Using EPMA, Raman LS, Hyperspectral CL, SIMS, and EBSD to Study Impact-Melt-Induced Decomposition of Zircon

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Using an integrated multi-instrument approach we investigate two exceptionally well-preserved zircon grains in a obsidian-like (holohyaline) impact melt glass from the 28 km diameter Mistastin Lake Impact Structure (Labrador, Canada). The zircon grains (Fig 1) contain an un-shocked relict core and a 20–50 micron thick quenched decomposition rim, formed by the dissolution reaction of zircon to $ZrO_2 + SiO_2$ phases when the grains were entrained in impact melt during the impact event ~36 Ma [1, 2]. Using electron-probe microanalysis (EPMA), laser Raman spectroscopy (LRS), hyperspectral imaging cathodoluminescence (CL), secondary ion mass spectrometry (SIMS), and electron backscatter diffraction (EBSD), we determined the composition and phases present in the zircon core, decomposition rim, and surrounding glass, and we investigated the rim-core dissolution interface, correlating REE zoning with hyperspectral CL in the zircon core.

The zircon grains were identified in thin-section. EPMA analysis included backscattered electron (BSE) imaging, compositional x-ray mapping, wavelength-dispersive (WDS) spot and traverse analyses, including selected REEs, using a JEOL JXA-8200 at Washington University in St Louis. Mineral phases in the core and decomposition rim were identified and mapped using a Renishaw In-Via LRS with 0.6 µm pixel resolution. CL data were collected with a Gatan MonoCL4 Elite system. Ion mapping (U-Th-Pb and Y, Dy, Er, and Yb) was conducted for comparison to EPMA analyses and CL zoning, and spot measurements were made to determine the age of the zircon core using the NORDSIM Cameca 1280 in Stockholm, Sweden.

LRS data show that the decomposition rim is a predominantly vermicular intergrowth of baddeleyite and amorphous glass (sourced from impact melt infiltrating the rim during decomposition) and confirm the presence of an unaltered zircon core. LRS data also reveal relict blebs of poorly crystalline tetragonal ZrO_2 associated with baddeleyite intergrowths, suggesting a minimum impact melt temperature of 1676ºC (and possibly much greater [e.g., 3]). EPMA x-ray maps show that interstitial material in the rim has nearly the same composition as the surrounding glass and that some components diffused into, and others out of, the rim zone (i.e, Al and other impact melt components moving into the grain, and Zr and other zircon components moving out to the surrounding melt), suggesting that surrounding melt infiltrated the grain as the heat of the melt decomposed the zircon crystal rim. CL data exhibit broad spectra with superimposed sharp peaks interpreted to represent specific REE and spatial patterns related to magmatic zoning and zircon decomposition (Fig 2).. Within the zircon core, crystallization zoning patterns in CL display broad spectral features, in addition to high-frequency sharp peaks interpreted as resulting from HREEs (Tm^{3+}, Er^{3+}, Dy^{3+}) based on correlation with the CSIRO luminescence spectral database (http://www.csiro.au/luminescence/). High resolution WDS trace-element analyses (traverse seen in Fig 1b; 2 µm beam, 15 kV, 150 nA) indicate an inverse correlation between Y concentrations and CL intensity (Fig 1b). Dark areas in CL within the core contain low concentrations (measureable, but at detection limits) of Er (20-30 ppm) and Dy (~10 ppm), and relatively higher concentrations of Y (~1500 ppm). It is known that REE (including Sc and Y) are important activator elements, and that Dy^{3+} is the main CL activator in zircon by virtue of more efficient excitation in the zircon lattice ([4, 5, 6]. We see Y^{3+} quenching in the brightest areas of the zircon core (Fig 1b), but a measureable concentrations of Th^{4+} and Er^{3+} in bright areas. It may be that Y^{3+} quenching dominates the CL signal in dark areas, and activators (Dy^{3+}, Er^{3+}, and Th^{4+}) are enough to cause the bright CL, even in very low concentrations (< 100 ppm). Distinctive blue CL is observed along the core-rim interface and along cracks in the zircon grain, and must be related to the dissociation of zircon to $ZrO_2 + SiO_2$. Although not well understood, blue CL in zircon has been attributed to a delocalized electron on the $[SiO_4]$ group [5, 6], suggesting the interface records the initial stage of breakdown. Blue CL along fractures in the grain may be related to the infiltration of melt, which imparted heat energy into the lattice, delocalizing electrons in the zircon. If left undisturbed it is likely that zircon along these fractures would have begun decomposing, but the process was halted by the quenching of the impact melt. As with the LRS data, we do not observe CL features in the zircon core that indicate structural lattice changes due to shock processes, suggesting

that the grains were only affected by the high heat of impact melt immersion. The lack of shock alteration in the core is also supported by the lack of petrographic shock features and SIMS data that show no resetting of the age of the grains (original crystallization age of 1417 ± 22 Ma (within analytical uncertainty of 1451 ± 12 Ma; [2]). Age dating of the zircon core and recently completed EBSD work will be discussed at the meeting.

