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APPLICATIONS OF ELECTRON MICROSCOPY IN GEOLOGY/EARTH SCIENCES

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Iris Buisman has been a microanalysis laboratory manager in the Earth Sciences Department, University of Cambridge since 2011 overseeing the electron microprobe and SEM. She has a PhD in Experimental Petrology, a method whereby Earth Scientists make synthetic 'rocks' (or sometimes crush actual rocks) and subject them to high pressures and/or temperatures to study the emergence (and disappearance) of different phases to help construct phase diagrams to better help understand the world beneath our feet. During her PhD she drifted towards microanalysis due to her experimental products proving tricky to analyse. Currently she finds herself involved in many different projects that involve active volcanoes and adding to the expanding knowledge in understanding their plumbing systems, in addition to enabling users to fully explore the potential of correlative microscopy and the data cube it produces. She has over 18 publications.

1. ABSTRACT

In this presentation, an introduction is given into the various ways an electron microscope might be used in an Earth Sciences Department. The focus here will be on the two instruments most geologists would use: a scanning electron microscope (SEM) and an electron probe microanalyser (EPMA). A brief introduction will be given on an EPMA instrument as this is not covered by previous lectures. This presentation will aim to illustrate, by means of examples and case studies, how the 'bread and butter' of the techniques such as secondary electron (SE) and backscattered electron (BSE) imaging, electron backscattered diffraction (EBSD), cathodoluminescence analysis (CL), quantitative/qualitative chemical analysis by means of energy-dispersive X-ray spectrometry (EDS) and wavelength-dispersive X-ray spectrometry (WDS) are used and then applied to the broader landscape of geological questions.

2. INTRODUCTION

The scanning electron microscope (SEM) is a versatile tool that can be used by various groups that have very different research interests. Today the instrument has evolved from a high resolution/magnification imaging machine to giving the researcher the opportunity to combine several analytical techniques in conjunction with imaging. The result is a correlative data cube: a powerful packet of data that can be interrogated to a greater depth particularly due to improved available computer power.

The electron microprobe microanalyser (EPMA) is often used in conjunction with an SEM. This tool allows for a nominal non-destructive compositional analysis of solid materials by means of wavelength-dispersive X-ray spectrometry (WDS). This technique allows for high precision and accuracy in addition to being more sensitive compared to energy-dispersive X-ray spectrometry (EDS).

3. ANALYTICAL TECHNIQUES

Although more complicated analytical techniques can now be exploited through a SEM, a lot of research still requires 'simple' imaging. Additionally, most studies require more than on analytical technique.

3.1. Secondary electrons (SE)

Palaeontologists are often interested in the structure/morphology of an organism preserved as a fossil. Sometimes these fossils are one of a kind, meaning the sample cannot be carbon coated or sectioned in any way. Other examples include studying the morphology of tephra (volcanic glass) or forensically examining pollen grain shapes to understand the species of plant and therefore origin of this pollen (Fig. 1a) in archaeological digs.

