Soft X-ray and cathodoluminescence measurement, optimisation and analysis at liquid nitrogen temperatures

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Abstract. Advances in field emission gun electron microprobes have led to significant gains in the beam power density and when analysis at high resolution is required then low voltages are often selected. The resulting beam power can lead to damage and this can be minimised by cooling the sample down to cryogenic temperatures allowing sub-micrometre imaging using a variety of spectrometers. Recent advances in soft X-ray emission spectrometers (SXES) offer a spectral tool to measure both chemistry and bonding and when combined with spectral cathodoluminescence the complementary techniques enable new knowledge to be gained from both mineral and materials. Magnesium and aluminium metals have been examined at both room and liquid nitrogen temperatures by SXES and the L-emission Fermi-edge has been observed to sharpen at the lower temperatures directly confirming thermal broadening of the X-ray spectra. Gains in emission intensity and resolution have been observed in cathodoluminescence for liquid nitrogen cooled quartz grains compared to ambient temperature quartz. This has enabled subtle growth features at quartz to quartz-cement boundaries to be imaged for the first time.

1. Introduction
Field emission gun equipped electron probe microanalysers (FEG-EPMA) offer high beam power density at a range of accelerating voltages, with excellent beam stability over days of operation. However, with high beam current densities the onset of specimen damage occurs faster [1]. It has been observed that destruction of the specimen and defect transformation is time dependent, and provided spectral measurements can be performed quickly enough, “undamaged” hyperspectral maps can be collected. To slow the onset of beam damage we have integrated a liquid nitrogen (LN) cold stage into a modern FEG-EPMA. The LN cold stage has been optimised for stage mapping, offering an advantage over normal cold stages in that large area maps up to several mm² can be collected at cryogenic temperatures using a variety of detectors such as grating optical and X-ray spectrometers for hyperspectral cathodoluminescence (CL) [2-5] and a soft X-ray emission spectrometer (SXES) [6, 7]. Lower accelerating voltages increase the chemical spatial resolution, but also increase the beam power damage, and so reducing the onset of specimen damage through cryogenic cooling allows lower accelerating voltages to be employed.
2. SXES configuration
The SXES offers the ability to acquire soft X-ray spectra with higher energy resolution than either energy-dispersive (ED) or wavelength-dispersive (WD) X-ray spectrometry. When operated in a mapping mode the SXES can collect a spectra at every pixel of a map, in acquisition times down to 200 ms. The minimum time in this case is governed not by the signal strength but by the time to readout the charge coupled device (CCD). In our system we employ a Princeton CCD which has a 2K × 2K back-thinned detector optimised for the collection of soft X-rays. The CCD is operated at -60 °C using a Peltier cooling device with water cooling to remove the heat and stabilise the temperature of the detector. The CCD is open to the vacuum of the spectrometer, and thus the EPMA, necessitating a clean high vacuum during the operation of the SXES. In our system we collect hyperspectral maps, with the SXES spectra being collected in parallel with other spectral signals acquired from the ED and CL spectrometers, as well as WD spectrometry and electron signals at every pixel. Hyperspectral mapping or analysis has significant advantages over traditional mapping, in that it removes the need to have a priori knowledge about what the important X-ray lines are, and when combined with the other signals being acquired from the EPMA, offers a wealth of information.

3. SXES alignment and calibration
For optimum performance the SXES must be correctly aligned through a two-step process. Firstly, the energy range required is set, which involves shifting the CCD up and down using a grub screw. In our case we often select the energy range to allow Li-K (54 eV) X-rays to be observed using the 50XL reflection diffraction grating. Typically the 50XL grating has an operational energy range of 48 - 180 eV [8]. However, in our system we can observe X-rays as low as 44 eV, which allows direct observation of the Mg L-line (49 eV) and up to 195 eV at the high end. For the 200N grating a typical range is 55 - 235 eV, however measurements up to 285 eV are achievable, allowing the first order C K-line to be observed. Thus the SXE spectrometer can have differing energy ranges selected for specific analytical tasks. Once the energy range has been selected the second step is align the SXES to achieve the maximum peak-to-background or resolution. This is achieved by rotating the CCD around its central axis until the best resolution is achieved. We usually perform this task on aluminium metal using the Al-L (77 eV) Fermi edge, which at zero Kelvin would be a vertical X-ray line. At room temperature the Al L-edge has, on our spectrometer, a resolution of 223 meV. These two steps complete the alignment procedure, and next one must calibrate the observed X-ray spectrum which involves converting the 2048 channels of the CCD into energy steps. This calibration takes into account that the crystal diffracts in wavelength and the energy scale conforms to the formula $E = \frac{hc}{\lambda}$, where $\lambda$ is the wavelength and $h$ is Planck’s constant.

