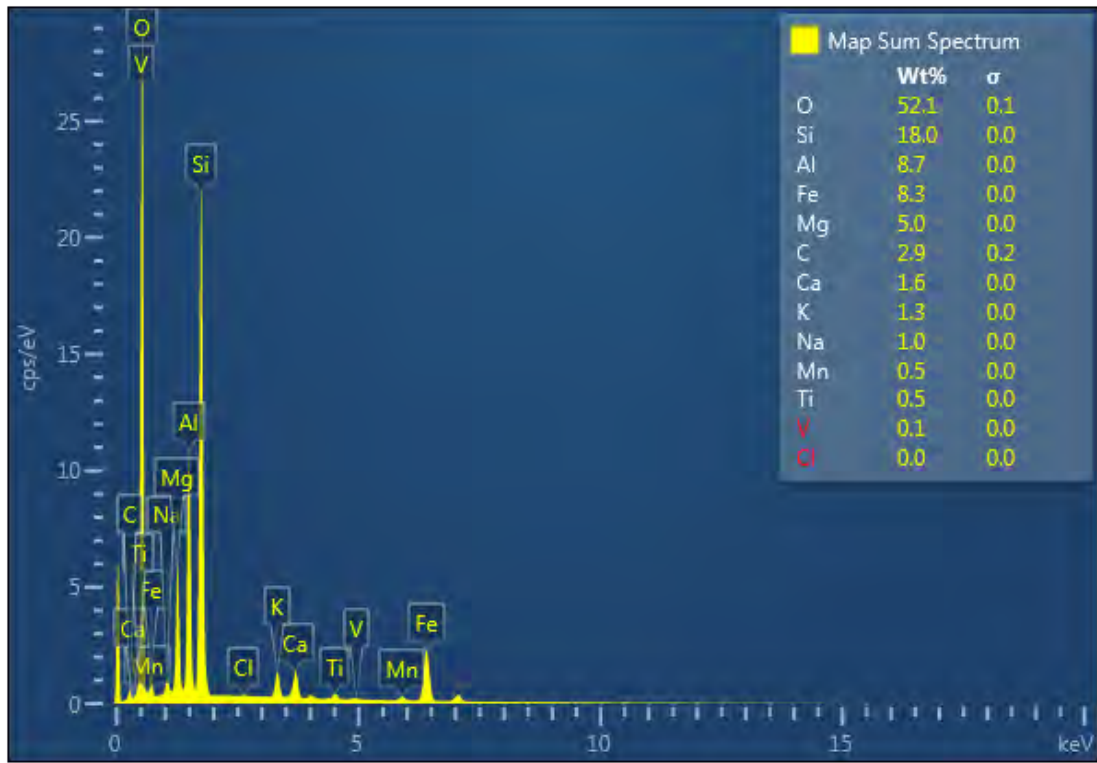
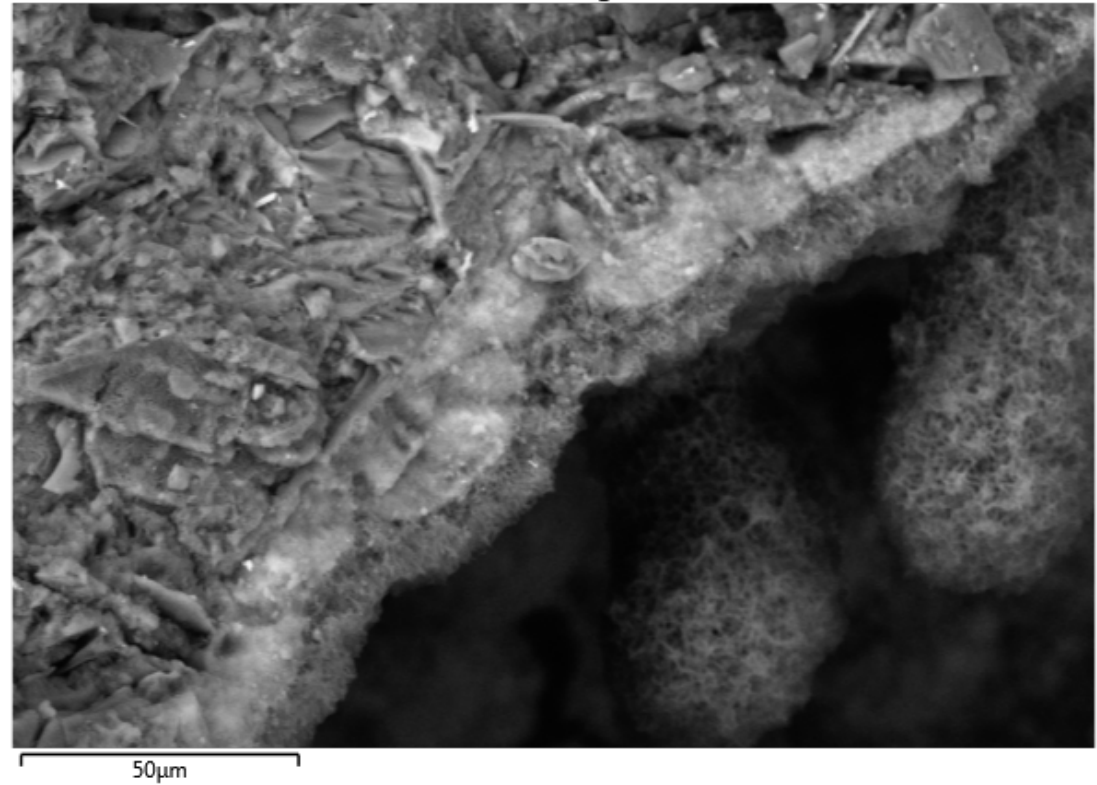






