

## A Closer Look At Hydrothermal Alteration and Fluid-Rock Interaction Using Scanning Electron Microscopy

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### ABSTRACT

Traditional techniques routinely used for hydrothermal alteration studies are X-ray diffraction (XRD) and petrographic microscopy. The addition of scanning electron microscopy (SEM) to these standard mineralogical analyses greatly enhances our knowledge and understanding of fluid-rock interactions in our geothermal systems. SEM observations on core from geothermal fields in New Zealand and USA show the advantages of adopting SEM to better understand subsurface processes. SEM imagery reveals detailed nano to micron scale information on crystal-crystal relationships. For example significant changes in subsurface environmental conditions such as cooling after boiling, or an increase in acidity at depth over time, can be tracked using SEM. The advantage of SEM is that it examines intact rock samples while XRD requires samples to be crushed and samples for petrographic thin sections are ground down to produce smooth surfaces. These crushing and grinding processes remove much of the mineralogical detail. SEM imagery also reveals crystal-clay relationships which are important, as in some settings clays attach to and alter crystal surfaces which influence porosity, permeability and rock strength. In other cases the clays do not alter crystal surfaces. Furthermore, SEM findings in this study include detail on clay-clay relationships, such as clay inter-bedding, differences in clay maturity, crystallinity and/or quantity. SEM observations allow fundamental questions to be addressed such as: (1) What influence do crystal and clay morphologies have on permeability? (2) How do crystal and clay inter-relationships affect permeability and/or rock strength? (3) How are the rocks reacting to ongoing changes in subsurface environmental conditions? (4) Are certain lithologies better suited for production or injection? (5) Which stratigraphic units are more likely to compress resulting in subsidence at the surface? SEM is a useful technique to examine fine-scale, fluid-rock interactions on core from production or injection wells.

### 1. INTRODUCTION

Traditional techniques used for mineralogical studies such as petrographic microscopy and X-ray Diffraction (XRD) require rock samples to be prepared in such a manner that often much of the information about fluid-rock interaction is lost. In the case of petrographic microscopy, thin sections of rock samples are ground down to create a flat surfaced, thin veneer of rock. XRD requires rock samples to be ground into a powder prior to analysis, losing all record of visual mineralogical relationships between individual crystals and their matrix. While both techniques provide useful information about the mineralogy of rock samples and fluid-rock interactions, Scanning Electron Microscopy (SEM) extends and enhances these traditional techniques. The advantage of SEM is that sample preparation enables whole rock samples to be used. This preparation method preserves vital information such as subtle fluid-rock reactions and crystal-clay interactions. Presented within this study are SEM images that show the level of detail that can be obtained from SEM. Examples shown in this paper are from a number of different geothermal reservoirs within New Zealand and the USA. Specific geothermal fields are not stated as it is the technique used to examine the rocks that is of importance in this paper, not the location of the fields.

