Elemental nano-imaging and chemical U-Th-Pb dating of monazite and zircon using synchrotron radiation induced XRF

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A wealth of geoscientific information on rock formation can be derived from trace elements such as rare earth elements (REE) or U, Th and Pb in accessory minerals. While REE patterns are widely used to study conditions present during continental crust formation, U, Th and Pb contents are used for age dating of metamorphic and igneous processes. So far, age dating and trace element detection have been performed with different methods. In this study, we apply combined elemental imaging with chemical age dating at sub-micrometer resolution using synchrotron radiation induced XRF mapping. The study was performed on the accessory minerals monazite (LREE, Ca,Th,U)PO_4 and zircon ($ZrSiO_4$) which incorporate U and Th during formation, are stable over a wide P-T (pressure-temperature) range up to ultra-high temperature conditions (> 900°C) and widespread in different bulk rock compositions.

Measurements were performed at the nano-imaging beamline ID22NI at ESRF, Grenoble. The excitation energy was set to 17.6 keV in order to allow the simultaneous detection of REE and Pb, Th and U via L-shell excitation and elements with Z between 14 and 39 via K-shell excitation, but exclude the excitation of the Zr K-edge. A 1.5 mm thick Al absorber was introduced to reduce the background in the low energy region. The incoming beam was focused with a KB-mirror system to a spot size of 190 nm horizontally and 164 nm vertically. This configuration resulted in a photon flux of 5 x 10^9 ph/sec on the sample. Fluorescence signals were recorded with an energy-dispersive SDD detector in confocal geometry using a polycapillary half-lens on the detection side. The confocal geometry resulted in a detector acceptance of less than 15 µm in the energy range with the emission lines of interest for chemical age dating (Pb-Lα, Th-L3M1 and U-L3M1) and between 20 and 26 µm for L-lines of REE. 2D elemental maps were performed in the layer of the sample yielding maximum fluorescence signal. Sample times varied between 0.4 and 50 sec and maximum step sizes were 0.25 µm. Peak areas were fitted using PyMCA (Solé et al., 2007).

Chemical age dating was performed with confocal fluorescence intensities of Pb, Th and U using the Ranchin formula as shown by Schmitz et al. (2009). Six known age reference samples for monazite ranging in age between 101 Ma and 1821 Ma were measured at a sub-micron resolution. Chemical ages were obtained at the nano-scale with a precision of 10 % for the age references and an accuracy better than 7 %.

Elemental nano-imaging reveals different states of mineral growth and alteration in the selected sample set: while one example shows that the boundary between the inherited core in zircon and the overgrowth at ultra-high temperature was sharp on the 250 nm scale, indicating this to be a true overgrowth with minimal or no recrystallisation and scavenging of the core, two monazite examples from different localities document either polymetamorphic growth with diffuse boundaries or later changes due to hydrothermal activity.

References:

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