Use of Environmental Scanning Electron Microscopy to Study Uncoated Minerals

J. Theo Kloprogge1, Loc V. Duong1,2, Ray L. Frost1 and Thor E. Boström1,2
1. Inorganic Materials Research Program, School of Physical and Chemical Sciences; 2. Analytical Electron Microscopy Facility, Faculty of Science, Queensland University of Technology, Australia

INTRODUCTION
Scanning electron microscopy (SEM) with or without energy or wavelength dispersive X-ray detectors for chemical analysis (also known as microprobe or electron probe microanalysis) has been and still is routinely used in the study of rocks and minerals. In order to use SEM and microprobe facilities the samples have to be coated with a thin conducting layer of gold or carbon in order to prevent charging of the sample. In the past twenty years the technique of low voltage SEM (LVSEM) has been developed to overcome the problem of charging of minerals without a coating. The use of LVSEM permits the imaging of uncoated samples since the secondary electron yield coefficient of the sample at low electron beam voltages either approaches or exceeds unity with as a result no net charging of the mineral surface [1,2]. However, the use LVSEM is limited by its relatively low spatial resolution of about 50 nm compared to normal SEM with a resolution of up to 6 nm.

The environmental scanning electron microscope was developed in the mid 1980s [3,4]. This electron microscope offers many extras compared to the normal SEM. The term environmental in the name indicates that one can vary the environment inside the vacuum chamber through a range of pressures, temperatures and gas compositions. But at the same time it retains all the performance advantages of the normal SEM but removes the high vacuum constraint on the sample environment. This enables one to study all sorts of materials, no matter whether they are wet, oily or non-conductive, with high-resolution secondary electron imaging conditions in a gaseous environment of practically any composition [5].

In this article we will demonstrate the use of low voltage ESEM to study minerals in their natural setting in rocks at much higher resolution and better image quality than can be achieved in normal LVSEM. In addition we will shortly show that ESEM can also be used to study mineral reactions like decomposition due to heating in situ as well as to study the behaviour of minerals as a function of relative humidity in a low vacuum chamber.

MATERIALS AND METHODS
All the mineral samples used in this study were from the private collection of one of the authors (JTK). For the decomposition experiment, synthetic weddelite was prepared by slowly mixing stoichiometric amounts of sodium oxalate and calcium chloride at 0°C. The resulting material was filtered and washed with deionised water until free of chloride (checked by the silver nitrate method). Montmorillonite SWy-1 was used without any further purification for the wetting and drying cycle experiment.

Scanning electron microscope images were obtained on a FEI Quanta 200 Environmental scanning electron microscope operated at an accelerating voltage less than 5 kV on uncoated mineral samples. In most cases the mineral of interest was still sitting in the host rock without any further preparation. Under normal high vacuum SEM the sample would have been coated with either carbon or gold in order to avoid charge buildup on the sample. After coating however, it is very difficult to remove the coating again from the very irregular surfaces present in rough mineral/rock samples.

The microscope was fitted with an FEI Peltier cooling stage with a temperature controller and K-type thermocouple for monitoring the temperature for the wetting and drying cycle experiments. A gaseous secondary electron detector with a pressure limiting aperture, mounted directly above the specimen on the heating stage, was used for electron imaging. During the wetting and drying experiments,

Figure 1:
(a) Needles of cyrilovite growing around a large quartz crystal together with another iron phosphate, possibly dufrénite or strengite. (b) Close-up of the area below the large quartz crystal. (c) Close-up of a single rounded grain of dufrénite or strengite on a needle of cyrilovite.
the detector-specimen distance was about 10 mm. The specimen chamber pressure and temperature were adjusted around 5ºC and 4 to 6 torr (water vapour).

The ESEM was fitted with an FEI water-cooled 1000°C specimen heating stage with a high-temperature controller and K-type thermocouple for monitoring the temperature. A high-temperature gaseous secondary electron detector with a pressure limiting aperture, mounted directly above the specimen on the heating stage, was used for electron imaging. During heating, the detector-specimen distance was about 8 mm. The specimen chamber pressure was maintained at 2 torr (267 Pa) water vapour. A small amount of the calcium oxalate powder was mounted onto a small aluminum cup with a thin layer of carbon paint, to ensure the particles were attached to the surface and to maintain reasonable heat conductance to the sample. No precoating with carbon or gold, as is done for standard high-vacuum SEM, was required for the ESEM observations. The oxalate sample was heated from room temperature to 750°C, at a rate of about 10°C min⁻¹, however a constant temperature was maintained during image acquisition or microanalysis. Prior to the analysis an equilibration time of approximately 10 minutes was applied.