### 2. SECTIONS THAT FOLLOW

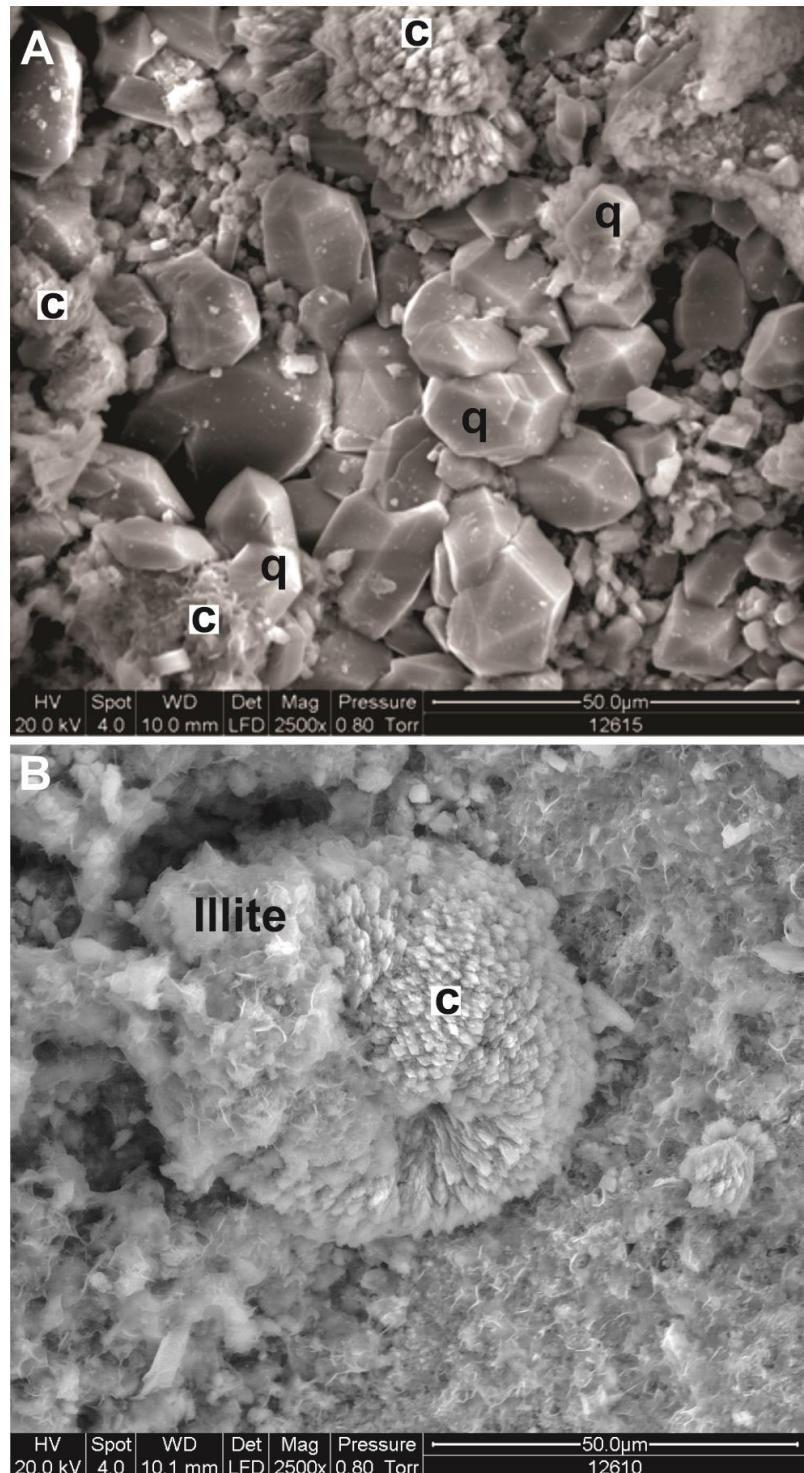
Fine-scale alteration components such as dissolution textures, water-rock interactions, clay morphologies and crystal-clay relationships were tracked using scanning electron microscopy (SEM) and standard petrographic microscopy. SEM sample preparation consisted of mounting a representative section of core onto an aluminum stub and powder coating it with platinum (10 nm coating thickness) for ~ 7 minutes at 10 mA using a high resolution Polaron SC7640 sputter coater. Samples were examined under the SEM using a Phillips (FEI) XL30S field emission gun. Operating conditions were 5 keV accelerating voltage, a spot size of 3  $\mu$ m, and a working distance of 5 mm. Electron Dispersive Spectroscopy (EDS) analyses were performed on samples to obtain semi-qualitative compositional data. EDS operating conditions were 20 keV accelerating voltage, with a spot size of 5  $\mu$ m, and a working distance of 5 mm. EDS shows the elemental composition of the crystal you are analyzing enabling its mineralogy to be determined. Standard petrographic microscopy was used to determine microscale textures, which were compared with the SEM results. X-ray Diffraction (XRD) was used to determine the mineralogy of the samples.