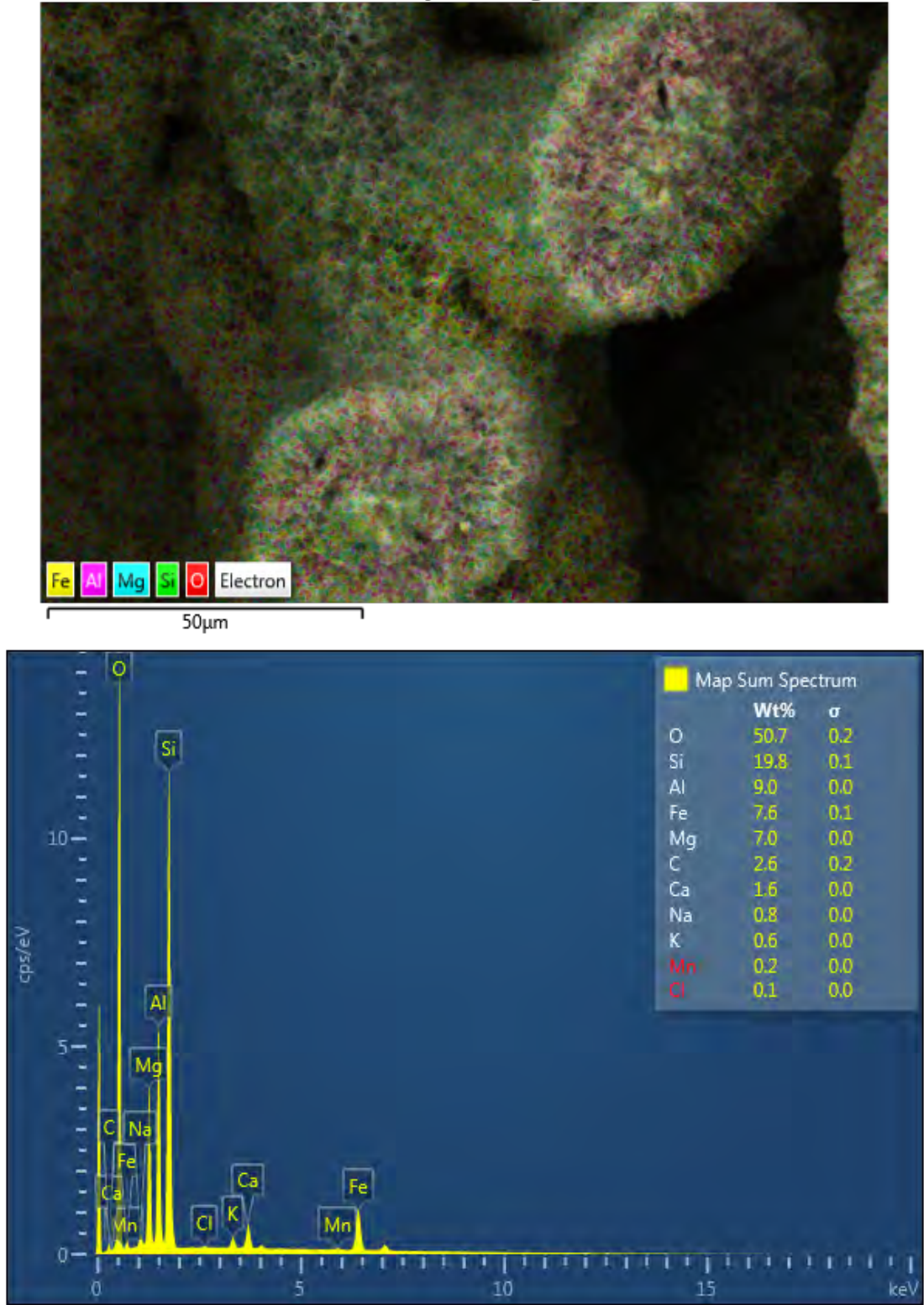
B10

Electron Image 11



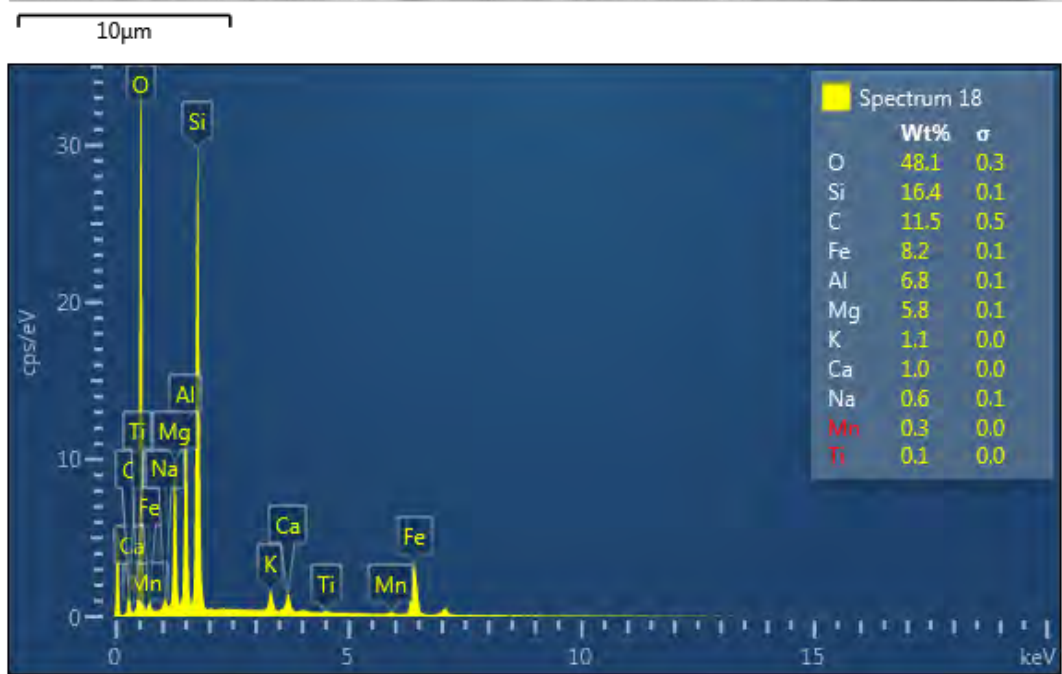
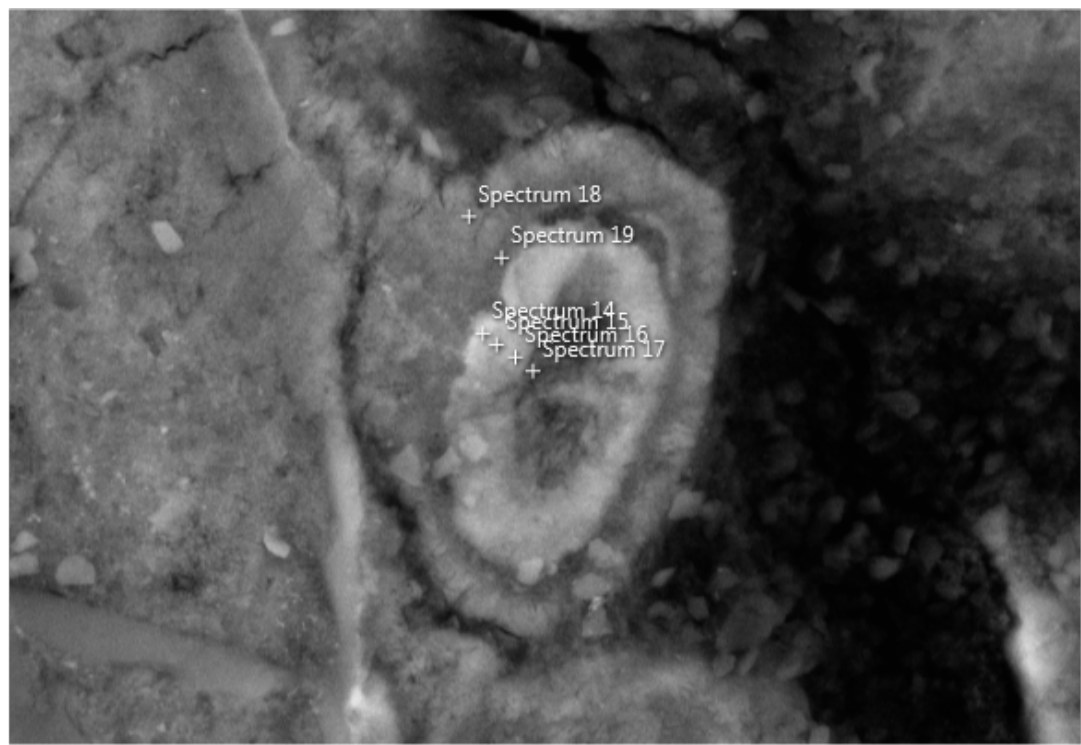
B11

