xCLent - Application Note

Quantitative trace REE analysis in Scheelite by CL

A method for the analysis of cathodoluminescence spectra is described which enables quantitative trace-element-level distributions to be mapped within minerals and materials. Cathodoluminescence intensities for a number of rare earth elements (REE) are determined by Gaussian peak fitting, and these intensities show positive correlation with independently measured concentrations down to parts per million levels. The ability to quantify cathodoluminescence spectra provides a powerful tool to determine both trace element abundances and charge state, while major elemental levels can be determined using more traditional x-ray spectrometry. To illustrate the approach, a Scheelite ($CaWO_4$) from Kalgoorlie, Western Australia, was hyperspectrally mapped and the cathodoluminescence was calibrated against microanalyses collected using a laser ablation ICP-MS. Trace element maps show micron scale zoning for the rare earth elements Sm^{3+}, Dy^{3+}, Er^{3+} and Eu^{3+}/Eu^{2+}.

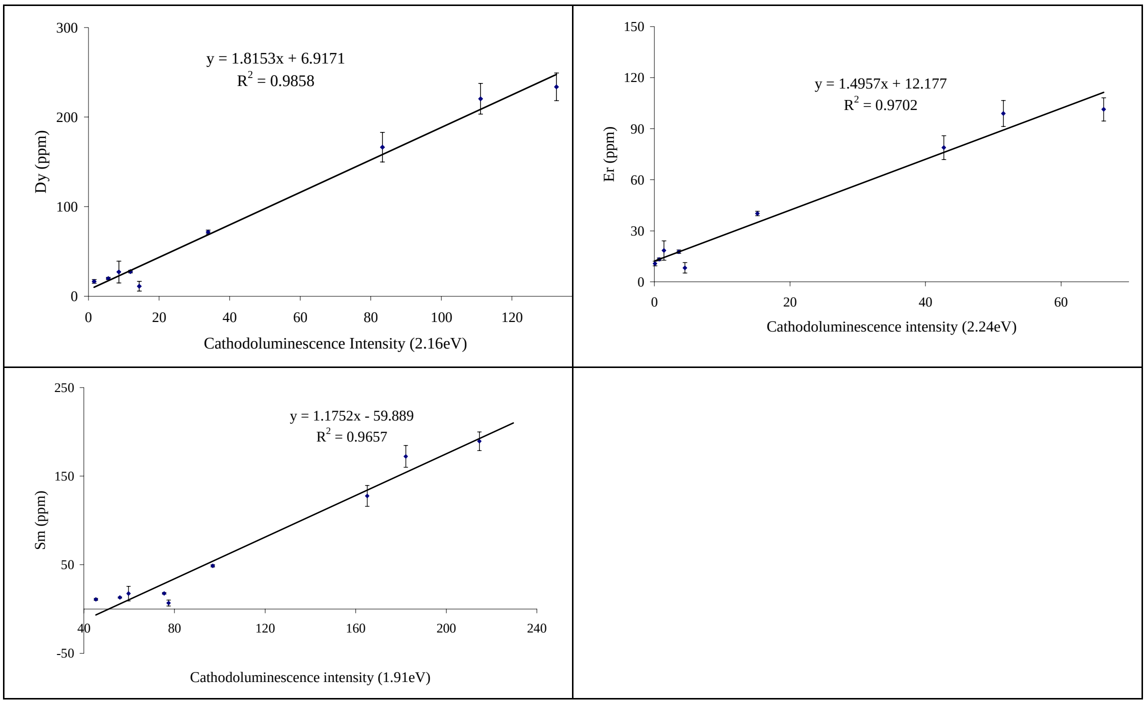
To identify lines for quantification, both selected area and sum spectra from the map were examined. Peaks were identified and compared to known rare earth lines in scheelite as listed in Table 1. From the data in Table 1, a list of spectral lines from REE dopants and the intrinsic ion band, WO_4^{2-}, was generated. XCLent Image - software was then used to fit a series of Gaussians, in energy space, to each of the major and minor peaks within the CL spectra, in this case a total of thirteen Gaussians were used, each corresponding to one of the identified spectral lines. The fitting was performed on the spectrum from each pixel within the CL map, with the peak positions and width of Gaussians kept constant and only the heights of the Gaussians allowed to vary during the fitting.

To calibrate each fitted REE line, the CL peak height intensity at each laser analysis spot was averaged, and compared to the LA ICP-MS analysis for the corresponding element, Fig. 1. This was repeated for all the laser spot analyses. This gives a calibration for the fitted CL peak height intensities of the various REEs identified in the spectrum which was then applied to peak intensity maps. These results are the basis for CL-quantified concentration maps. The comparison of LA ICP-MS analyses with measured and fitted peak intensities for Sm^{3+}, Dy^{3+}, Er^{3+}, Eu^{3+} and Eu^{2+} were produced and the Er^{3+} speciation map is given in Fig. 2.

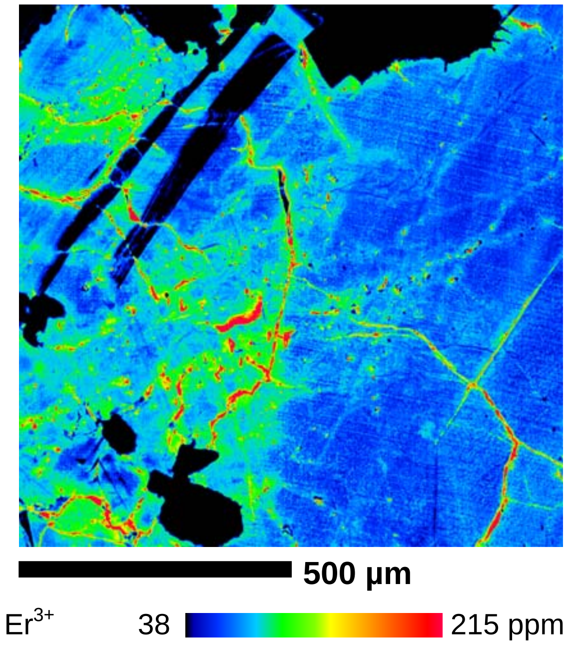
This enables subtle REE zoning to be revealed at down to 15 ppm levels with micron spatial resolution. This information is critical for the interpretation of the geochemical significance of REE incorporated in minerals.

Peak ID	Energy (eV)	FWHM (eV)
WO_4^{2-}	2.75	0.43
Dy^{3+}	2.54, 2.16, 2.13, 1.69	0.012, 0.012, 0.09, 0.007
Er^{3+}	2.24, 2.28, 2.34	0.015, 0.019, 0.018
Eu^{3+}	2.01	0.08
Sm^{3+}	1.80, 1.91, 2.08	0.05, 0.008
Eu^{2+}	2.96	0.125

Table 1. List of identified cathodoluminescent peaks positions and associated full width half maximums in Scheelite from Kalgoorlie



Comparison of fitted CL spectra with the elemental levels measured by LA ICP-MS for Dy^{3+}(2.16eV), Er^{3+} (2.24eV) and Sm^{3+} (1.91eV).



Fitted and calibrated speciation map for Er^{3+} (2.24 eV) showing fine zoning across the map.

Reference:

1. MacRae *and Wilson.* Microscopy and Microanalysis 15: 222-230 (2009) Quantitative cathodoluminescence mapping with Application to Kalgoorlie Scheelite.
2. MacRae *et al.* (2001). Holistic mapping in an electron microprobe. In Microscopy and Microanalysis, G. W. Bailey (Ed.), pp. 146-147. New York: Springer.