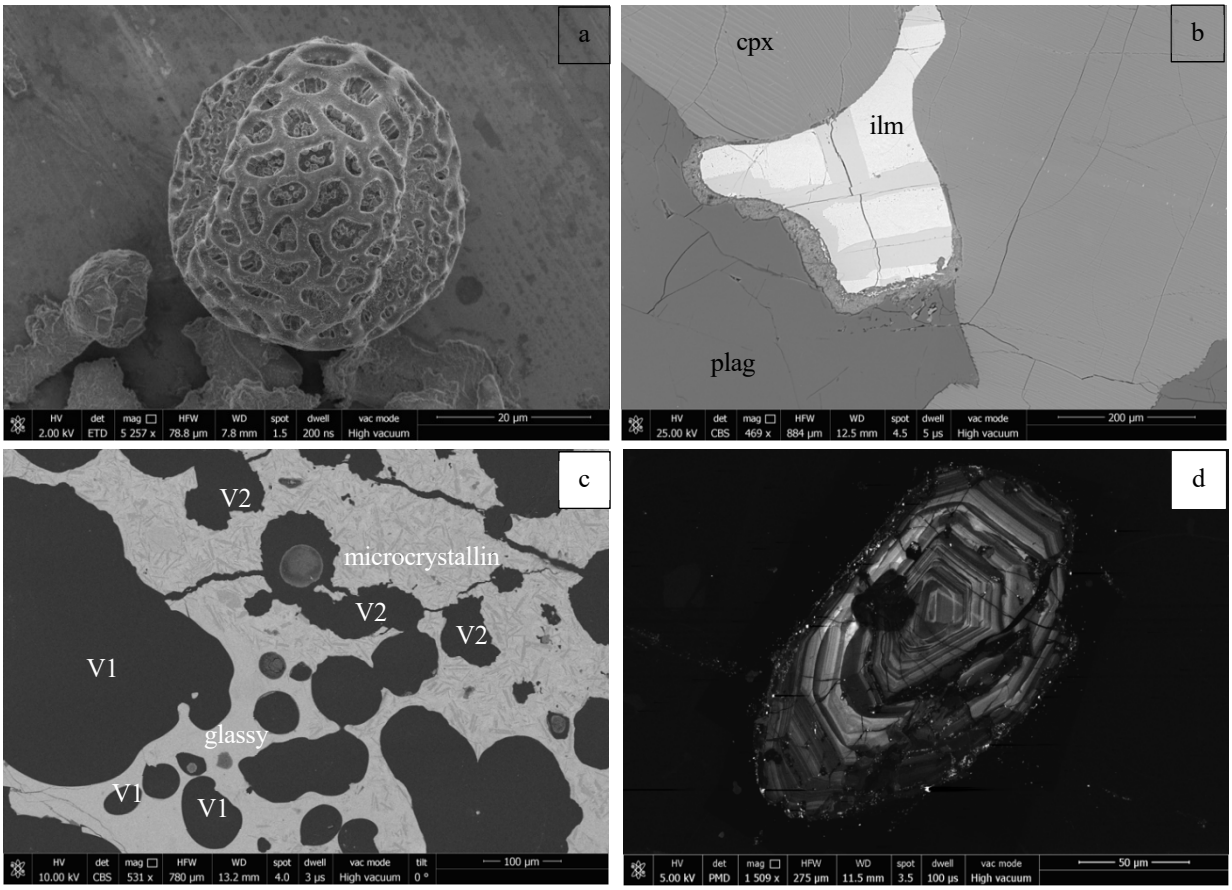

Figure 1. a) SE image of pollen. b) BSE image of an intruded rock in Skaergard, Greenland. Plag - plagioclase, Cpx – clinopyroxene and ilm – ilmenite. Note how both ilmenite and cpx show exsolution features of different scales. c) BSE image of lava. Note how the vesicles have smooth edges and generally more round when next to glassy basaltic melt (V1) and those surrounded glass with many crystals (i.e., microcrystalline) show rougher edges (V2). These kind of observations are important when considering the eruption dynamics of this sample. d) CL image of a zircon grain. In BSE this grain would seem to be homogenous.

3.2. Backscattered electrons (BSE)

Geologists often prepare their samples as thin sections; a rock slice up to 2 by 35 mm in size, polished down to a slither of 30 micrometres, which is mounted on a glass slide. A BSE image is essentially a phase map without definitive information on the chemical composition but rather an image of the relative average molecular mass differences of adjacent phases (Fig. 1b). Other useful image analysis done on BSE images is looking at vesicles (bubbles) in lava samples (Fig. 1c). This provides information on the viscosity of the melt before eruption and, therefore, an important insight into the mechanism of a volcanic eruption. This is essential when considering the hazards a particular eruption can pose. Shape, zoning and any exsolution features (Fig. 1b) in crystals are typical other examples how BSE images prove useful to geologists.

3.3. Combined EDS and BSE phase mapping techniques

An example of combining these techniques is quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN), which is a fully-automated microanalysis system that enables quantitative chemical analysis of materials and generation of high-resolution mineral maps and images as well as porosity structure [1]. Today many different approaches have been used to enable geologists to make large area (> 2 cm^2) phase maps. Phase mapping, and particularly larger areas of mapping that are now accessible to us, aids geologists to, for example, more readily and accurately measure (and, therefore, quantify) the modal proportions of different minerals present in a sample in addition a visual representation of the sample allowing for textural and spatial distribution of different minerals (Fig. 2).