For the calibration of the 50XL grating, we use the C-K X-ray line from graphite, the Zr Mζ-line from zirconium metal and the Mo Mζ2-line from molybdenum metal. Given that the SXES has such high energy resolution it can therefore observe shifts in X-ray lines that are due to bonding. Consequently, one must be careful to use single element metals for energy calibration so that the measured X-ray lines from these materials will match X-ray line databases. With the 50XL diffraction grating we can observe the C-K 2nd, 3rd, 4th, 5th and 6th order X-ray reflections. Since the diffraction grating is holographically produced it is highly efficient at reflecting higher order X-ray lines and quite often 8th and 9th order lines are observable. The peak positions of C K reflections together with Zr-Mζ 1st (151 eV) order and the Mo-Mζ2 1st (193 eV) order are recorded and these positions are then fitted using a polynomial expression to provide a calibration curve for the CCD. As an example, figure 1 which shows the calibration curves for the 50XL and 200N gratings. The non-linear response is a property of the grating and its reflectivity curve. This completes the alignment and calibration of the SXES.
4. Soft X-ray emission and transmission though films

To observe soft X-ray emission in poorly electrically conductive materials, such as ionically bonded minerals (e.g., fluorite, CaF$_2$) or sulphides (e.g., pyrite, FeS$_2$), one needs to coat with a thin conductive film. To determine whether it is possible to observe soft X-rays (e.g., Li-K) through a carbon coat, we performed a test in which varying thicknesses of carbon were applied to a surface using a carbon arc coater (Cressington 208carbon). An integrated quartz thickness monitor was used to measure the carbon coat thickness and it was assumed the density of the film was 2.2 g/cm$^3$. The curves in figure 2, are of the Li-K (54 eV) and Al-L (72 eV) peak intensities versus carbon coat thickness, as measured from an aerospace alloy AA2099 at 5 kV accelerating voltage. This alloy contains ~1.8 wt% Li and ~95 wt% Al. At a carbon coat thickness of 80 Å the measured intensity of the Li-K drops by 63 % and the Al-L intensity drops by 75 % compared to the uncoated metal. While the intensity of the Li K-line drops off faster than the Al-L with increasing coat thicknesses, the intensities of these peaks are still sufficiently high to allow mapping and analysis of coated minerals and materials.

**Figure 1.** Calibration curves for SXES gratings 50XL and 200N.

**Figure 2.** Measurement of Li-K (54 eV) and Al-L (72 eV) emitted intensities through varying film thicknesses of carbon. All measurements were performed at 5 kV with a 10 µm defocussed beam.
X-ray yield curves are not available for many soft X-rays as the mass absorption coefficients (MAC) have either not been measured or determined. To do this one must measure the X-ray lines of interest (ideally within the material to be examined), from low through to high accelerating voltage. By plotting the emission intensity versus the accelerating voltage one can produce an x-ray yield curve and this can be used to determine the optimum voltage to analyse the X-ray.

Figure 3 shows the effect of changing accelerating voltage on the emitted intensity of Al-L in aluminium and Si-L (91.5 eV) in silicon. A repeat set of measurements were performed from 4.5 - 7 kV on the aluminium to check the reproducibility and both curves show a similar trend with a maximum emission at 6.5 kV. In the case of Si L in silicon the maximum intensity was observed at 9.5 kV. Similar curves have been generated for a wider set of materials and reported in Demers et al. [9].