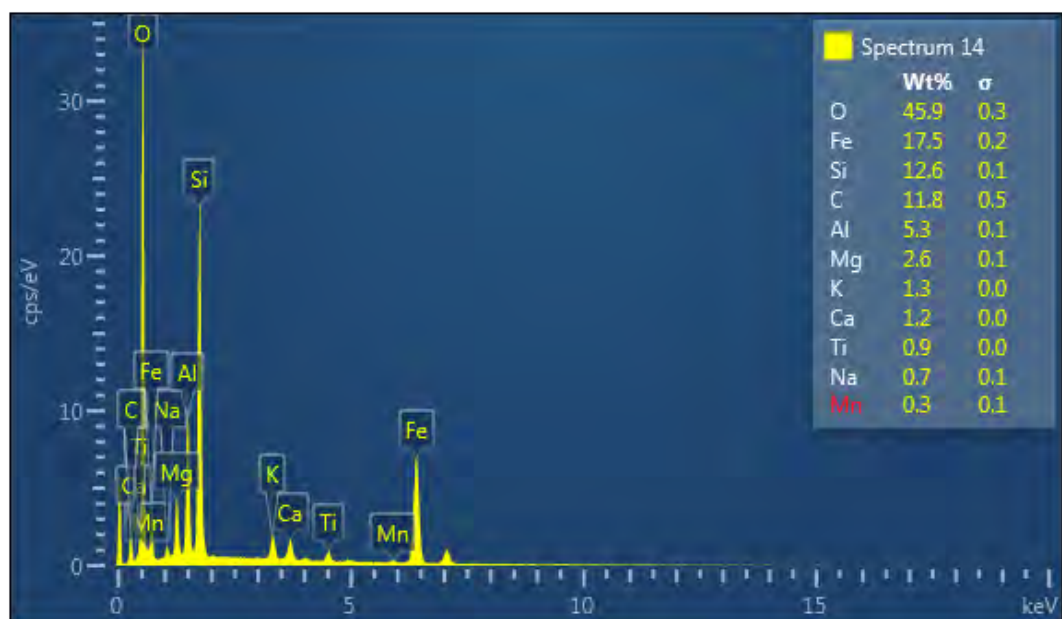
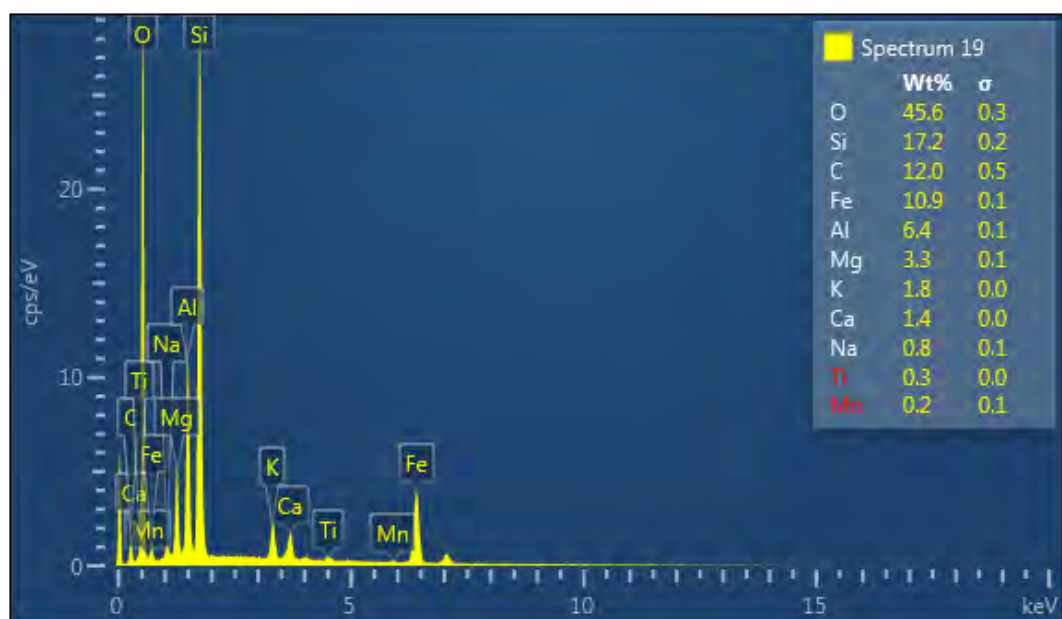
EDS Layered Image 2