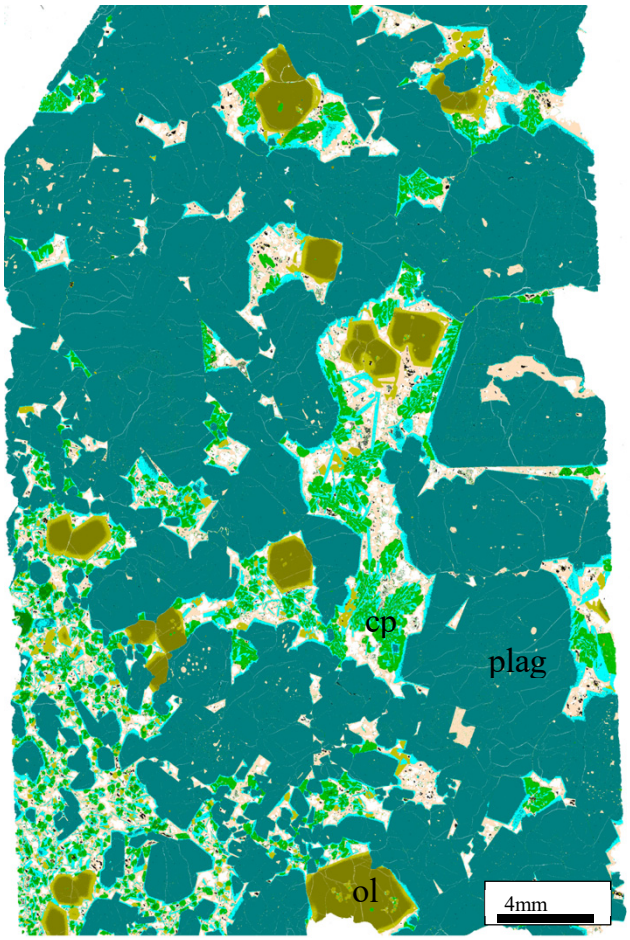

Figure 2. A QEMSCAN image of a basaltic rock from Iceland. Here the data was processed to pick out zoning of different phases to be able to see the cores and rims (i.e., zoning) of each phase. By measuring the change of certain elements across a zoned crystal, one can apply diffusion modelling to elucidate how long this crystal was in a magma chamber before the magma erupted. This information is important when trying to understand volcanic eruption dynamics. Plag – plagioclase (turquoise with brighter/lighter turquoise pointing out different Na content in the rim of the phase), ol – olivine (yellow green with lighter rims showing higher Fe content) and cpx – clinopyroxene (bright green).

3.4. Wavelength-dispersive X-ray spectrometry (WDS)

One might find one of these detectors mounted on an SEM, but usually these are mounted on specialised machines with up to 5 WDS around a single electron column; an electron probe microanalyser (EPMA). A lot of work performed using WDS analysis, focusses on changes in chemistry in a crystal; in major elements (those present in concentrations greater than 10 wt%) but more crucially trace elements (those present in concentrations below 500 ppm). For example, Cr-spinel found in Icelandic lavas were found to be chemically zoned. Using the diffusion of Cr and Al across these grains (Fig. 3), it was demonstrated that these magmas are stored for hundreds to thousands of years at the crust-mantle boundary. This discovery elucidates the time scale for understanding how magma is created and stored and how it erupts [2].

