Invited keynote lecture:

Hyperspectral cathodoluminescence

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The development of hyperspectral mapping on an electron microprobe equipped with wavelength dispersive spectrometers (WDS), energy dispersive spectrometers (EDS) and a cathodoluminescence (CL) spectrometer has provided the ability to collect both X-ray and CL spectra in parallel (MacRae et al., 2005). The combination of these data sets has wide application in the study of minerals and materials. While x-rays have been traditionally used in both qualitative and quantitative ways to describe elemental concentrations and distributions within samples, CL has been used only qualitatively on mapped samples. The ability to quantify CL map data offers the potential to map minerals and materials with lower detection limits compared to standard X-ray trace element mapping by electron probe microanalysis. Cathodoluminescence can have greater sensitivity to trace element levels, particularly on strongly active materials such as scheelite (MacRae et al., 2009) and quartz (Leeman et al., 2012). The energy and intensity of CL is sensitive to the material composition and crystal structure, as well as more subtle effects such as trace level concentrations of luminescence activator and quencher ions, and their chemical valence. The most common activators are metal ions such as Cr^{3+}, Mn^{2+}, Mn^{4+}, Sn^{2+}, Pb^{2+}, Fe^{3+} and rare earth elements ($REE^{2+/3+}$). Due to orbital splitting, REE ions with different valence or coordination may emit spectral lines at different energies, which can be used to identify the emitting ion. These can help provide insight into rock formation and mineralisation processes as well as information on the band structure within a material. Recent advances in hardware associated with CL detection have resulted in better system stability, faster data collection, improved sensitivity, while software improvements has led to enhanced spectra analysis and hyperspectral data collection. The recent development of a luminescence database has provided the means for identification of intrinsic and extrinsic peaks. A web based version of the database can be viewed online at ***www.csiro.au/luminescence*** (MacRae et al., 2008).

Using identified peaks spectra can be analysed for both major and minor peaks more rigorously, leading to improved CL spectra fitting. With independent measurement of elemental abundances using, for example X-rays or laser induced inductively coupled mass spectrometry, the CL fitted peaks can be calibrated which allows for the quantification of hyper-spectral cathodoluminescence datasets. In order to be quantitative we need to be assured that the CL spectra will behave with a linear response. A dual CL spectrometer collection system has been integrated with an electron microprobe to collect luminescence generated by the electron beam across the wavelength range from 200 nm to 1700 nm. The CL signal is collected and focused through a series of mirrors and lenses into two Peltier cooled CCD spectrometers, which simultaneously measure the UV–Visible (UV–Vis) spectrum from 200–980 nm, and the near infrared (NIR) spectrum from 900–1700 nm. The spectrometers overlap in the range 900–980 nm, which allows an intensity scaling factor to be calculated to give a smooth transition across the overlap region. The ability to simultaneously measure UV–Vis and NIR transitions is advantageous for measuring CL transitions associated with rare earths ions, which have emission lines spread across the spectrum from visible to NIR that are detectable and quantifiable (e.g. Nd^{3+} in Scheelite, Tb^{3+} and Dy^{3+}in Fluorite) (Pagel et al., 2000). To quantify the concentration of rare earth elements within an area mapped by CL, a set of Gaussian /

Lorentzian peaks are first fitted to the spectra of every pixel in the map. An independent measurement of trace elemental abundances from areas within the mapped region is then performed by electron probe microanalysis or laser induced inductively coupled mass spectrometry. From this data, a calibration line is calculated for each CL peak by regression of the trace analyses against the fitted CL intensities from the same areas. This calibration line allows quantitative speciation maps to be plotted with a sensitivity of parts per million. A grain of Wilberforce apatite ($Ca_5[PO_4]_3[F,OH]$) has been investigated using the dual CL spectrometer system. The combined UV–Vis–NIR cathodoluminescence spectrum from the grain is shown in Fig. 1. A map collected at 20kV and 40nA shows clear differences in spectral response between the UV–Vis spectrum that is