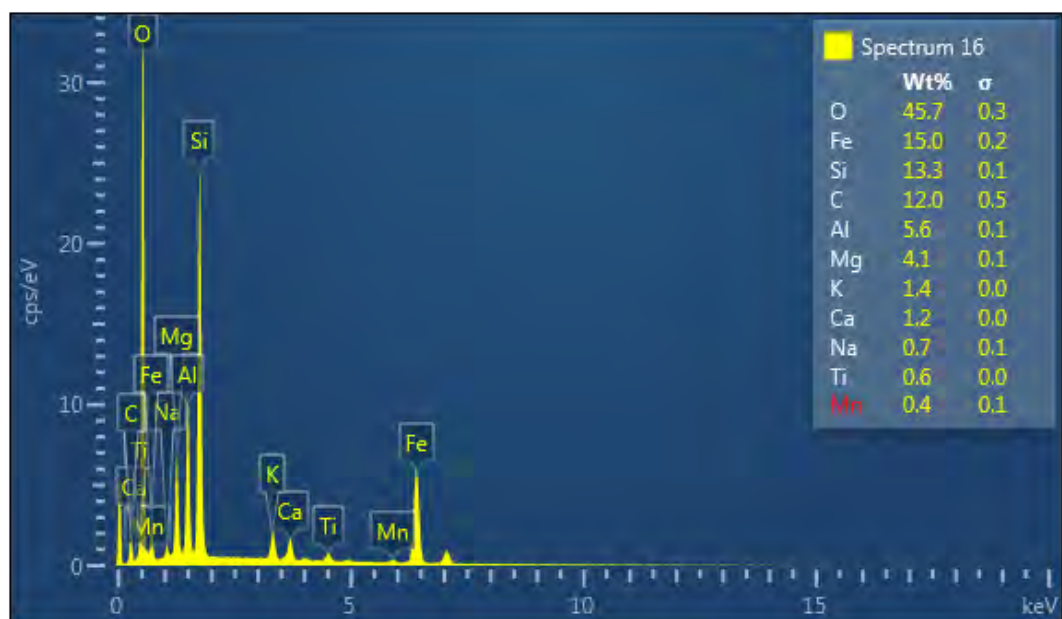
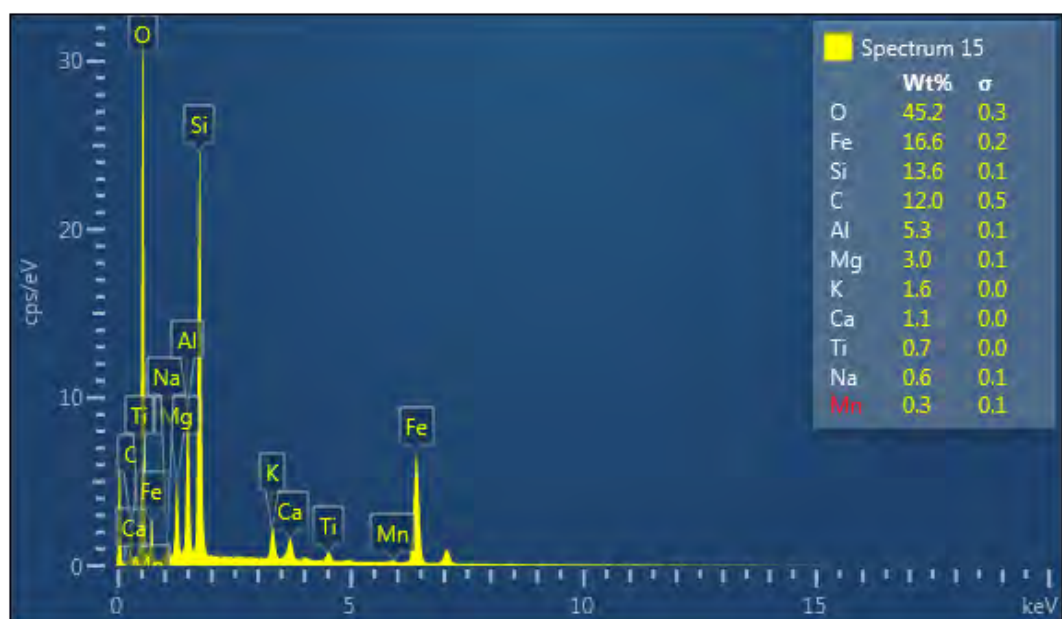