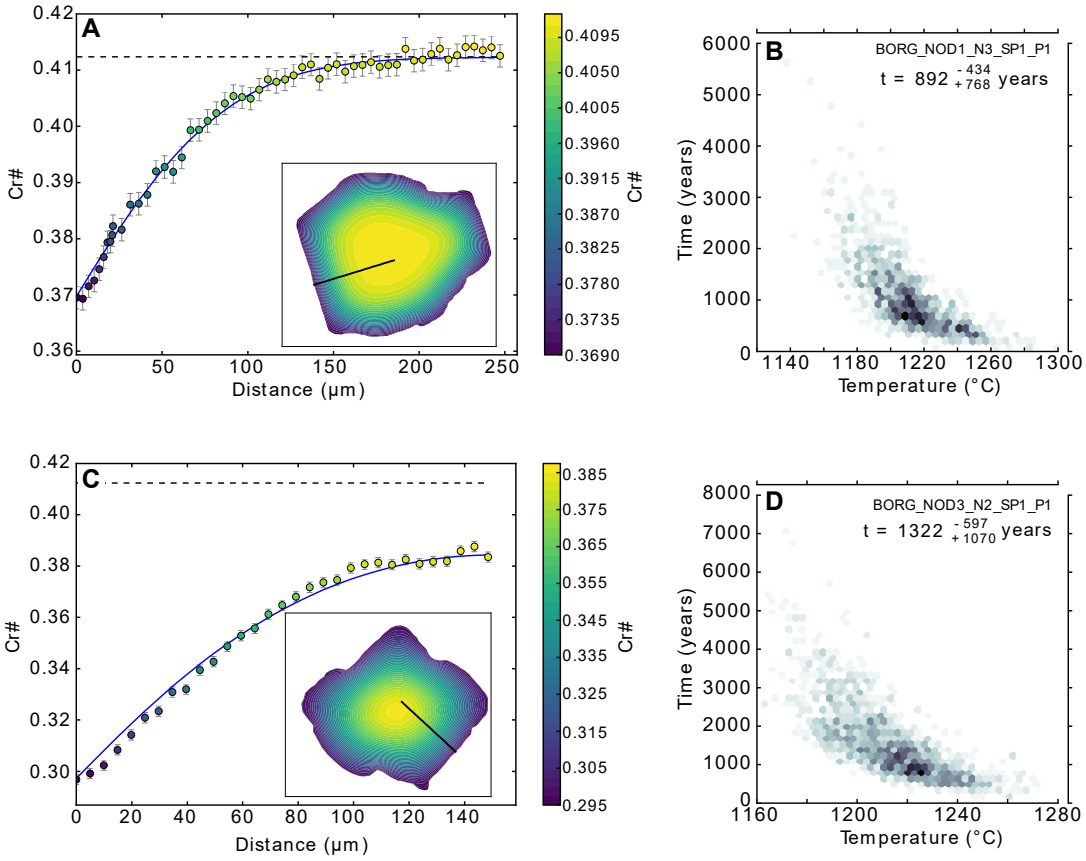

Figure 3. Timing diffusive equilibration of Borgarhraun (Iceland) spinel crystals. A and C) 1D Cr# profiles measured by electron microprobe microanalysis across Borgarhraun spinels. Blue curves show the modelled 1D fit from the 2D finite element diffusion model (insets). Dashed lines are model initial conditions. The error bars are 1σ standard deviations based on analytical uncertainties. B and D) Temperature-time density plots for posterior distributions from the Bayesian inversion [2].

3.5. Cathodoluminescence (CL)

Some minerals are seemingly chemically homogenous and thus show very plain BSE images. However, trace quantities of particular elements in some phases fluoresce giving rise to very beautiful images demonstrating a variation in composition.

Geochronology – Zircon ($ZrSiO_4$) grains are often referred to as 'geological clocks' due to small amounts of radioactive uranium isotopes and their decay products that are trapped into the crystal structure during crystallisation. These minerals are extraordinarily resistant to erosional processes, and are often exposed to different crystallisation events, thus each crystallisation period will have a U/Pb isotope ratio (U does not move in the zircon crystal). These different growth histories are not visible in conventional SE or BSE imaging techniques, but vital to illustrate as then areas can be careful selected to date them by means of ion microprobe techniques. Using CL, these different areas (and thus ages) of zircon are easily identified (Fig. 1d). This method was used to identify good candidates for dating zircons, which lead to dating the oldest terrestrial material found on Earth – The Jack Hills zircons (Australia) at 4,404 6 8 Myr [3].

Geo-thermobarometry– is the quantitative determination of the temperature and pressure at which a metamorphic or igneous rock reached chemical equilibrium. In this example, we use CL to identify different zoning regions in quartz grains that are subsequently analysed for trace amounts of Ti on the EPMA. Titanium is one of many trace elements to substitute for silicon in the mineral quartz. This substitution is temperature dependent, providing an opportunity to calculate what temperature a particular quartz grain has experienced [4].

4. A CURRENT STUDY USING THIS TECHNIQUE IN MY LABORATORY

The overall purpose of the project is to use temperature estimates from contact metamorphosed sediments that occur around granite intrusions. The temperature versus distance profiles of the metasediments provides important constraints on the thermal evolution of the region during granite emplacement and may provide insights into potential emplacement mechanisms of the granite. As the granite is emplaced into the crust it progressively heats the surrounding rocks. The temperature estimates and distances of the samples from the granite can be used in conjunction with thermal models to better constrain the mechanisms of granite body emplacement (Fig. 4). The data may also be used together with larger scale tectonic models to see how large scale granite emplacement episodes may impact the amount of heat within the crust and its influence of crustal deformation.

