



	<b>Experiment title:</b> Trace element diffusion in accessory minerals: implications for geochronology of metamorphic and igneous rocks	<b>Experiment number:</b> EC652
<b>Beamline:</b> ID22	<b>Date of experiment:</b> from: 24.2.2010 to: 1.3.2010	<b>Date of report:</b> 24.10.2010
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**Report:**

In this experiment, we performed in-situ trace element diffusion studies of accessory minerals with the aim to elucidate element redistributions during subsequent magmatic or metamorphic events. Such information is essential for the retrieval and correct interpretation of magmatic and metamorphic ages and has the potential to establish links between mineral ages and magmatic and/or metamorphic events. The most important minerals to retrieve magmatic and metamorphic ages are the accessory minerals monazite and zircon. So far, ages are either retrieved with a high precision by laser ablation mass spectrometry isotope dating or at a high spatial resolution based on U-Th-Pb composition by electron microprobe analysis (EPMA). However, the results are either restricted to a spatial resolution of around 4-5 micrometer (laser ablation techniques) or to high lower limits of detection for Pb i.e. minerals of old ages (EPMA). Changes in the ages due to chemical diffusion has been demonstrated recently for experimentally altered monazite (Harlov & Hetherington, 2010), but has never been accessible in the sub-micrometer regime nor studied for natural samples. The present study, for the first time aims at chemical age dating in the sub micrometer regime. We selected samples from well studied polymetamorphic terranes where isotopic ages are already known and from six widely used age reference samples. Samples were either prepared as thin sections on a glass slide or embedded in a resin mount and then polished. Care was taken that the chemicals were free of elements heavier than silicon to avoid contaminations. Measurements were performed at the micro-fluorescence beamline L at HASYLAB to test the glass slide backing materials used for preparation of thin sections. From those measurements, Suprasil® was identified to be the best backing material for thin section preparation.

Monazite and zircon from polymetamorphic terrains as well as six age reference monazite samples were selected with the Jeol electron microprobe at CAU Kiel, based on cathodoluminescence (zircon) and on back scattered electron images and results obtained from single point chemical ages following the procedure of Braun & Appel (2006) for monazite. SR XRF measurements were performed at the nano imaging beamline ID22NI at ESRF, Grenoble, with a beam size of 190 nm horizontal and 164 nm vertical. 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. Fluorescence signals were recorded with an energy-dispersive SDD detector situated at 15° from the sample in confocal geometry. We performed elemental mappings as well as line and point scan measurements. For elemental mappings, the exposure time was normally set to a second or below. Line scans were performed at longer counting times in order to retrieve better statistics on elements with low concentrations. Exposure times for single point measurements were as high as 100 sec per point. Those measurements were only performed on the reference samples used for age dating in order to get very precise concentrations of the elements Pb, Th and U.

It can be shown that the analytical settings and conditions allowed simultaneous detection of K, Mn, Fe, Rb, Ce, Dy, Er, Yb, Lu, Hf, Pb, Th and U in zircon. In a zircon from an area with multiple magmatic and metamorphic events within a short time interval, a correlation could be found between the elements Dy, Er, Hf, Lu, Pb, Th, U and Yb with features revealed by cathodoluminescence in a zircon with an older core and overgrowth rim. The boundary between the inherited core and the overgrowth was sharp also for U, Th and Pb on the 250 nm scale, indicating this to be a true overgrowth with minimal or no recrystallization and scavenging of the core. First results have already been presented at a conference.

Another case study environment was a polymetamorphic terrane: three different ages were found with chemical age mapping using an EPMA (Fig. 1) in a monazite. Figure 1 shows the results for a tricoloured U-Th-Pb elemental map of the monazite obtained from nano-imaging at ID22NI in comparison to the BSE image.