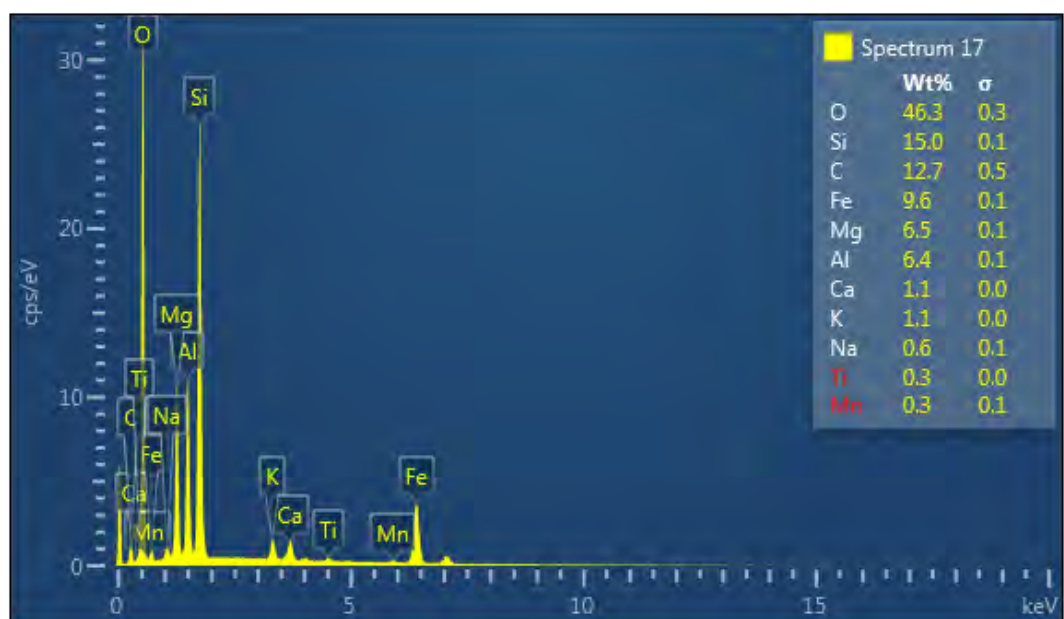
B12

07Ba_3









Appendix C: Raman data

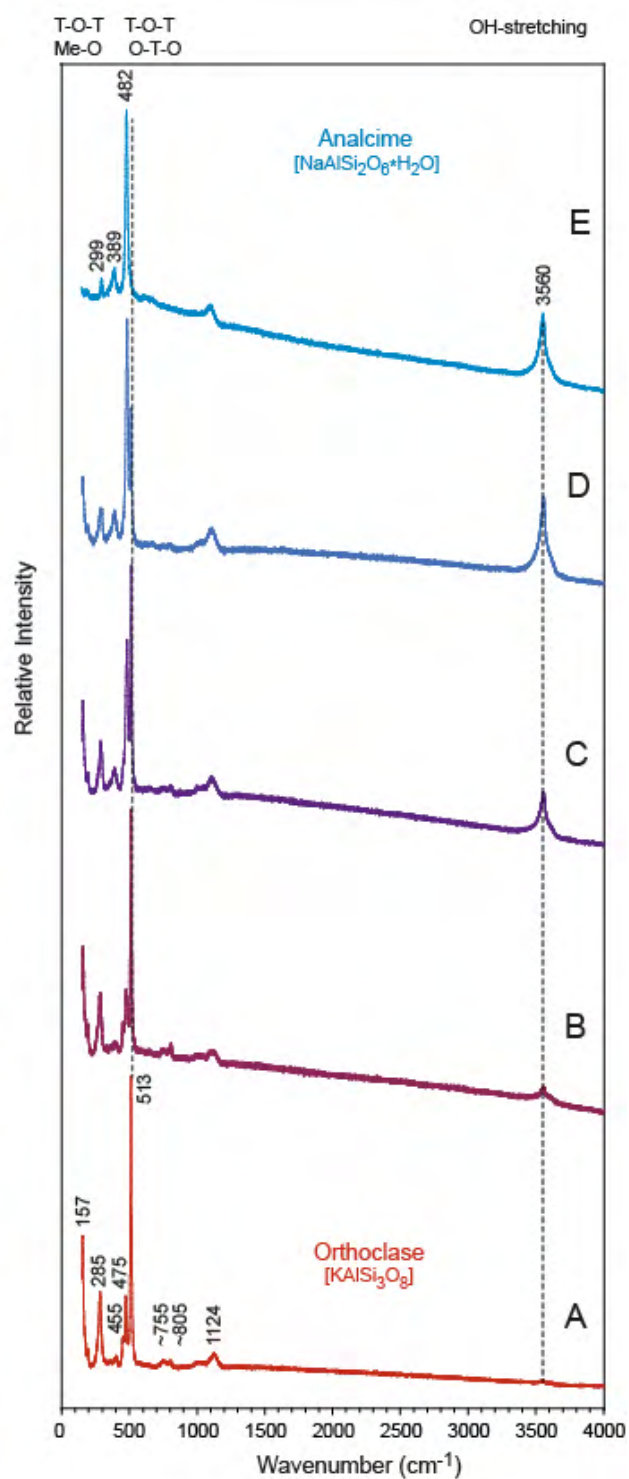
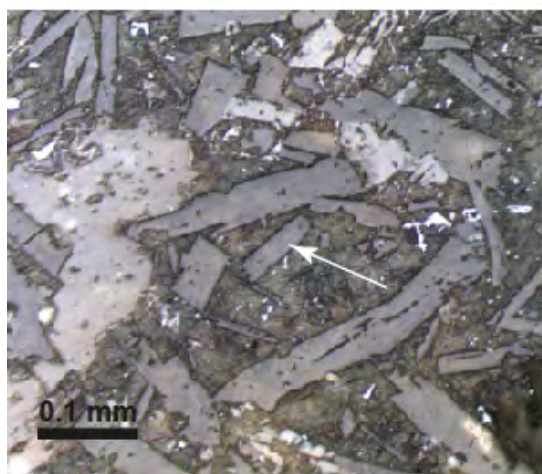
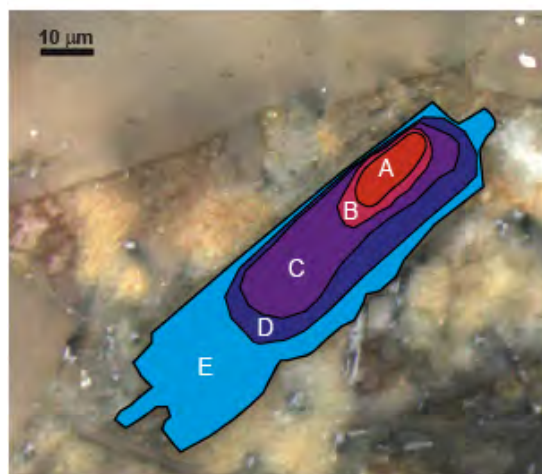
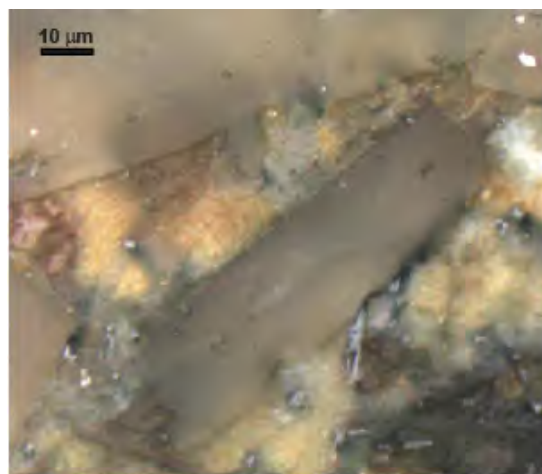