Elemental analysis was carried out using a thin-window EDAX energy-dispersive X-ray (EDX) detector and microanalysis system. For the heating stage experiments it was not possible to analyze samples at temperatures above 400°C because the infrared radiation from the heating stage would swamp the X-ray detector. However a constant temperature was maintained during image acquisition or microanalysis. For temperatures above this value, the sample temperature was first lowered to 350°C for the analysis, and then restored to its prior setting. Since any evolved gas was constantly being pumped away and the pressure inside the chamber was kept constant, the chances of reverse reactions taking place were absolutely minimal.

RESULTS AND DISCUSSION

Figure 1a shows needles of cyrilovite grown on a large quartz crystal together with smaller quartz crystal covered by a thin coating and rounded aggregations of a second iron phosphate, possibly dufrénite or strengite. A close-up of the area under the large quartz crystal clearly showed the second generation of quartz crystals and the second iron phosphate (Fig. 1b), while Figure 1c shows a close-up of a single rounded aggregate of the second iron phosphate on a single cyrilovite needle.

The second example concerned a single crystal of bixbyite. Due to the low voltage of the electron beam, surface properties were more pronounced than under normal SEM conditions of 15 to 25 kV. This is very clearly visible in Figure 2a, where we identified the (111) face in the middle of the image surrounded by three intermediate faces before reaching the {001} zone with one face visible at the right hand top of the image. Figure 2b shows a sample of radial fibrous glaucocerinite with a fine structure visible on the surface. A broken aggregate clearly exhibited the radial fibrous nature (Fig. 2c). A close-up of the surface showed that the crystals were not so much fibrous but more platy in nature (Fig. 2d).

Figure 3 shows a number of other mineral examples including tarbuttite crystals showing both etching on one face and growth steps on other faces (Fig. 3a), and very well-formed arsenolite crystals in a matrix of fibrous unidentified mineral (Fig. 3b). Although this material was not identified with certainty, chemical analysis pointed in the direction of a cobalt carbonate mineral spherocobaltite. Figure 3c shows needle-like prisms with nicely developed faces on the top of wavellite crystals. The last example concerned very thin platelets of straczekite (Fig. 3d), some of which are slightly rolled up (at the right side of the image).

Figure 4a shows an image of synthetic leconite, which did not form well-developed crystal
faces although some are visible in between rounded edges. This mineral is a hydrated ammonium sodium sulphate. At the low voltages applied in this study it was still possible to obtain evidence of its chemical composition through the energy dispersive X-ray detector but it could not be used to quantify the analysis. The observed spectrum is shown in Figure 4b. Under low voltage conditions one has to realise that the analysis will only be from a very thin layer at the top of the crystal due to the strongly diminished penetration depth of the electron beam but also that because of the low accelerating voltage only low-energy transitions of the elements can be observed. This means in practical terms that only a very limited number of elements can be observed under these conditions, such as C, O, Mg, Al, Si, S, N, etc., but elements with higher transitions energies will not be observed, for example Fe, Cu, Ni, etc.

Figure 5a shows a dry aggregate (after the first rapid wetting and drying) at the starting pressure of 4.7 torr and 2ºC. Very characteristic here is the open morphology caused by the fast evaporation of the water from between the clay layers. This is the structure often reported in the literature for SEM observations of smectitic clay samples. Wetting of the montmorillonite aggregates started at the edges of the clay layers and could be observed as slight rounding and softening of the edges. This can be explained by the fact that the clay 001 faces are rather hydrophobic compared to the charged sites on the edges formed by, for example, hydroxy groups on the unsaturated Al and Si bonds at the edges of the clay sheets. Further increase of the pressure to 5.3 torr resulted in the rapid wetting of the whole particle. Figure 5b shows the wetted sample after increasing the pressure to 5.3 torr and then slowly decreasing the pressure to 5.2 torr to prevent the clay aggregate from floating in the liquid water inside the sample holder. Full details of this wetting and drying study will be published in the near future.

In an earlier study [6] the thermal decomposition of weddelite was followed in situ using a heating stage Environmental Scanning Electron Microscopy and observed as a decrease in the oxygen and carbon content. The final reaction of CaCO3 to CaO while evolving CO2 around 600°C involved the formation of chains of very small oxide particles pseudo-morphic to the original oxalate crystals (Fig. 6b). The change in chemical composition could only be observed after cooling the sample to 350°C because of the effects of thermal radiation.

CONCLUSIONS
The use of an environmental scanning electron microscope in combination with low voltage, a heating stage or variable gas composition has been proven to be very successful in observing the morphological and chemical changes of minerals. In the case of high temperature ESEM, however, changes in chemical composition at high temperatures can only be observed after cooling the sample to 350°C because of the effects of thermal radiation (black body radiation).

These first examples of the decomposition of weddelite, wetting and drying of montmorillonite and the high resolution imaging of uncoated minerals shows that this technique can be developed into a very useful tool for geologists, mineralogists and materials scientists to test materials at high temperatures and observe their behaviour.