### 3. RESULTS

#### 3.1 Reservoir Conditions

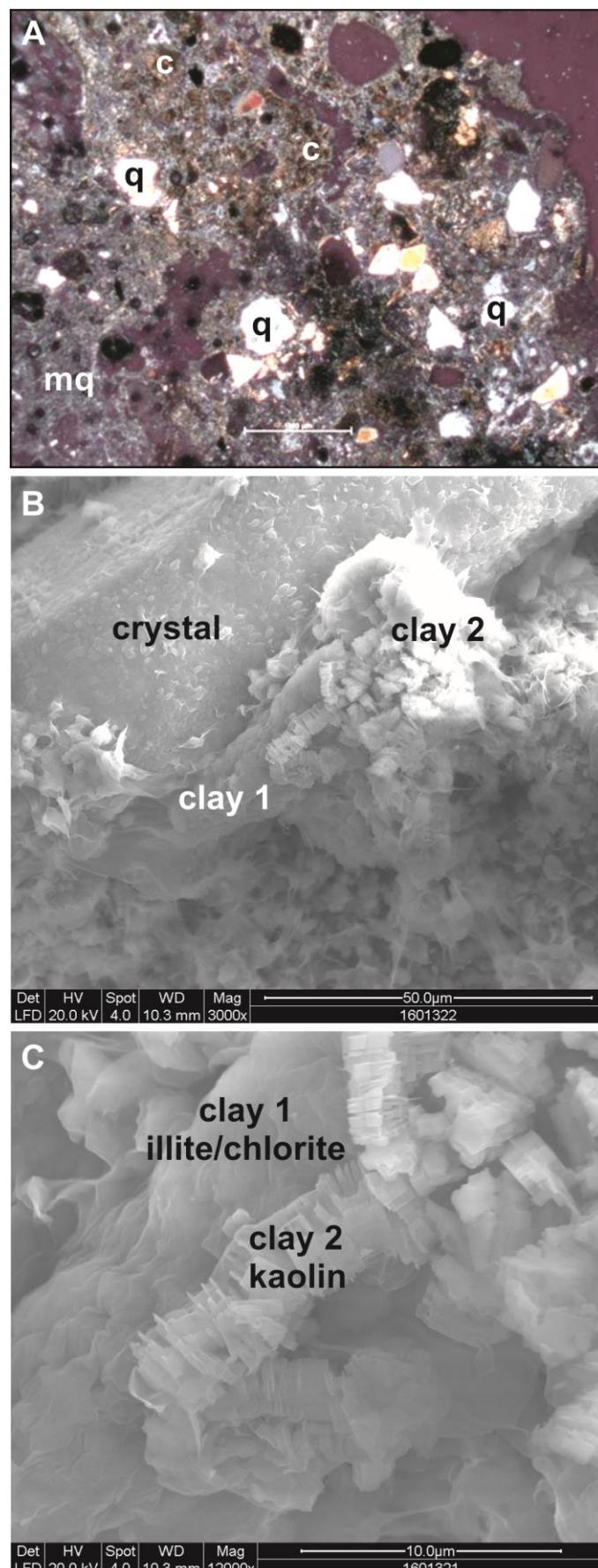
The examination of cored rocks from geothermal drillholes using SEM can assist in our understanding of reservoir conditions. Often such changes are subtle requiring high resolution, fine-scale imaging of intact samples to appreciate the full extent of the host rock and thermal water interactions. Figures 1 and 2 provide examples of SEM imaging that capture the subtleties of fluid-rock interactions within geothermal reservoirs. Figure 1A displays the relationship between bladed calcite and quartz where at two sites newly-forming quartz crystals can be seen growing from bladed calcite. This relationship occurs when deep, near-neutral alkali chloride fluid flashes and boils as it ascends through volcanic host rocks, causing the fluid to lose steam and dissolved gases such as CO<sub>2</sub>. The rapid loss of CO<sub>2</sub> near the site of first boiling results in the deposition of bladed calcite (Browne, 1978, Tulloch, 1982,