Figure Raman 1

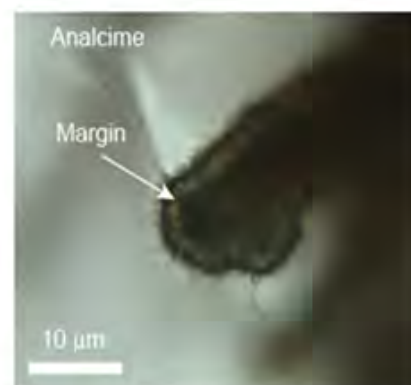
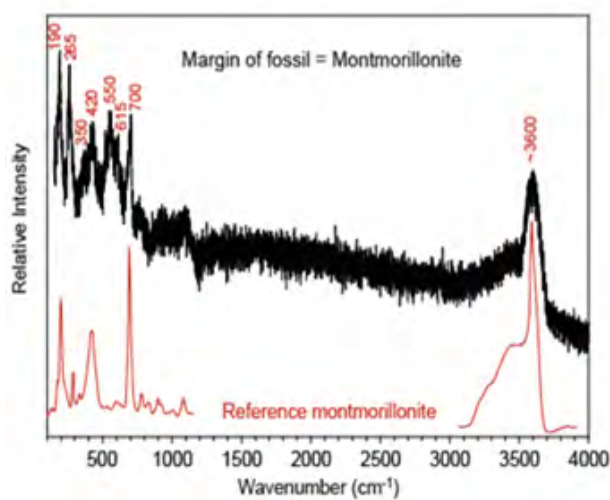
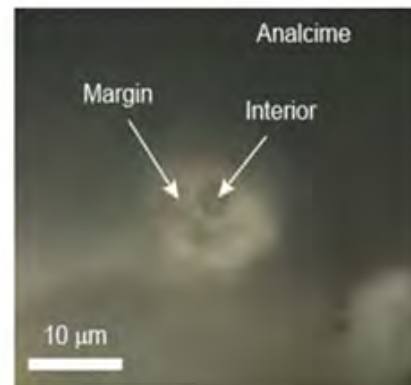
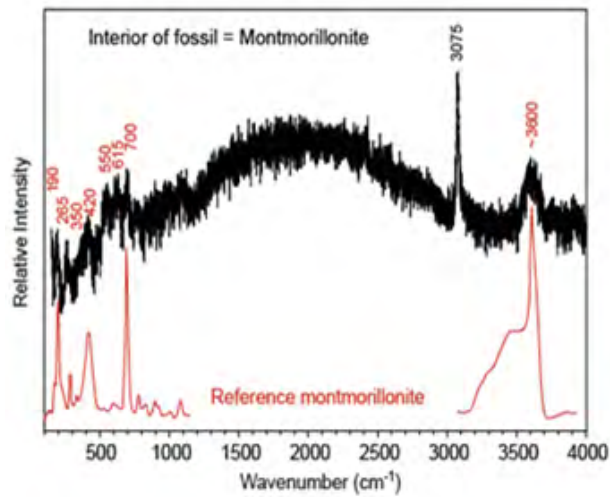
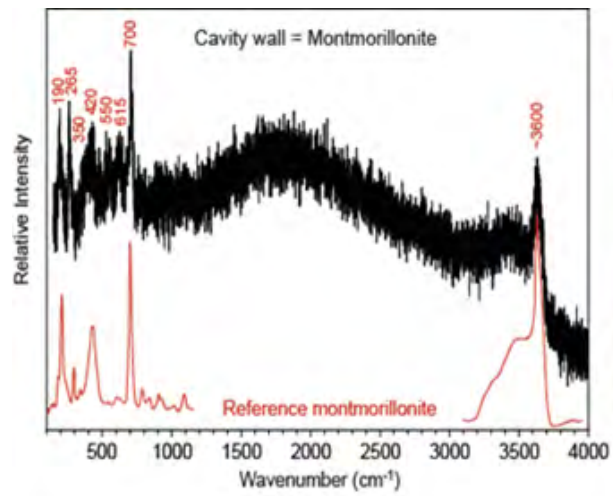


Figure Raman 2

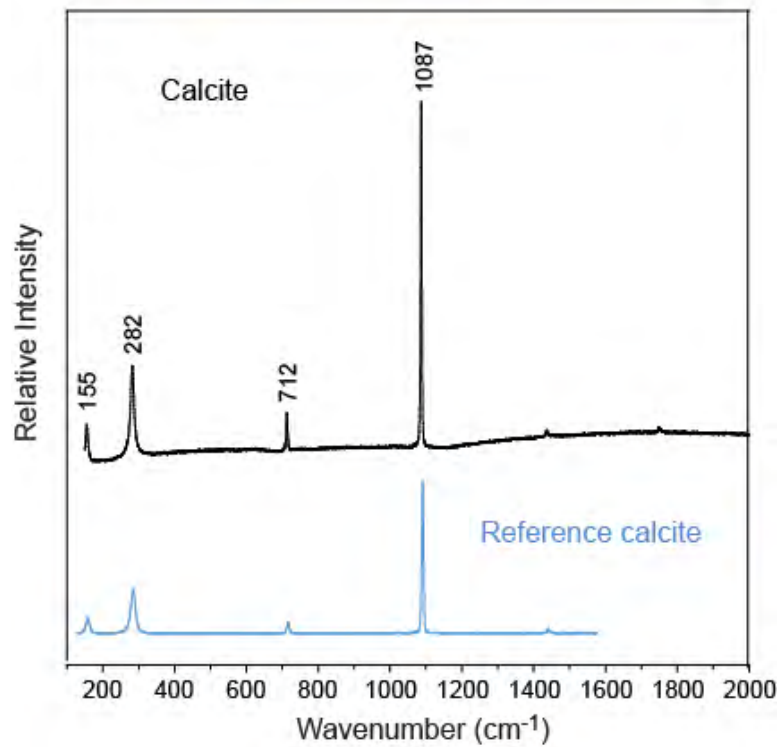
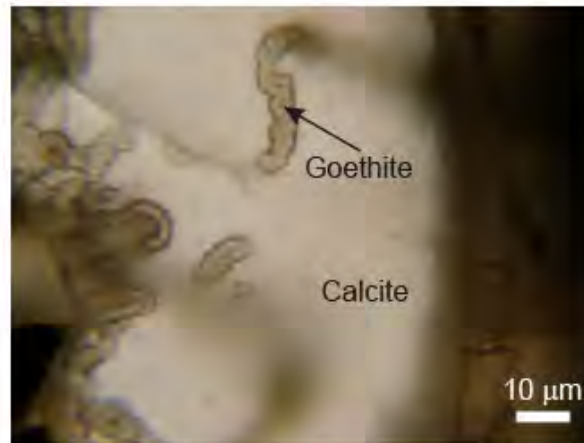
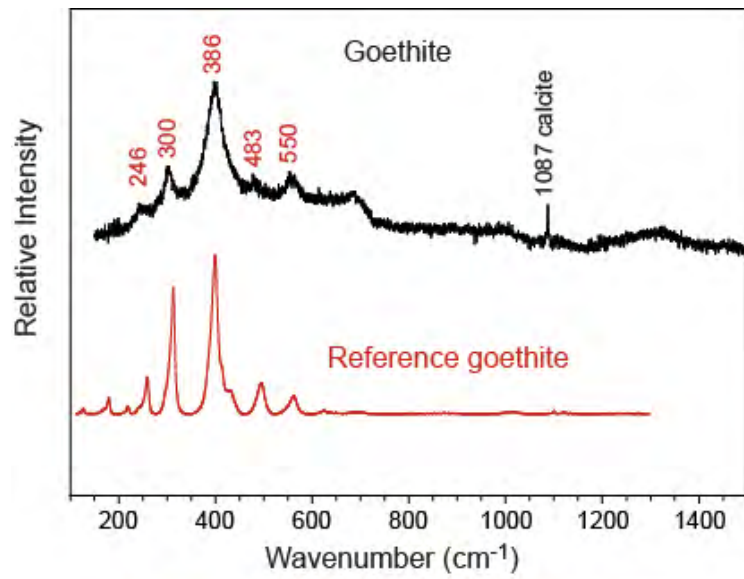