The curvature of the gratings and dispersion gives rise to a change in resolution of the spectrometer with energy. This can be observed by measuring the energy width between the 75 % and 25 % edge height of X-ray peaks that have Fermi edges. Figure 4 shows a plot of the Fermi edge resolution versus X-ray line energy measured using Mg-L (49 eV), Al-L (73 eV) and B-K (183 eV) in all cases the lines were measured on the pure metal at ambient temperature. The Al-L peak position indicated here is the Fermi edge position, 73 eV, which is different from the peak position of 72 eV. The resolution moves from a maximum of 115 meV (Mg-L) through to 1030 meV (B-K).

5. Calibration and alignment of cathodoluminescence spectrometer

We employ a factory aligned, fixed grating spectrometer containing no moving parts. Cathodoluminescence from the specimen is collected by the integrated light optics of the EPMA and transmitted to the optical spectrometer by means of a fibre optic. Our standard optical spectrometer has a wavelength range of 200 - 980 nm and has interchangeable slits with varying sizes ranging from a 25 µm slit giving 1 nm resolution and up to 300 nm slit providing 10 nm resolution. Each slit requires a minor adjustment of the alignment optics after replacement, and on the electron microprobe this is usually performed on a non-beam sensitive CL material such as zircon or ruby.
6. Cold stage operation

The cold stage we used in these measurements utilises a GATAN C1001 stage integrated by JEOL (Japan) onto a purpose built carriage and door assemble, figure 5. The design accommodates a 10 mm diameter sample, which is mounted flush within the holder for good thermal conductivity. The sample is pumped down in the airlock to a base pressure of better than 10^-2 Torr and then inserted into the JEOL 8530II electron microprobe using the supplied high precision stage. The teflon tubing is initially coiled, as in figure 5, and during insertion stretches out but does not interfere with the operation of the stage. Thus the stage movements are uninhibited and either stage or beam mapping can be used. In our case we use the former to cover large areas. To prevent ice build-up on the surface of the sample during use of the cold stage, a liquid nitrogen (LN) cold trap below the pole piece is operated with an auto-filler to allow unattended operation for up to three days. In addition, we have engineered a cascade turbo pumping arrangement so the backing turbo for the main chamber is backed by a smaller turbo pump, with the ultimate pressure of the instrument being below 3 × 10^-7 Torr during operation. This minimises surface contamination which is important for detection of low level Li by either windowless SDD or SXES.

Figure 5. JEOL-GATAN cold stage, which uses cryo-cooled nitrogen gas to cool the stage. The white teflon tubing allows the cold stage to be inserted from the airlock into the microscope during operation. Thermocouple wire and heater cabling are visible.
7. Collection of hyperspectral maps
The electron microprobe software and hardware have been modified to allow hyperspectral collection from two Bruker SDDs, a CL spectrometer and the SXES in parallel, together with the wavelength-dispersive and electron signals [10]. This enables single pass mapping with full registration of all signals at the pixel level. The electron beam easily damages many minerals and materials during analysis/mapping and structural retention is as important as elemental stability for CL and SXE spectroscopy, making single pass mapping the key to reducing damage artefacts in the map data. The EPMA has been equipped with a sub-micrometre beam defocus allowing maps with a sub-micrometre step size to be matched with an equivalent beam spot size. This is possible in steps of 100 nm. At the completion of mapping, all data is combined into a single file and offline data processing is performed in the Chimage software [11].

8. SXES mapping
An application of the SXES is in the study of aerospace alloys which have been studied previously by EPMA using a combination of WDS and EDS [12, 13]. The SXES equipped EPMA was used to determine the distribution of alloying elements in an aluminium alloy, AA2099, containing Cu (2.4 %) and Li (1.6 %) as the active alloying components. The focus in this study was on constituent intermetallic (IM) particles (large particles, typically > 1 µm, comprising significant levels of impurities and alloying elements), where corrosion is observed to occur. One gap in the previous studies is that it was not possible to determine whether Li was present in the constituent particles. We have observed a number of IM particles and see copper depletion at high angle grain boundaries but not sub-grain boundaries, figure 6. The map is generated by summing intensities in a region-of-interest centred on Al-L. The map was acquired at 7 kV, 80 nA and 200 nm step size with a 1500 ms dwell per pixel. The Li in these grain boundaries does not appear to vary but fine copper particles are aggregated near or along grain boundaries giving rise to enhanced Al. This illustrates both the high spatial resolution and surface sensitivity of the SXES when coupled to an EPMA.