Simmons and Christenson, 1994). Upon cooling after boiling, quartz crystals form. Figure 1B illustrates the relationship between bladed calcite and illite where illite formed after bladed calcite. Illite formation is favoured by the cooling of CO<sub>2</sub>-rich fluids. Therefore identifying bladed calcite/quartz/illite sites within a core by SEM imaging enables the tracking of locations and depths of subsurface flashing and the identification of CO<sub>2</sub>-poor versus CO<sub>2</sub>-rich reservoir fluid.



**Figure 1: SEM images of core from a geothermal field. (A) The formation of quartz (q), bladed calcite (c), followed by further quartz formation. (B) Illite visible on top of bladed calcite (c) indicating it formed after the calcite.**

Tracking changes within the reservoir fluid is important for maximizing the potential of both production and reinjection wells, as well as identifying possible sites of future subsidence. In Figure 2, SEM reveals the occurrence of illite and kaolin, whereby kaolin is observed resting on top of illite (Fig. 2B-C). Micro-environmental conditions for illite and kaolin differ. A pH of approximately 5 favours illite formation and a pH of around 3 favours kaolin formation (Allen et al., 1996). This finer-scale detail is not visible using petrographic microscopy (Fig. 2A). Such information is useful in many ways. For example, (i) it assists with assessment of well conditions with respect to well corrosion and fluid composition, (ii) mapping sections of a geothermal field that may be heating up or cooling down, (iii) identification of potential subsidence sites due to acidic alteration of the host rocks leading to a weakening and subsequent compaction of the rocks (Lynne et al., 2011).



**Figure 2: Tracking changes in the geothermal reservoir environmental conditions based on mineralogical observations of cored rock samples. (A) Petrographic microscope image shows quartz crystals (q) in a fine grained micro-crystalline quartz (mq) and clay matrix (c). (B-C) SEM images reveal illite/chlorite underlying kaolin inferring a decrease in temperature and increase in pH of the subsurface environment. Such detail is not evident in (A).**

### 3.2 Clay minerals

Within geothermal systems clay minerals are known to often cause problems, specifically with decreasing permeability of wells. XRD clay mineral analysis provides a quick and easy way to identify which clay minerals are present within rock samples while petrographic examination reveals an overview of clay distribution within a host rock. SEM imaging coupled with EDS analysis offers additional information not retrievable using other techniques. SEM imaging reveals the degree of clay crystallinity (Fig. 3A-C), and shows the variation in morphological characteristics related to the degree of maturation within the same clay type (Fig. 3A-C). This information is not recoverable from petrographic microscopy (Fig. 3D). Also SEM is useful for documenting morphological differences that can be related to subtle variations in the composition of mixed clay assemblages (Fig. 3E-G). Petrographic microscopy cannot offer this fine-scale detail (Fig. 3H). Such morphological and/or compositional differences may affect well permeability therefore it is beneficial to include SEM imaging of clay minerals when studying the mineralogy of core from geothermal systems.

### 3.3 Crystal degradation and crystal-clay relationships

Fluid-rock interactions often result in hydrothermal alteration of host rocks which affect measurable parameters of the rock such as density, porosity, permeability, clay content and rock strength. For example, precipitation of new minerals decreases the rocks porosity and potentially its permeability. Dissolution however, can increase its porosity and permeability and weaken the formation if sufficient dissolution takes place.