Figure Raman 3

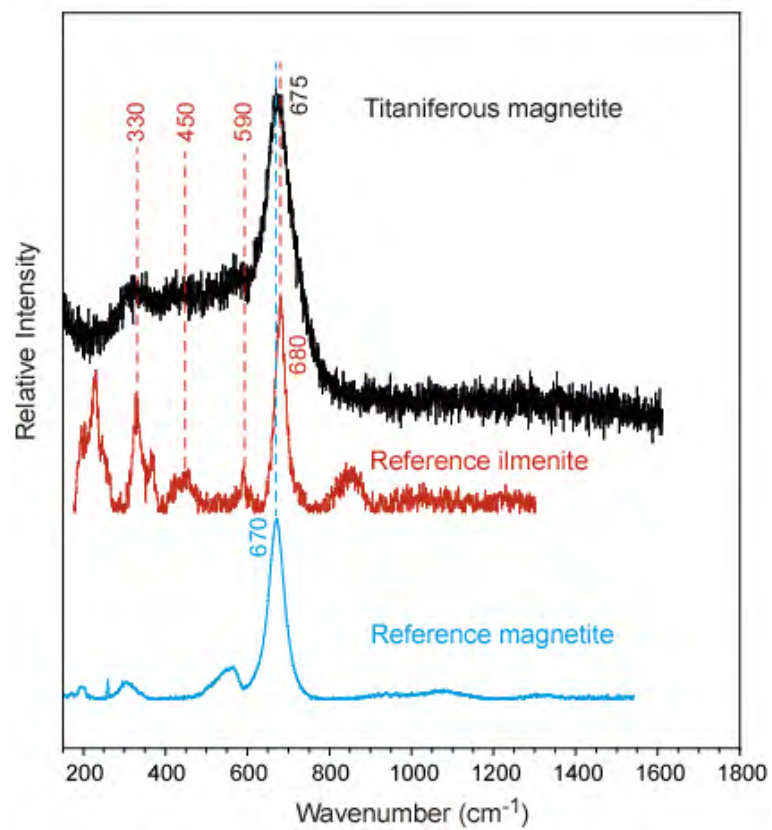
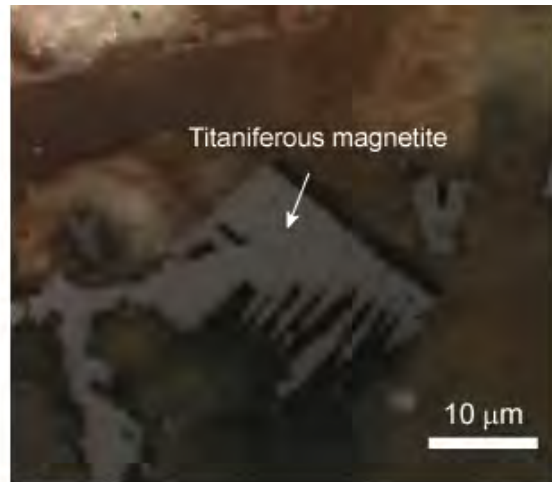


Figure Raman 4

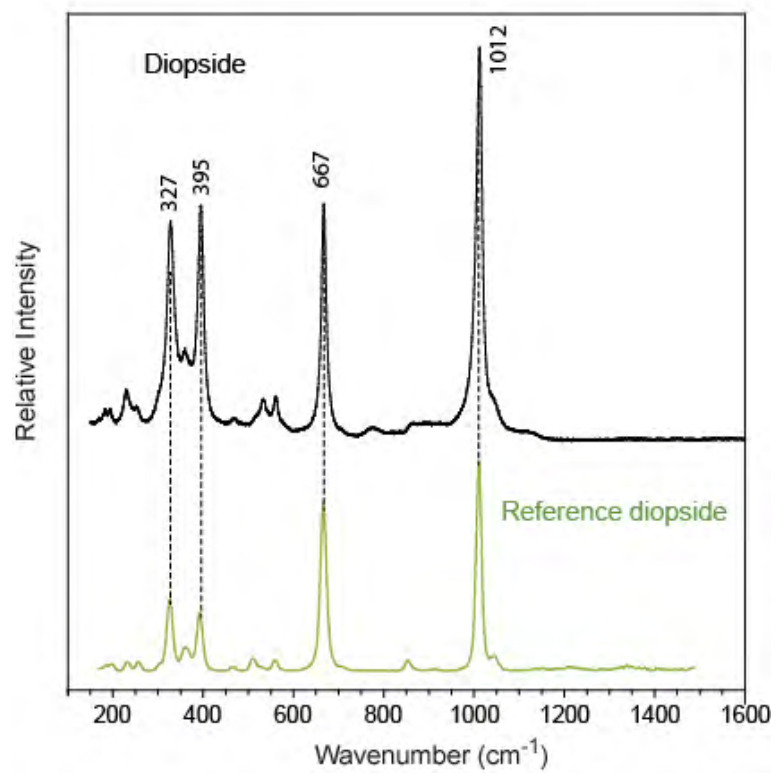
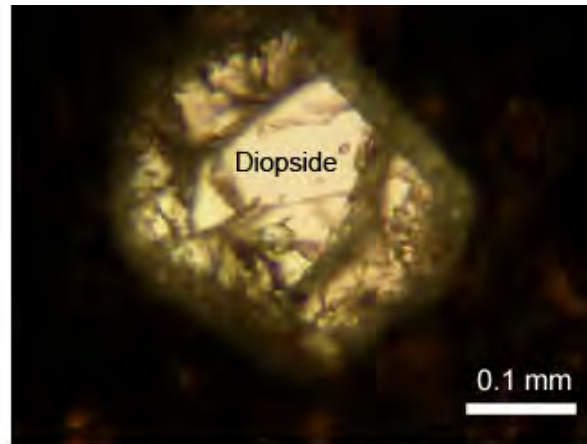