9. Cold stage analysis using SXES

9.1. Thermal broadening
Measuring spectra at low temperature has the advantage of reducing thermal broadening of peaks and hence increasing the spectral resolution [14]. In the case of SXES we have examined the Al-L Fermi
edge (72.5 eV) [15] at both room and LN temperatures (figure 7) and observed that the Al-peak shifts to higher energy by up to 30 meV at LN temperatures, but the base does not move, resulting in a sharper edge. Spectra were collected on the Al specimen at 7 kV, 40 nA, 1.5 s acquisitions averaged over 200 s. Using the energy difference between the 25 % and 75 % of the Al-peak height as a measure of the energy spread, we fit a line to the Fermi edge and at room temperature the energy resolution is measured to be 257 meV, while at LN 246 meV is observed. The broadening seen here is consistent with the Fermi-Dirac distribution at room temperature which follows the $4kT$ rule which for SXES has been described by Terauchi et al [6]. Previous work by Skinner has shown changes in Fermi-edge shapes with temperature although with lower spectral resolution [16].

![Figure 7. Al-L spectroscopy observed at 296 K and 80 K temperatures showing the Fermi edge at ~72eV. The zoomed in region, insert, shows the Fermi edge at room temperature becoming sharper at LN temperatures, 246 meV compared to 257 meV at room temperature.](image)

9.2. Lithification of LiF

The spectroscopic analysis of ionically bonded materials such as LiF by SXES needs to be performed without inducing beam damage. When a focused electron beam is employed then we have observed the lithification of the LiF. In figure 8, a Li-K peak at 54 eV is seen on LiF which is associated with the growth of Li metal. In addition we also observe a lower peak which we attribute to a Li oxide peak at 47.8 eV. To observe undamaged spectra from LiF we collected a spectra by defocussing the electron beam and collecting a map. The resulting sum spectra shows a split Li-K peak at 44.5 eV and 61 eV. By comparison the Li-K peak in metal is 54 eV. This measurement is in agreement with Li-K measurements performed using a zone plate installed at BESSEY II, where they reported Li-K in LiF at 46.5 eV and 61 eV [17]. The discrepancy in the lower Li-K peak, 44.5 eV, may be due to an energy calibration issue at the lower end of the SXES.
Figure 8. Spectra collected from LiF using a focused electron beam, orange, which induces lithification resulting in a Li metal peak (54 eV) and Li oxide (47.8 eV). The low dose spectra from LiF reveal two Li-K peaks at 44.5 eV and 61 eV.

10. Cold stage mapping using cathodoluminescence

10.1. Carbonado diamond
Cathodoluminescence analysis performed on a carbonado diamond specimen mapped at room temperature and LN temperatures show marked differences. In figure 9a shows two CL spectra from the carbonado diamond; one collected at room temperature (blue) with the other at LN temperature (red). A slight sharpening of the main peak at 2.8 eV is observed in the LN spectra, while a dramatic sharpening of the nitrogen defects centred at 2.43 eV is observed in the LN spectra compared to the room temperature spectra. The diamond spectral resolution improves at LN temperatures due to the peaks associated with the nitrogen defects becoming narrower [18, 19]. In addition the intensity of the luminescence increases at LN temperature by at least a factor greater than two. Previous work on carbonado diamonds at room temperature showed a wide variety of defect peaks associated with diamond including the nitrogen with a neutral vacancy (N-V0), the nitrogen pair with a vacancy (N2V) and the group of three nitrogens with a vacancy (N3V) [19-21]. The peaks from these defects are complex and are each composed of a zero phonon line and a set of lines from the vibronic system. However, at LN temperatures the finer peak resolution improves the stability of peak fitting. Figure 9b shows a panchromatic map of a carbonado diamond shows the intersection of two distinct crystal planes and enhanced emission is evident at the grain boundaries, possibly due to the incorporation of trace elements. The map was collected at 10 kV, 48 nA with 1 µm step size and the beam was defocussed to 1 µm, with the surface coated with a 3 nm carbon film.