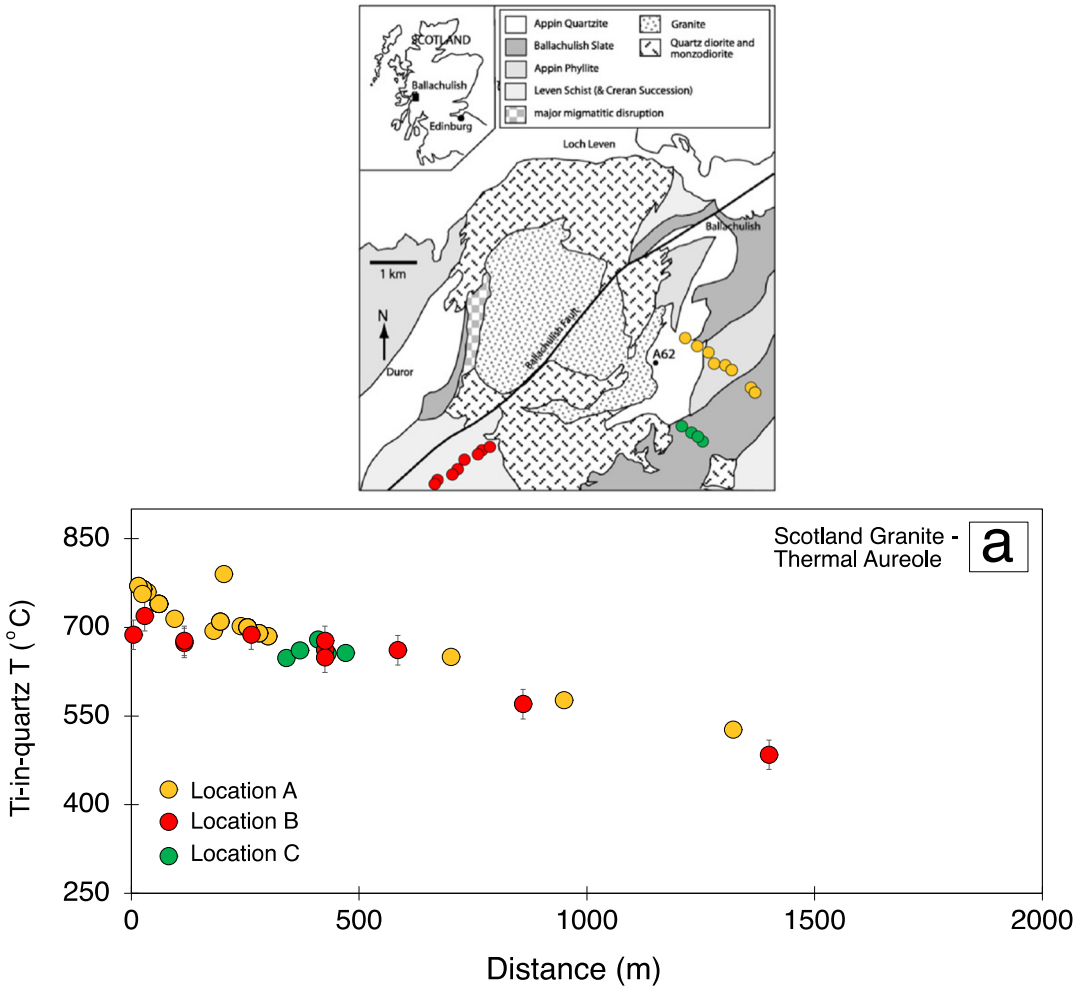

Figure 4. a) The locations of all samples used in this study. The samples are from the metasediments that surround a granite in north-west Scotland. Samples were taken along traverses from the contact of the granite to regional metasediments; b) The temperature versus distance profiles for each of the traverses shown on the map in a). All temperatures are from Ti-in-quartz thermometry obtained on an EPMA machine. The temperature versus distance profiles are consistent between the locations and are consistent with earlier thermometry done on similar rocks.

