Zircon zonation and metamictisation revealed by cathodoluminescence and chemical imaging and analysis

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Zircon ($ZrSiO_4$) exhibits an extraordinary memory. Its stability, durability, low solubility and low elemental diffusivities combine to preserve in it a record of most of the important events that have affected it, its host rocks, and the crust of which it is a part. The zonation in zircon grains delineate the boundaries of discrete geochemical processors that occurred at different times. Zircon grains often contain high levels of Th and U either as inclusions of discrete mineral grains, or as a solid solution in the crystal lattice. Radiation generated by these impurities leads to metamictisation which is partial or complete destruction of the optical, physical and chemical characteristics of zircon crystals over time if they are not subjected to natural healing processes (e.g. heating through metamorphism). If significant modification to the structure of the zircon grains occurs, they can lose their opacity and hence their commercial value to the ceramics industry. To lower the Th and U levels to acceptable levels it is essential that the chemistry and structure of the zircon grains are well understood. It is also important to understand how any potential radiation removal technique may modify the structure. Cathodoluminescence (CL), backscattered electron (BSE) and chemical imaging reveals detailed zonation patterns that are commonly invisible or barely visible with conventional transmitted and reflected light microscopy (Hanchar and Miller, 1993). Many of the factors that contribute to the CL spectra from zircon are well established. Studies of natural and synthetic zircon have shown that the presence of various CL-active impurity ions, such as trivalent rare earth elements (REE^{3+}), causes narrow luminescence emission peaks at characteristic wavelengths, a summary of which can be found in a luminescence database (MacRae and Wilson, 2008). In natural zircon, narrow REE peaks are commonly superimposed on a broad emission however the origin of this broad CL peak is contentious and has been attributed to point defects, OH- defects, or defects within the silica tetrahedra (Timms and Reddy, 2009). The sum of all of the luminescence bands gives the integrated intensity seen in panchromatic CL images or an equivalent image can be produced by summing the intensities in each spectra of a hyperspectral CL map.

A zircon concentrate from a heavy mineral sands deposit has been investigated using combined hyperspectral CL and x-ray data collection to examine the relationship between metamictisation and trace element speciation and chemistry as revealed through CL and x-rays, respectively. The grains were mapped using a JEOL 8500F equipped with wavelength dispersive, energy dispersive and CL spectrometry at 20kV, Fig. 1. Subsequently the CL images were used to guide the selection of quantitative analysis points. By selecting varying CL intensities ranging from bright to dark points were chosen and then were analysed for Zr, Si, Al, Hf, Y, La, Th, U and Pb. A correlation between the CL intensity versus the uranium content was consistently observed for the series of samples examined, Fig 2. The zircon grains containing high levels of uranium, greater than 1000ppm, are relatively dark in CL which is attributed to higher rates of alpha particle emission as uranium decays through to lead, leading to higher levels of metamictisation.