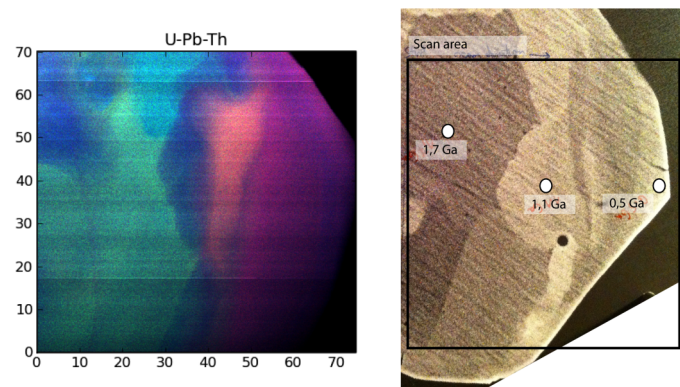


Figure 1: Monazite from a polymetamorphic terrane. Left: Pb-Th-U map obtained at ID22NI. Scales are in micrometer. Right: BSE image with chemical ages from EPMA.

During the experiment, we obtained results from all our preselected case study samples and trace element distribution patterns could be linked to features observed with CL and BSE images. The method of age calculations based on Pb-Th-U concentrations is still being improved aiming at the best possible precision. However, the data show already that trace elemental mapping on the nanoscale of monazite and zircon is an extremely powerful tool with a clear potential in the future.

#### References:

Harlov & Hetherington (2010), *Am Mineral*, 95, 1105 – 1108. Braun & Appel (2006), *Eur J Mineral* 18, 415 – 427.

### Elemental nanoimaging of monazite and zircon using SR XRF

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Monazite and zircon are among the most important accessory minerals used for U-Th-Pb geochronology of metamorphic and igneous rocks. Additionally, both minerals have a high potential to be used as geothermometers [1,2,3]. Although widely used in geochronology, the chemical stability and growth mechanisms of monazite and zircon are poorly understood. Using synchrotron radiation induced X-ray fluorescence analysis (SR XRF) at a high spatial resolution below 250 nm, we studied trace element distribution in monazite and zircon from case study localities with the aim to identify and characterize growth domains and their boundaries. This information will be correlated with age information obtained from chemical age dating by the procedure described by [4]. A similar technique is to be developed for chemical age dating of zircon with SR XRF.

Monazite and zircon from polymetamorphic terrains as well as six age reference monazite samples were selected with the Jeol electron microprobe at CAU Kiel, based on cathodoluminescence (zircon) and on back scattered electron images and results obtained from single point chemical ages following the procedure of [5] for monazite. SR XRF measurements were performed at the nano imaging beamline ID22NI at ESRF, Grenoble, with a beam size of 190 nm horizontal and 164 nm vertical. 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. Fluorescence signals were recorded with an energy-dispersive SDD detector in confocal geometry.

It can be shown that the analytical settings and conditions allowed simultaneous detection of K, Mn, Fe, Rb, Ce, Dy, Er, Yb, Lu, Hf, Pb, Th and U in zircon. A correlation could be found between the elements Dy, Er, Hf, Lu, Pb, Th, U and Yb with features revealed by cathodoluminescence in a zircon with an older core and overgrowth rim (Fig. 1). The boundary between the inherited core and the overgrowth was sharp on the 250 nm scale, indicating this to be a true overgrowth with minimal or no recrystallisation and scavenging of the core.

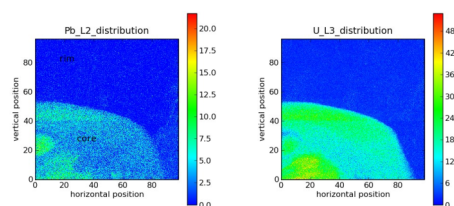


Fig. 1: Lead and U distribution maps of zircon with inherited core and metamorphic rim, axes dimensions in  $\mu\text{m}$ . Sample times were 0.4 sec per point, step sizes 0.25  $\mu\text{m}$  in both directions.

[1] Gratz & Heinrich (1998) *Eur J Mineral* **10**, 579 – 588. [2] Pyle et al (2001) *Journal of Petrology* **42**, 2083 – 2107. [3] Watson & Harrison (2005) *Science* **308**, 841 – 844. [4] Schmitz et al. (2009) *Eur J Mineral* **21**, 927 – 945. [5] Braun & Appel (2006), *Eur J Mineral* **18**, 415 – 427.