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Low Voltage FEG-EPMA in Earth Sciences – Problems and Solutions for Analysis of Unstable Materials

Stuart L Kearns[1], Ben Buse[1]

[1.] School of Earth Sciences, University of Bristol, Bristol UK

The high spatial (sub-micron or nanoscale) resolution analysis achievable with modern field emission gun electronprobe microanalysis (FEG-EPMA) instruments provide an enticing opportunity for earth scientists to investigate processes at previously unattainable length scales. Unfortunately the stability of some geological materials under electron beam bombardment is compromised by the need to operate at low accelerating potentials such that some minerals and glasses that are sufficiently stable at high (15-20kV) voltages prove extremely difficult to analyse at low (<10kV) accelerating potentials [1].

Many geological materials –minerals, glasses and some amorphous species prove difficult to analyse under standard EPMA conditions. For example, carbonates and phosphates undergo rapid degradation under a focussed high current beam, zeolites suffer a dehydration reaction [2], alkali rich glasses are subject to ion migration [3], sulphur bearing glasses demonstrate oxidation under the beam [4], even simple minerals such as quartz can undergo beam-induced amorphisation [5].

Here we review the methods that can be employed to mitigate the deleterious effects of beam bombardment on a range of geological materials; coupled with time dependent intensity (TDI) modelling to conclude a series of protocols which will assist instrument operators in the successful generation of high quality quantitative data and X-ray maps.

As nearly all geological materials are dielectric and variable pressure conditions are here considered inappropriate, a conductive coating is essential for EPMA. Traditionally, carbon is the preferred material but this may not offer the optimal condition for protecting the sample against negative impacts of the beam. Experimental analyses are here performed on carbonate, phosphate and mica to demonstrate the effects. The case of dolomite (fig 1) illustrates the benefits of using metal coatings. The use of a silver coating clearly mitigates the effects of CO_2 loss. Thermal modelling demonstrates an effective heat dissipation using highly thermally conductive metal coatings. However our results demonstrate that silver or gold coatings do little to stabilise ion migration in alkali rich glasses. Contrastingly, the use of a cryogenic stage to cool the sample to 100K limits alkali diffusion [3], but the cryo-stage alone has very little mitigating effect on carbonate loss (fig 2) – TDI gradients at ambient and cryo temperature similar.

Contamination becomes increasingly important at low voltage as the contaminant layer occupies an increasingly large proportion of the interaction volume as the accelerating potential is lowered. The combined effects of energy loss in the contaminant layer and increased absorption impact variably on the X-ray emission depending on energy. The problem is most severe during generation of line profiles where points impact on the contamination ring of previous analyses. The use of a cold finger assembly or airjet and modelling contamination effects can minimise the negative impact on analyses [6]. Hirsch et al. [7] demonstrated that reducing contamination build up at low voltage can be controlled by the use of a cold finger assembly operating at relatively modest temperatures. This opens up the possibility of using Peltier cooling rather than liquid nitrogen to continually minimise contamination – Early experiments of this technique are effectively applied to FEG-EPMA (fig 3).

We conclude that thermally conductive metal coats provide a significant mitigation of temperature related beam damage e.g. carbonate and phosphate degradation but have little effect on ion migration. Continuous cold finger decontamination is important at low kVs. In all cases, the use of a chart recording system is invaluable to monitor the behaviour of the sample with time, both in terms of X-ray count rates and absorbed current reading. The latter whilst giving evidence of instability of the sample is not always straightforward to interpret.

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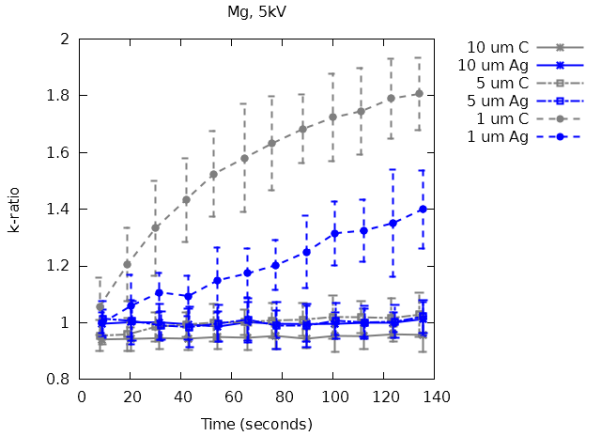

Figure 1. TDI curves for Mg in dolomite at 10nA, 5kV. The use of silver coat clearly mitigates grow-in of Mg for small spot size analysis.

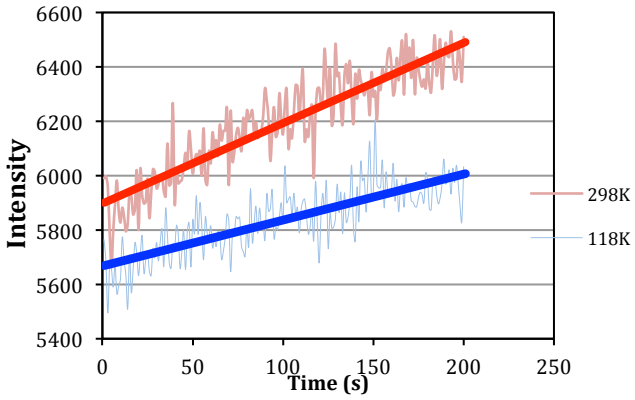

Figure 2. Calcite stability curve. Intensity change of Ca Ka at ambient and cryogenic temperatures. Ca intensity increases with time - a result of "grow-in" resulting from carbonate loss from the sample.

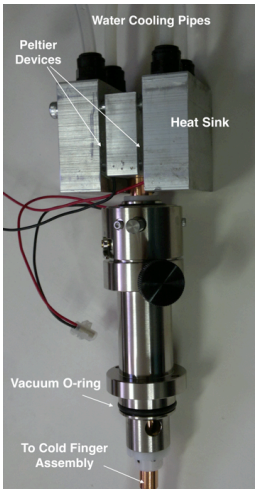

Figure 3. Peltier Cooled Cryo-Finger Assembley for a JEOL EPMA. Consists of dual 45W Peltier devices with water cooled heat sinks capable of reducing ambient temperature by about 40-50 degrees sufficient to reduce carbon contamination build up on the sample.

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