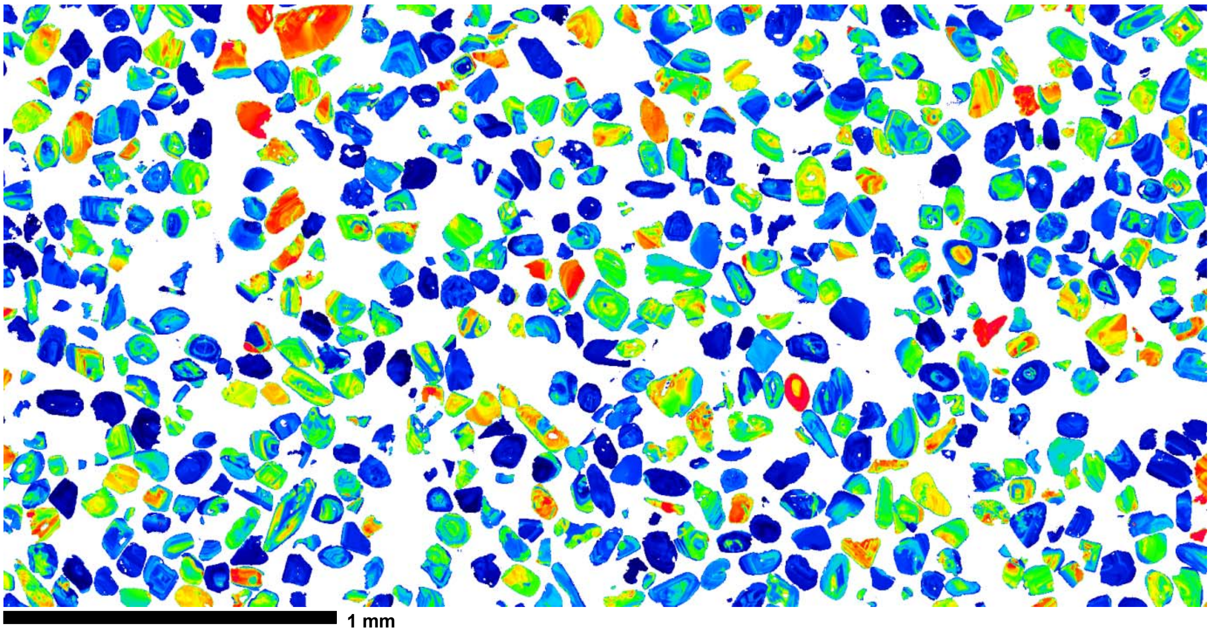

Fig. 1. *Cathodoluminescence image of zircon grains showing a range of different growth histories and recrystallisation as revealed by CL. The image illustrates the sensitivity of the CL imaging technique to identifying structural and chemical changes within zircon.*

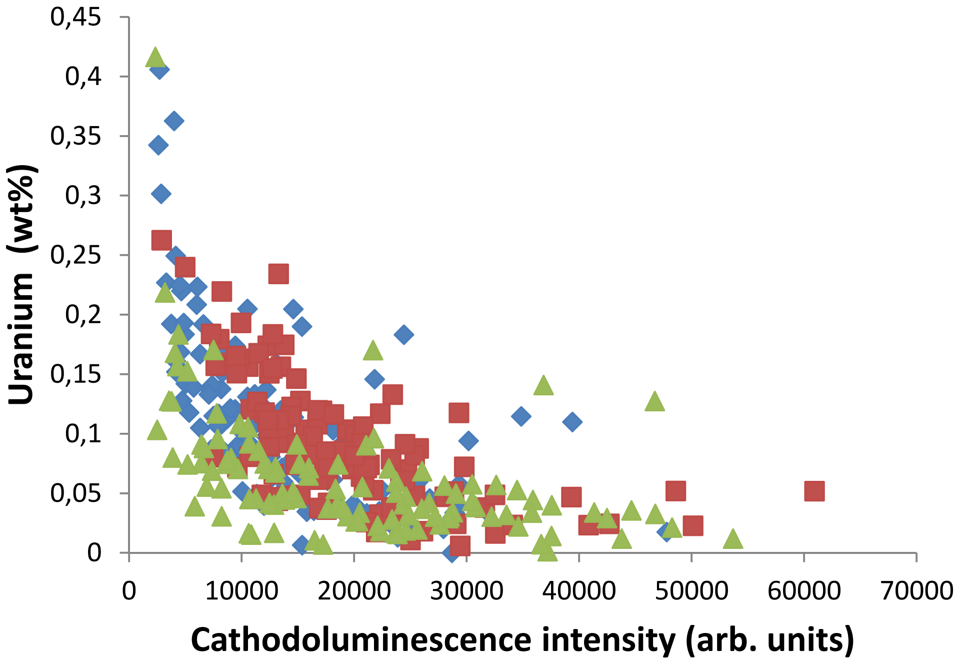

Fig. 2. *Scatter plot of uranium concentration versus cathodoluminescence intensity, for three different zircon concentrates. Bright zircons (red areas in Fig. 1) typically contain low uranium impurities and hence are likely to have undergone less metamictisation. Low CL intensity (blue areas/grains in Fig. 1) is associated with a high degree of metamictisation.*

References:

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