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Zircon Metamictisation study by Cathodoluminescence and X-ray Imaging

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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 processes 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 the 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 and also 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 [1]. 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. In natural zircon, these narrow REE^{3+} peaks are commonly superimposed on a broad emission peak [2]. However, the origin of the broad CL peak is contentious and has been attributed to point defects, OH-defects, or defects within the silica tetrahedra [3].

We have collected hyperspectral CL and x-ray data together with back-scattered electrons (BSE) to investigate the relationship between metamictisation and zircon trace element speciation and chemistry as revealed through CL and x-rays, respectively. Zircon grains were mapped using a JEOL 8500F microanalyser equipped with wavelength dispersive, energy dispersive and a high resolution CL spectrometry [4] at 20kV, Fig. 1. A correlation between the CL intensity versus the uranium content was consistently observed for a series of samples examined, Fig 2. 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. The CL images were used to guide the selection of analysis points by selecting varying CL intensities ranging from bright to dark which were analysed for Zr, Si, Al, Hf, Y, Dy, Nd, Pr, Th, U and Pb. Highly metamict zircon grains with characteristic weak CL and high uranium levels, were found to consistently exhibit a series of Dy^{3+} peaks similar to those observed in Dy^{3+} doped grown zircons, Fig. 3.

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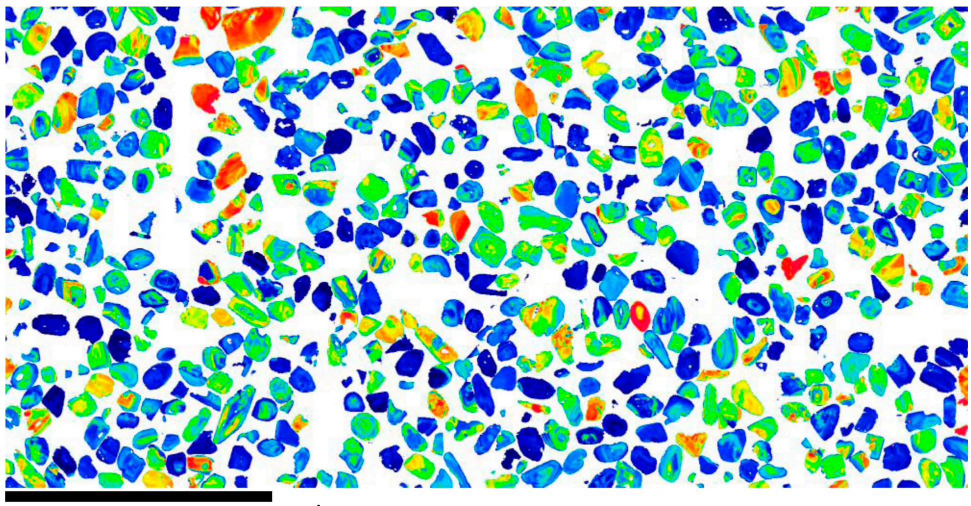

Figure 1. Cathodoluminescence image of zircon grains showing a range of different growth histories and recrystallisation as revealed by CL. Red indicates high total CL emission whereas blue represents low total CL. The image illustrates the sensitivity of the CL imaging technique to identifying subtle structural and chemical changes within zircon.

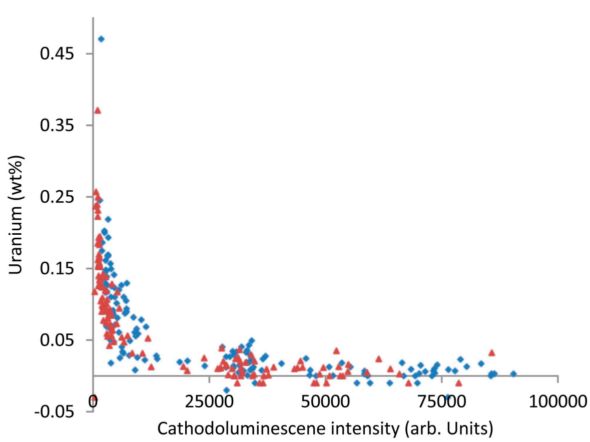

Figure 2. Two different zircon concentrates both showing similar UTOT versus CL trends. The low CL (blue areas/grains in Fig. 1) is associated with a high degree of metamictisation whereas bright zircons (red areas/grains in Fig. 1) typically contain low uranium impurities and hence have a lower degree of metamictisation.

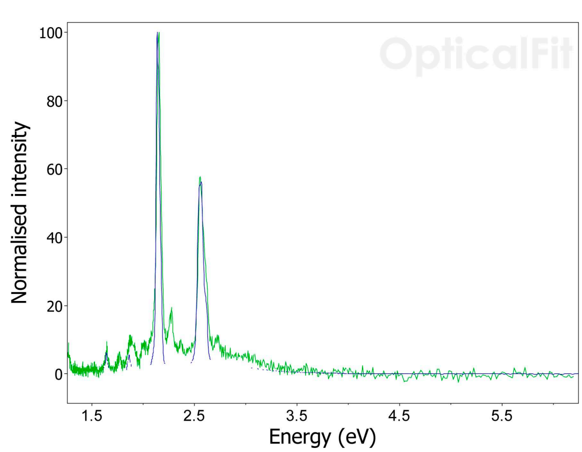

Figure 3. CL spectrum from a grain with low total CL containing 2800ppm uranium and associated with a high degree of metamictisation (green pattern). The grain exhibits distinct Dy3+ peaks similar to those observed from a Dy3+ doped synthetic zircon (blue pattern).

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