SEM provides insights to the subsurface processes taking place and altering rocks (Fig. 4). The initial formation of open chlorite platelets (Fig. 4A) and illite (Fig. 4B) reveals different clay morphologies and crystal-clay relationships. In Figure 4A, open chlorite platelets protrude from feldspar crystals but the crystals are relatively unaltered. In Figure 4B the initial formation of illite is shown as elongated strips attached to the entire surface of a partially degraded feldspar crystal surface. Figure 4C-D shows clay minerals with a mixed chlorite-illite composition and two distinctly different crystal degradation processes. Figure 4C reveals complete dissolution of half of a feldspar crystal as it transforms into chlorite-illite clay minerals. This process would increase the host rocks porosity and possibly permeability, as well as weaken the formation. Figure 4D shows partial dissolution of the elongated surface of a feldspar crystal and transformation of the crystal surface into clay minerals. Here, porosity, permeability and strength of the host rock would be less compromised than that shown in Figure 4C. Figure 4E-F show crystal-clay inter-relationships where the clay and crystals co-exist with little effect on the overall porosity, permeability or strength of the formation. Figure 4E illustrates how illite clay can be present in abundance within the matrix of a rock but not attach to or erode crystal surfaces. Figure 4F shows chlorite embedding a lithic fragment with no fragment degradation.

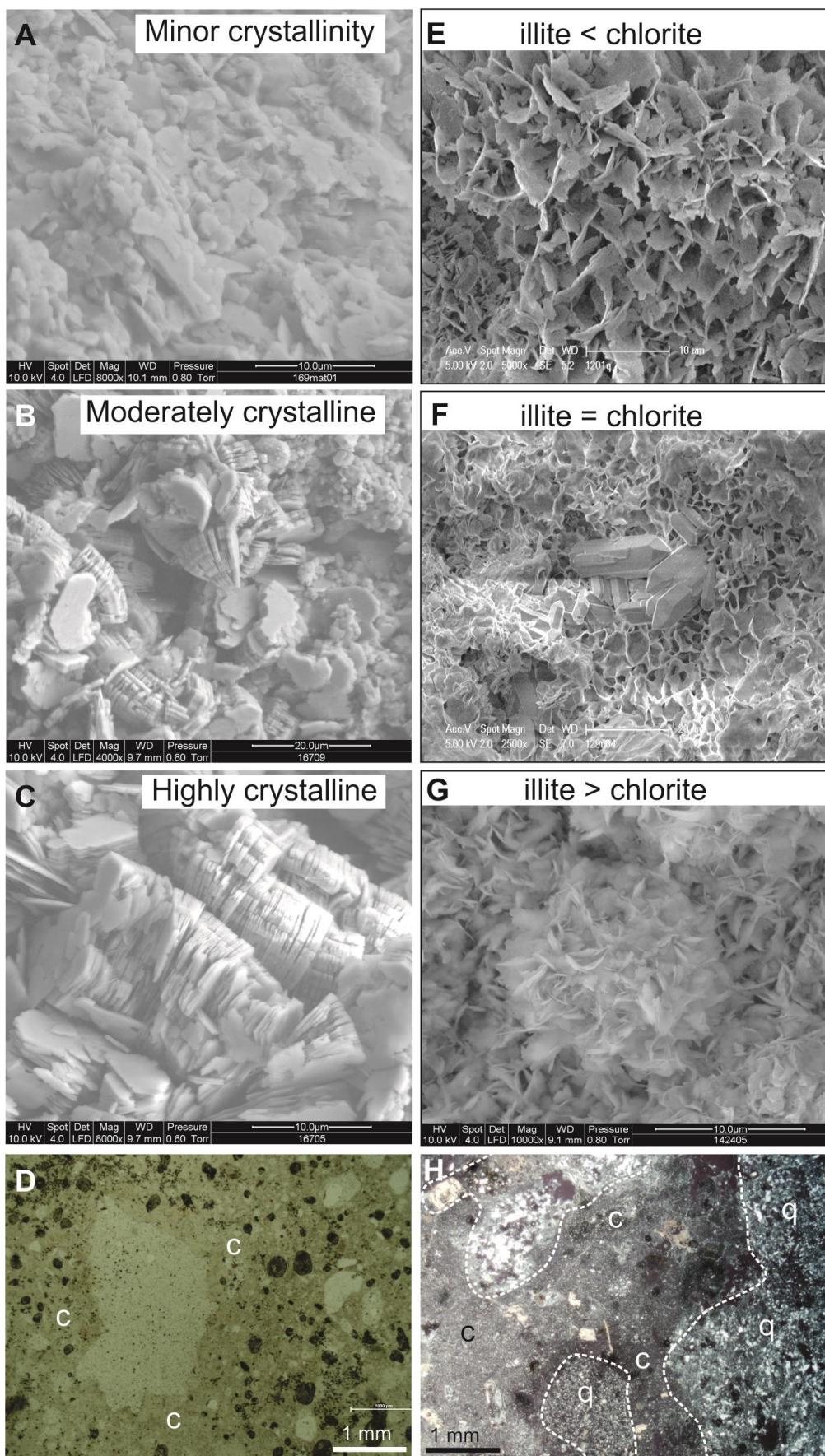
### 3.4 Minor quantities of minerals detectable using SEM