4.1. Electron backscattered diffraction (EBSD)

By tilting the sample to 70° with respect to the incident beam, the electron beam scatters to produce several bands that are related to the crystal structure and orientation. It is a powerful technique allowing for *in-situ* analysis and allows for exploring strain analysis in addition crystal orientation (Fig. 5). This technique aids us to look at single grains within a sample, and their relationship to neighbouring grains providing some insight into what kind of forces the rock may have experienced in its last stage of formation. EBSD has proven to be pivotal when understanding diffusion of elements across a grain of a given composition (i.e., mineral), as depending on the space group the mineral crystallises in, diffusion might be anisotropic,

therefore, it is important to know in what direction, and, therefore, along which axis you are measuring the diffusion profile. One such mineral, which is a very common mineral, used for diffusion modelling is olivine ($(Fe,Mg)_2SiO_4$).

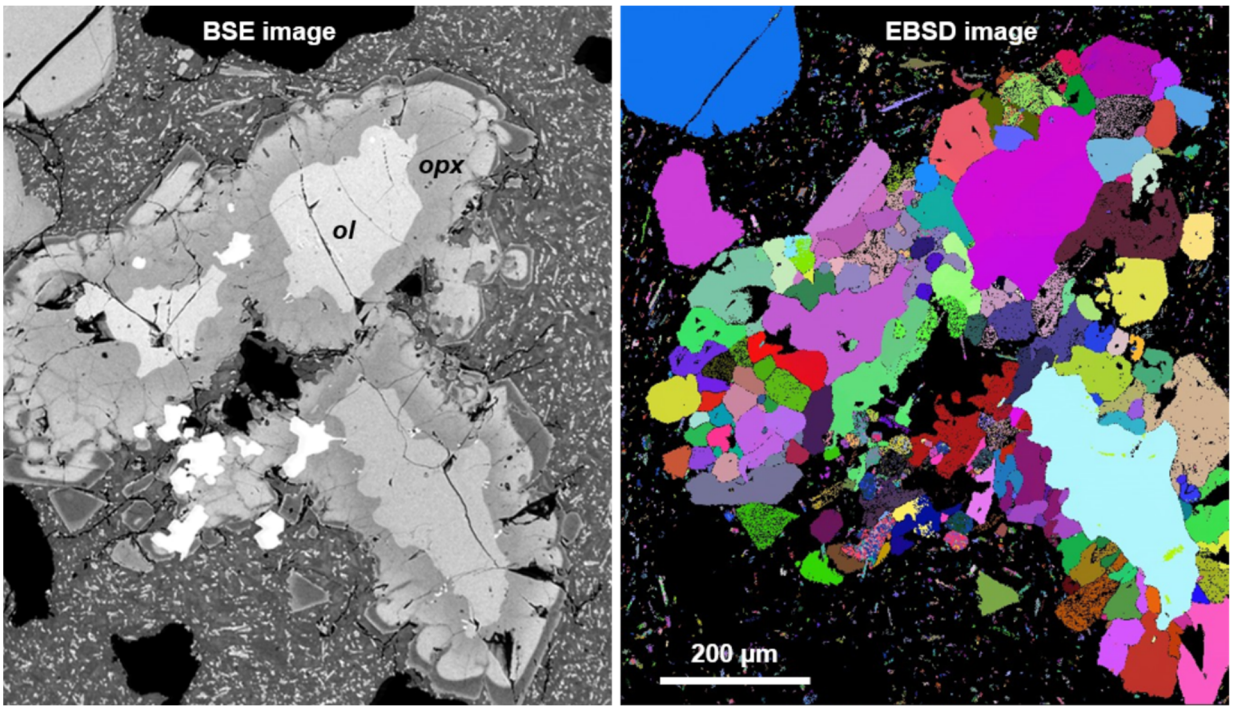

Figure 5. Olivine (ol) and orthopyroxene (opx) crystals in a lava flow from Mount Ruapehu, New Zealand. The EBSD image on the right demonstrates how sub grains of each phase have different orientations (different colours). This technique opens up ways to measure the crystal orientation and strain analysis *in situ*.