10.2. Quartz-cement sandstone
A Triassic quartz-rich sandstone sampled from a deep well in the Southern Perth Basin has been investigated as a potential target for CO2 geological storage [22]. Quantitative cathodoluminescence and trace analysis has been used to establish the magnitude and relative timing of diagenetic processes affecting the sandstone and their chemical fingerprint at the microscopic scale. Key to understanding the evolution of the quartz-cement has been the use of cathodoluminescence mapping and X-ray microanalysis to determine the source of the silica in the brine that has precipitated the quartz-cement [23]. The LN cold stage has been used in this study for two reasons; firstly as it offers the ability to map
Figure 9. a) Cathodoluminescence spectra at 296 K (RT in blue) and at 80 K (LN in red). The nitrogen vacancies (2.4 eV) become sharper and hence easier to analyse at 80 K. b) Map of carbonado diamond collected at 80 K showing crystal growth planes.

with significantly lower damage compared to ambient conditions. Secondly, at LN temperatures we have observed an increase in CL emission intensity by up to a factor of five in both detrital and diagenetic quartz, figure 10, enabling lower beam currents to be used for mapping. A minor sharpening of the peaks centred at 1.91 eV occurs and the peak centred at 2.7 eV moves down to 2.50 eV.

Figure 10. Cathodoluminescence spectra from a quartz-rich sandstone specimen collected at 296 K and 80 K (LN temperature). Both the intensity of the peak and resolution increase at LN temperatures.

The CL associated with the quartz-cement is usually weaker compared to the detrital quartz grains due to its lower formation temperature. To differentiate the quartz-cement from the detrital quartz we use a Si-K versus CL intensity scatter plot to show the different forms of quartz and then select the
quartz with low CL intensity cluster, as shown in figure 11. The higher CL intensity clusters are from the two main, detrital quartz grains. The map was acquired at 80 K (cryogenic nitrogen) with beam conditions of 10 kV, 20 nA, 20 ms dwell, 1 µm step and defocus. Typically the CCD in the optical spectrometer is cooled to -15 °C and a long background collection is run immediately prior to collecting the map to determine the CCD response at the regulated temperature. The spectrometer Peltier cooler is regulated to maintain the temperature within a 0.1 °C window but the response of the detector electronics changes slightly with room temperature and so this is tracked pixel-by-pixel and compensated for using the blanked off pixels within the CCD which respond to these subtle temperature fluctuations. In figure 12, all pixels are selected and the growth history within the quartz grains are evident. The highly angular nature of the quartz-cement may indicate it is growing following the grain boundary orientation of the quartz grain. The lower large quartz grain, figure 12, shows some evidence of a crack that has been healed by infilling with quartz-cement (green line through the quartz grain).

Figure 11. Scatter plot of CL versus Si K (WDS), the various clusters represent different quartz grain types, by choosing pixels from the lower CL intensity cluster we select the quartz-cement. The map shows the selected pixels in blue, which bond the quartz grains together.

Figure 12. Map of quartz, same as figure 11, with all pixels selected. The infilling between adjacent quartz grains by the quartz-cement is evident.
To understand the role of trace elements within the quartz, in particular Ti and Al, we have performed quantitative point analysis on a number of quartz grains and the associated quart-cement [24, 25]. The technique we used was firstly to map a large area, 4 × 4mm at 2 µm step size at 20 kV, 30 nA with spot size set to match the step size, 2 µm. Critical for good CL images the surface finish needs to be as defect free as possible and this usually involves finishing the sample with a 20 nm colloidal silica polish. The polish may be further refined using a low energy ion beam to remove the amorphous layer left by the mechanical polishing, which may be desirable for high resolution CL investigations. This procedure is similar to sample preparation for electron backscatter diffraction (EBSD). The ion beam polisher can also clean any residual hydrocarbons or contaminants from the surface prior to coating with 10 - 15 nm of amorphous carbon. The carbon coat provides a conductive path for the electrons and has little absorption of the CL signal. Light absorption in carbon films is approximately linear across a range from 400 – 1,000 nm [1]. Clearly thinner carbon films are more desirable for use in CL due to the lower absorption, however they do not introduce non-linear absorption artefacts.