References:

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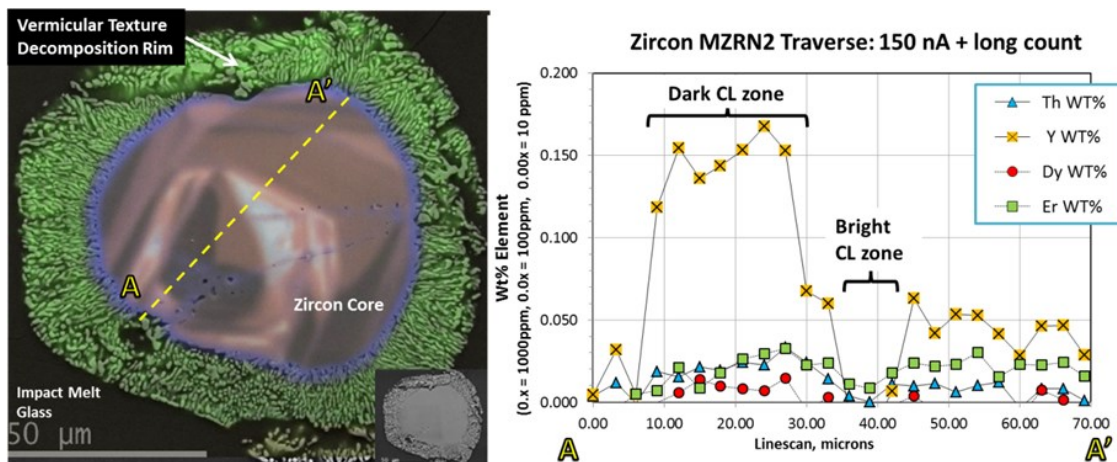

Figure 1: (left) False color RGB CL image overlain on a BSE image of partially decomposed zircon in impact melt glass. (Right) WDS spot-analysis traverse (yellow points) showing concentrations of selected REE CL activator and quenching elements.
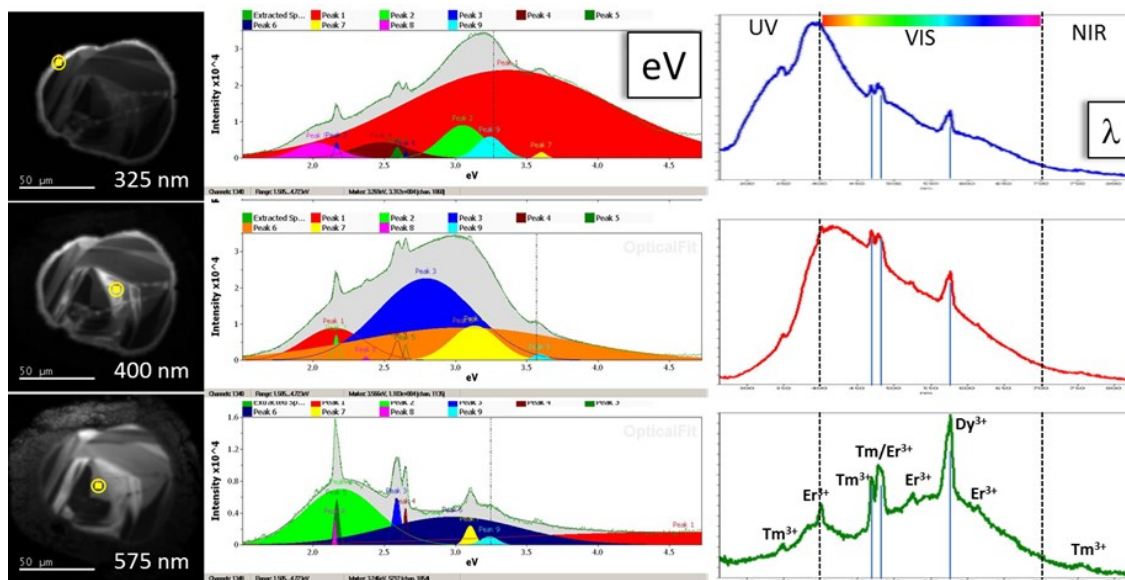

Figure 2: Hyperspectral CL data collected from various spot analyses. (left column) BSE images with spot analyses (yellow dots). Top row: decomposition interface (blue rim in Fig 1a); middle row: bright CL (white in Fig 1a); bottom row: intermediate CL (salmon color in Fig 1a). (center column) deconvolved spectra for spot analyses as a function of energy (eV). Broad humps may represent "intrinsic" CL, and sharp peaks are related to specific REE activation. (left column): same spot spectra as a function of wavelength.