5. *A CURRENT STUDY USING EBSD COMBINED WITH AN IN-SITU DEFORMATION STAGE IN MY LABORATORY*

Understanding and being to quantify the tectonic stress in lithospheric plates is key to evaluating a breadth of geological phenomena, such as the evolution of major ductile shear zones. One method of estimating past stress magnitudes is to measure microstructural elements that can be related to stress through experimental calibrations, a technique known as piezometry [5]. Once a sample has been deformed under controlled laboratory conditions, EBSD is used to quantify the relationship between this stress and the sub-grain size.

Further to developing this piezometer, faster EBSD detectors have allowed for *in situ* rock deformation experiments to take place in house without the need of going to a synchrotron. In the field, you are able to see the result of how deformation affects a given rock type. Here a specially designed stage, connected to a controller (Fig. 6), allows us to monitor the progress while applying a continuous steady force (and/or heat) to the sample. The stage is cooled by

water from a chiller. One of the experiments involved tracking the deformation of halite at 450 °C (sample was heated at a constant rate). The sample is heated to 450 °C, and then deformed by a pre-defined percentage during which a video is recorded of the SE signal while it gets squeezed. Once the sample has been squeezed by a certain percentage, it is left to cool, after which the EBSD camera is inserted to see the resulting deformation. Using the kernel average misorientation (KAM), which is a measure of how much the orientation of each pixel in the EBSD map deviates from its neighbours thus making it ideal for examining low-angle boundaries in deformed materials, it shows that the in-situ stage, together with EBSD, can be used to map the evolution of these low-angle boundaries with strain during deformation (Fig. 7).

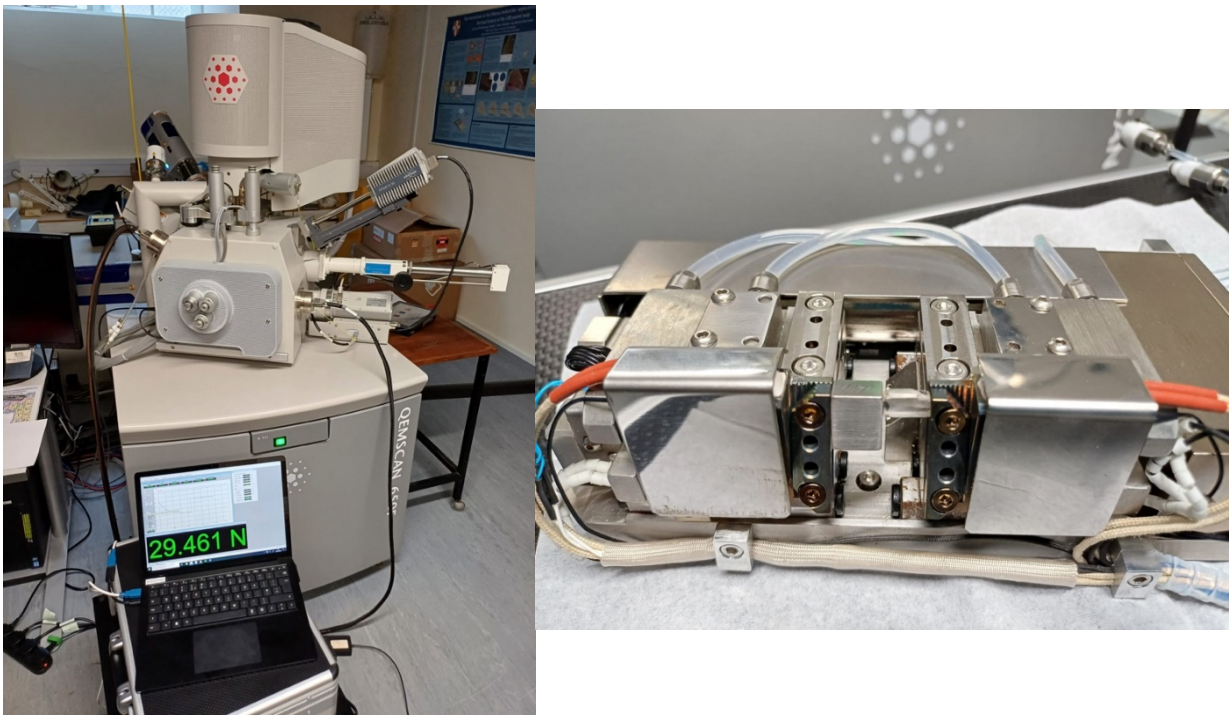

Figure 6. The set-up of the in-situ deformation stage (right), connected to a controller (left). Note the small crystal of halite (about 8 mm in length) mounted between the jaws. This is the setup of the in-situ stage before mounting it onto the stage of the SEM.