Figure Raman 5

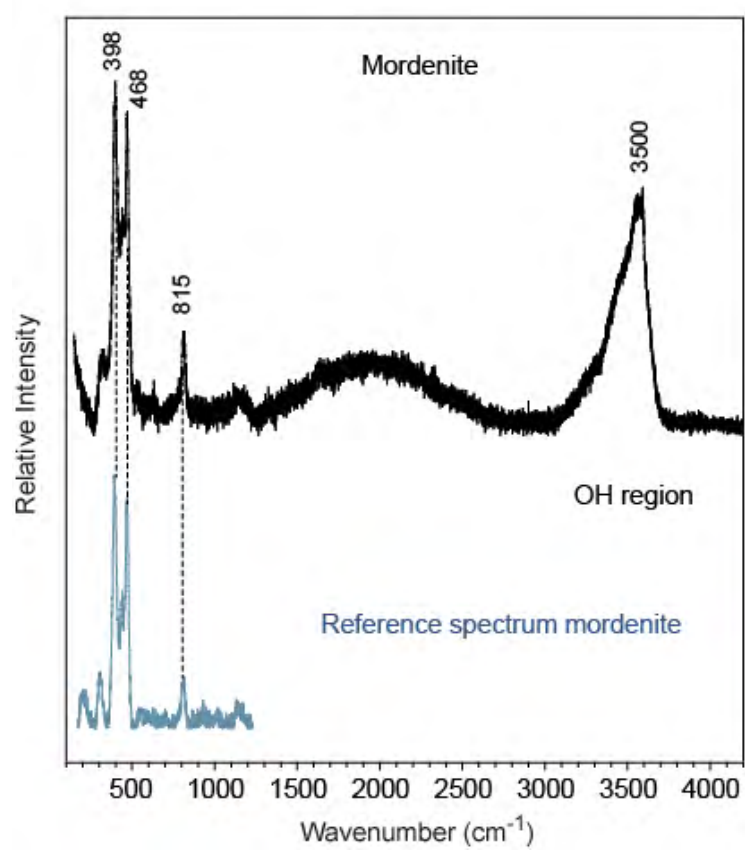
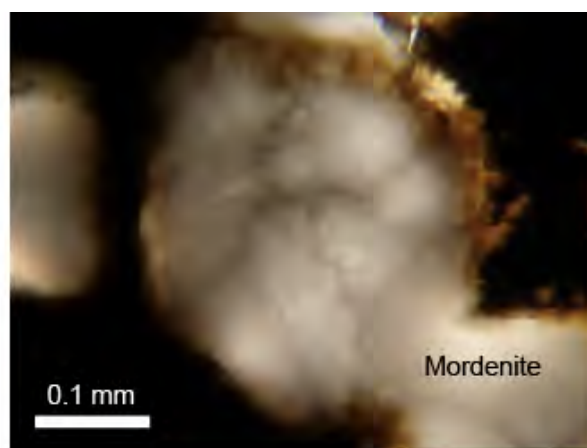
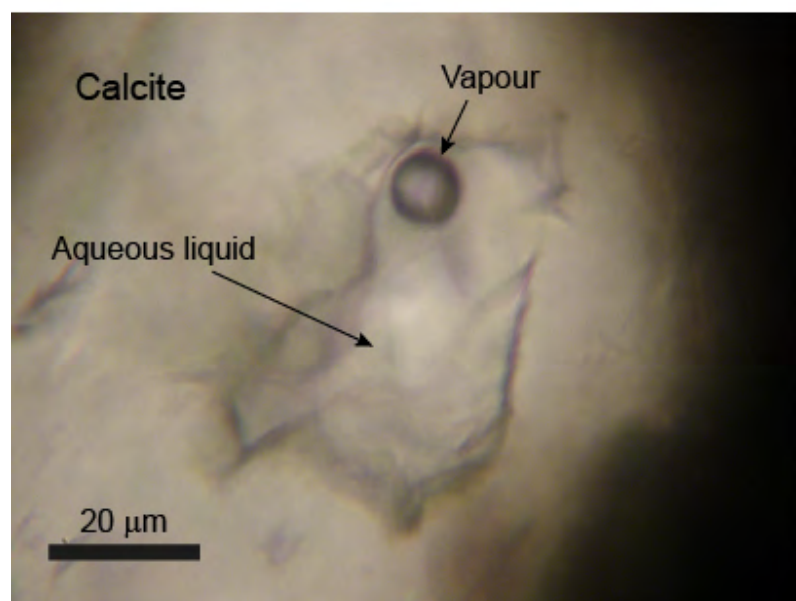
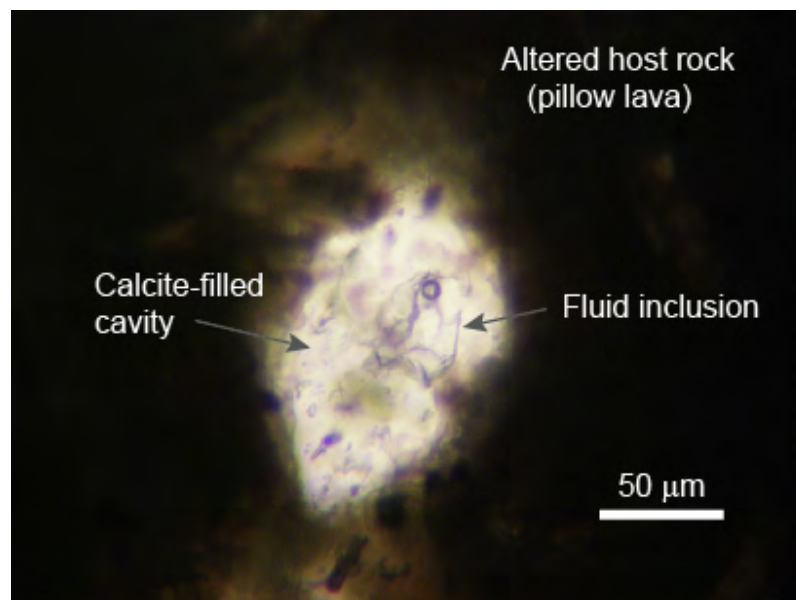


Figure Raman 6

Appendix D: Fluid inclusion data



Appendix E: XRF data