All analytical techniques are limited by their lowest detection limits. However, it may be that a trace element or mineral of significant importance is present in minor quantities and undetectable due to equipment limitations. SEM and EDS can determine subtle changes within a host rock, such as minor elemental changes across micro-fractures, at crystal or formation boundaries and can image crystals or clays even if only present in minor quantities. Often it is these minor elemental changes that provide important information about subsurface environments and are of significance for exploration of hydrothermal systems.

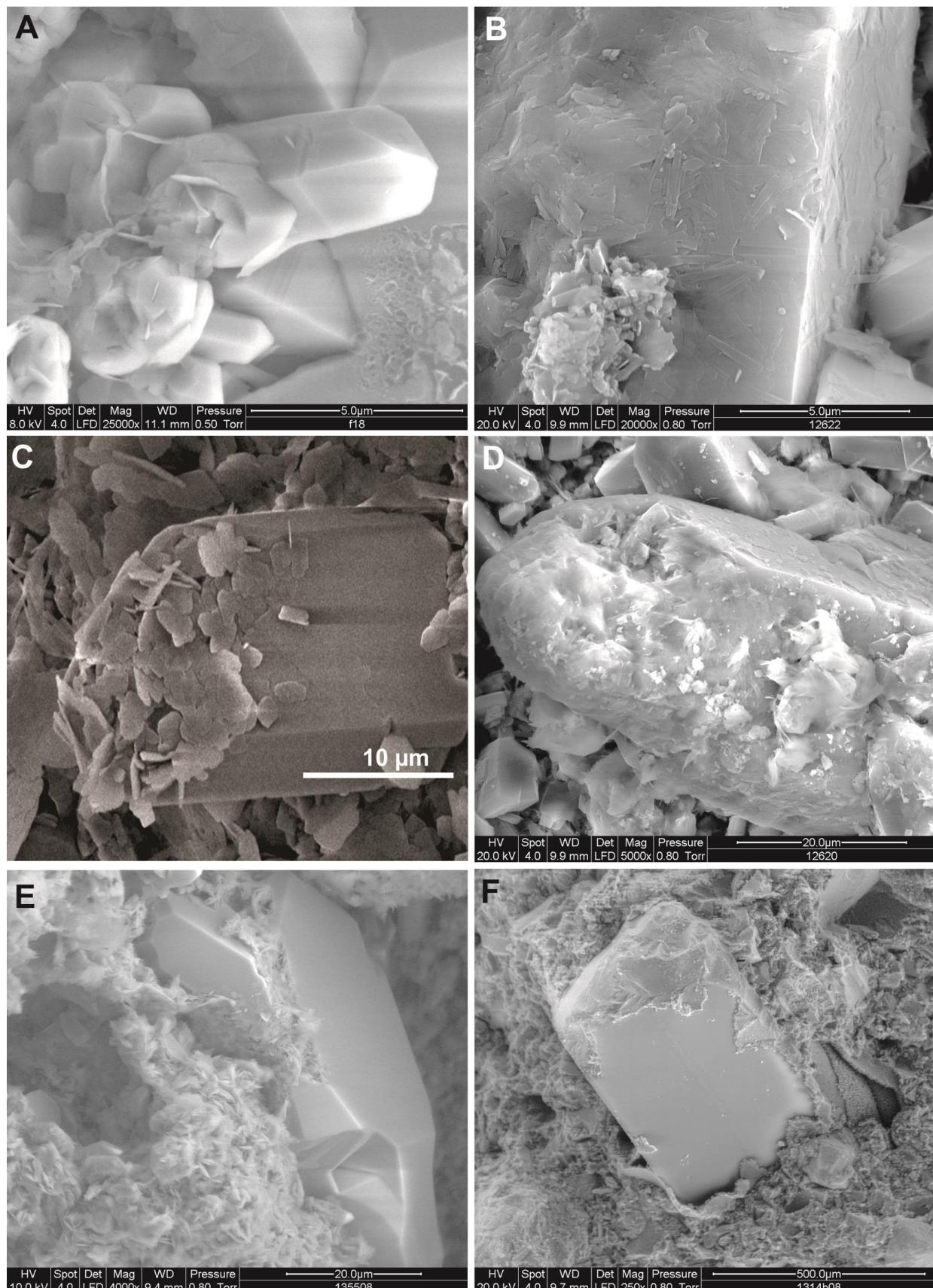
Figure 5A-B shows SEM images of gold within a siliceous sinter deposit (hot spring rock). This sample was recovered from a core taken within a geothermal field. XRD and XRF analyses of this sample only detected the presence of silica, as gold was not present in sufficient quantity to be detected by these methods. Figure 5A-B reveals the bulk of the rock consists of opal-A/CT silica where the opal-A/CT nanospheres are pseudomorphing botryoidal opal-A spheres (Lynne et al., 2005). Using SEM, banded gold was imaged within some of the low areas between silica spheres. The gold strands form long ribbon-like structures. EDS of the banded elongated structures confirmed it to be gold. This sample was collected from a sinter located within a known gold mining area, however, this example shows how useful SEM can be to detect subtle but significant mineralogical information about an area.