To quantify trace element concentrations by CL, the specimen is first mapped in the EPMA, with CL, EDS and WDS collected in parallel. Once the map is complete, coordinates for follow-up quantitative analysis are selected from quartz grains that have a range of CL intensities, since higher Ti-levels are generally associated with brighter grains [26, 27]. In addition a series of points on the quartz-cement were also loaded. The points were analysed at 20 kV, 120 nA, 10 µm spot and this gave detection limits on Ti of 20 ppm and Al was 55 ppm. A zero background synthetic quartz was analysed to determine the background offsets and these measurements were then used to correct the trace element levels. The vendor-supplied microanalysis software has been modified to allow negative k-ratios to be carried through the correction procedure. This allows a full scatter of trace levels and importantly the “zero” levels are scattered both above and below zero. The effect of allowing negative concentrations through can be seen in figure 13a, were the lowest Ti-levels scatter both above and below zero. To determine trace element correlations with CL peaks one first must determine the peak present, their positions and full width half maximum (FWHM). We use a CL database which has been described previously but now contains reference spectra and these can be used to compare with the collected spectra from the map [28]. The identified peaks in the quartz spectra are shown in Table 1. For fitting we describe the peaks using a Gaussian shape, which for quartz is adequate. Where forbidden transitions are observed in CL, lifetime broadening results in peaks with a Lorentzian or pseudo-Voight profile, which must be fitted appropriately. The described peaks are fitted at each pixel by locking each peaks FWHM but allowing the peak intensity to vary. Previous work has shown that the Ti$^{4+}$ concentration in quartz is associated with the 2.73 - 2.83 eV peak and the Al can be correlated with the non-bridging oxygen hole centre (NBOHC) 1.945 eV peak [29, 30]. Finally to correlate the trace element measurements with the CL spectra, we average the CL spectra from the same 10 µm region in which the analysis was performed. Thus a fitted CL peak versus trace element plot is generated as shown in figures 13a and 13b. The quartz grains show a linear correlation between the Ti$^{4+}$ centre and the Ti trace element analyses of the corresponding points, figure 13a. However, the quartz-cement does not show the same correlation due to the significantly lower formation temperature, resulting in a titanium solubility below measurable levels in the EPMA. The 1.95 eV peak shows a reverse correlation with Al-levels, figure 13b [31]. The detrital quartz and quartz-cement have differing linear gradients indicating that different incorporation mechanisms are likely to be involved, most likely associated with the temperature of formation.
Table 1. Peak centres and associated FWHM for the quartz map shown in figures 11 and 12.

| Peak | Attribution          | Position (eV) | FWHM (eV) |
|------|----------------------|---------------|-----------|
| 1    | undocumented         | 1.55          | 0.79      |
| 2    | NBOHC & Al           | 1.95          | 0.38      |
| 3    | Defect               | 2.05          | 0.49      |
| 4    | Ti⁴⁺                 | 2.73          | 0.99      |
| 5    | Dangling NBOHC       | 2.83          | 0.85      |
| 6    | Intrinsic            | 3.62          | 0.76      |

Figure 13. Quantitative elemental microanalyses compared to extracted emission centres. a) Ti⁴⁺ emission centre at 2.8 eV versus Ti shows a correlation in quartz with R² of 0.8641. b) Al emission centre at 1.95 eV shows negative correlations in quartz and to a lesser extent quartz-cement.

11. Summary
The EPMA offers the ability to collect a wealth of both chemical (EDS, WDS, SXES and CL) and structural information (SXES and CL) when used to map minerals and materials. To efficiently gather information from the array of spectrometers and detectors one wants to maximise the collected data but minimise the time to acquire. These conflicting criteria lead to operators employing large beam currents that in the case of the FEG can be quite destructive. To minimise the damage we cool the sample to LN temperatures and always defocus the beam to the step size of the map. Using this strategy we can minimise damage and achieve the desired fast collection and analysis of samples. The use of hyperspectral mapping or analysis, has significant advantages over traditional mapping in that it removes the need to have a priori knowledge and together with modern data processing strategies enables previously difficult to analyse elements and lines, i.e., Al-L and Li-K to be detected. This offers new insights into minerals and materials research.

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