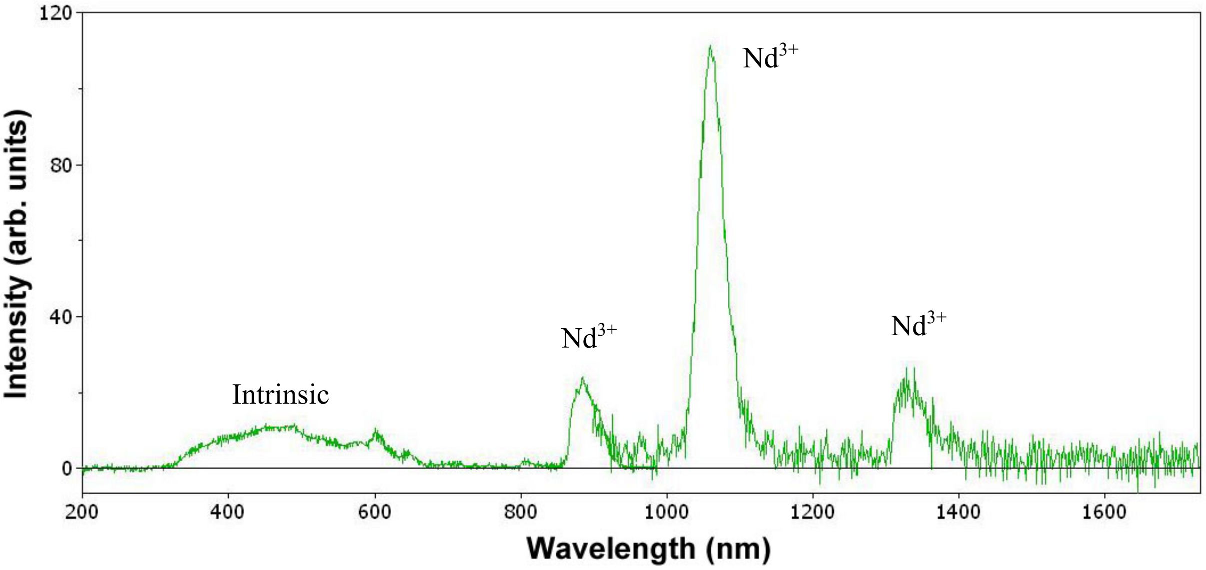

Fig. 1. *Cathodoluminescence spectrum from a Wilberforce-apatite grain, Ontario, Canada, collected by combined UV–VIS and VIS–NIR spectrometers.*

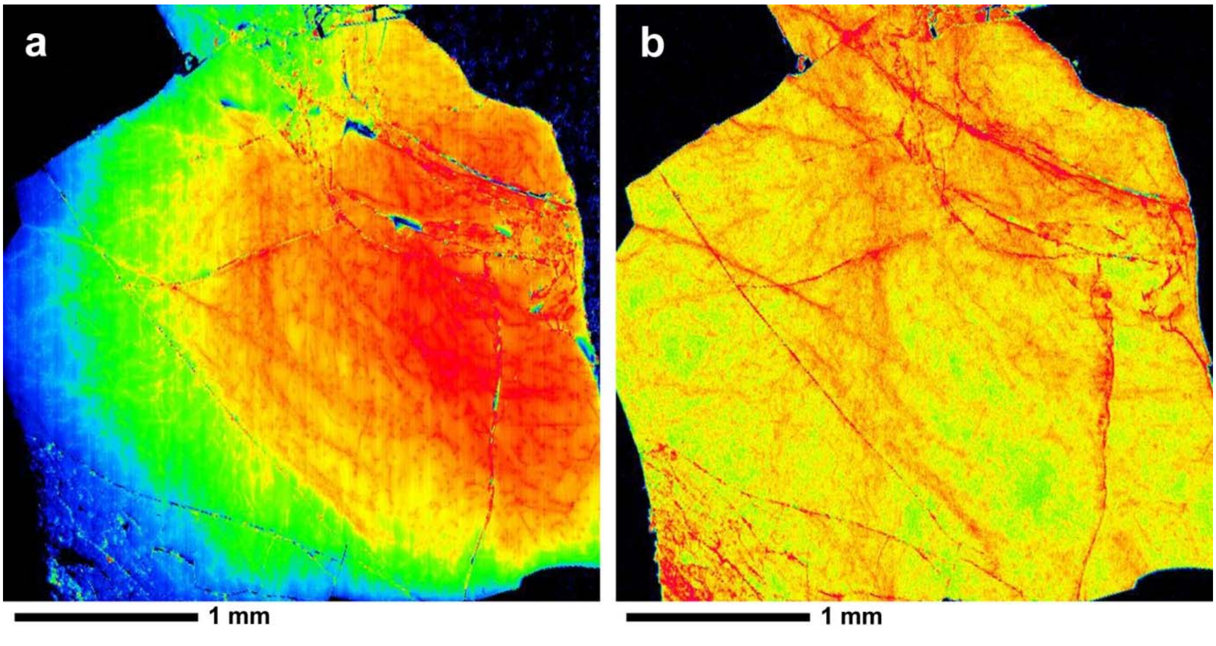

Fig. 2. *Visible sum-spectra map (**a**) and map of the Nd^{3+} peak centred at 1050 nm (**b**), collected on Wilberforce apatite at 20 kV, 2 µm step size and 80 ms dwell per pixel.*

dominated by the intrinsic response (Fig. 2a) and the NIR region that is dominated by Nd^{3+} peaks (Fig. 2b). This new technique offers the ability to characterise a greater range of CL transitions and will provide new information in many materials and mineral problems.

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