## 4. CONCLUSIONS

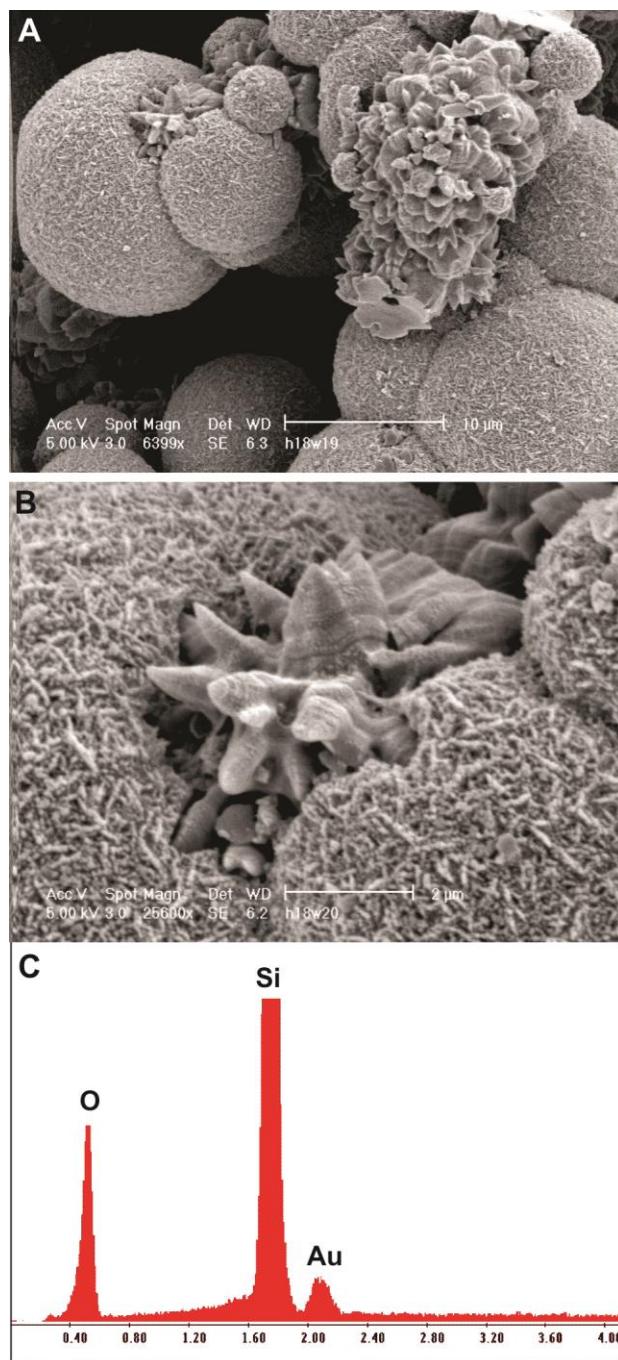
SEM is a useful technique for all aspects of mineralogical studies on rocks from geothermal systems and complements traditional analytical techniques such as petrography and XRD. SEM, petrography and XRD all offer useful data and when combined provide detailed information on fluid-rock interaction. Petrographic analysis documents large-scale, mineralogical relationships while XRD identifies mineralogical composition. The SEM high resolution detailed images taken at the nanoscale provide information about water-rock interactions and subsurface processes that are not obtainable using other techniques. Identifying subtle variations in crystal and clay morphologies, crystallinity, compositions and crystal-clay inter-relationships are important for our understanding of broader issues within our geothermal systems such as: (1) identifying boiling zones; (2) mapping the distribution of CO<sub>2</sub>-rich versus CO<sub>2</sub>-poor fluid movement in the reservoir rocks; (3) tracking temperature changes within a system, (i.e., is it heating up or cooling down with time); (4) identifying zones of potential weakness due to crystal degradation which may lead to subsidence at the surface; (5) documenting sites where environmental changes are taking place over time such as a pH decrease which may lead to a weakening of the formation; (6) mapping the distribution, composition and morphology of clay minerals as clays often play a significant role in decreasing productivity of both production and reinjection wells; and (7) identification of minor but significant minerals within a host rock.