6. CONCLUSION

This is just a small selection of ways a geologist might use and electron microscope technique for their research. Other instruments, not discussed here, such as a focussed ion beams (FIB) for sample preparation for transmission electron microscopy (TEM). Today a multi-disciplinary approach is often used in geology due to the complicated nature of natural samples. I hope I have been able to demonstrate how an electron microscope, and their attached detectors, are vital for researchers in Earth Sciences and Geology.

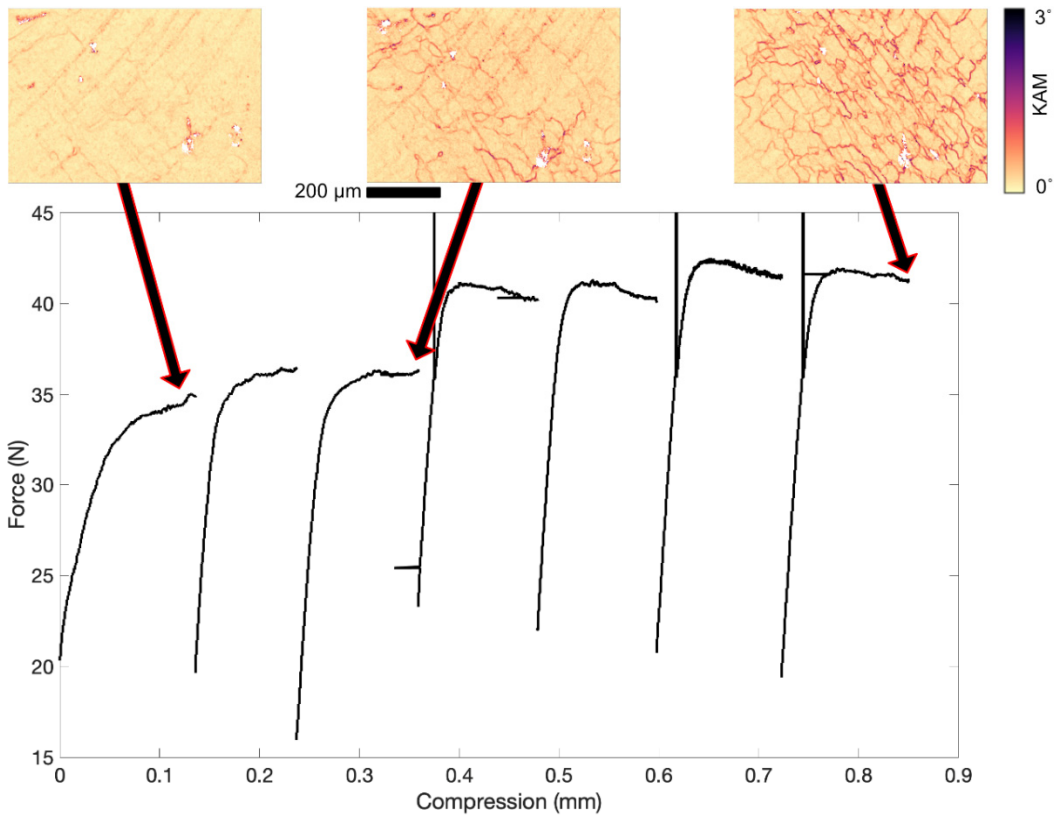

Figure 7. This image contains a plot of the mechanical data (force versus mm compression) for sample MGDi_0032 (a specimen of halite that was deformed *in situ* at 450 °C and a motor speed of 0.02 mm/min). Note the multiple cycles of deformation as described above. EBSD data was collected at the end of each cycle, and in this instance, three kernel average misorientation (KAM) maps are illustrated showing where in the deformation series they were taken. Note how the misorientation increases from left to right (increasing deformation).

7. *ACKNOWLEDGEMENTS*

Iris would like to thank Zach Sudholtz for providing her with images for an example of measuring Ti in quartz and many thanks to David Wallis, Catherine Goddard, Tom Breihtaupt, Harison Weissman for allowing me to use their most recent *in-situ* experiments results for this presentation.

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