**Figure 3: Clay morphologies.** (A-C) Kaolin clay in a minor, moderate and highly crystalline form reveals different morphologies for each degree of crystallisation. (D) Clay (c) shown in (C) appears as a tan coloured, fine-grained matrix under petrographic microscopic examination. (E-G) Mixed illite-chlorite clay minerals with different quantities of illite versus chlorite show a range of morphologies. (H) Petrographic microscopy image shows overview of (G) with clay (c) and micro-crystalline quartz (q).



**Figure 4:** SEM images display various degrees of crystal degradation and clearly reveal the spatial relationships between crystals and clays. (A) Early chlorite formation on some feldspar crystal surfaces. (B) Early illite formation shown as thin strips on uneven, partially degraded, feldspar crystal surface. (C-D) Transformation of feldspar crystals into mixed chlorite-illite clay minerals. (E) Illite clay surrounding and infilling fractures within a feldspar crystal but no illite has attached to the crystal surface. (F) Lithic fragment embedded in chlorite. No degradation of fragment surface.



**Figure 5: Banded strands of gold within an opal-A/CT siliceous sinter deposit identified in core recovered from a geothermal field. (A) Overview of gold strands within an opal-A/CT siliceous sinter deposit. (B) Elongated strand of banded gold in low area surrounded by aligned rows of opal-A/CT nanospheres. (C) EDS scan of elongated strand of gold shown in (B).**

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