

Alteration and electron probe micro-analyser dating of high-U zircon from a pegmatite from the Aduiskii Massif, Middle Urals

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Zircon (ZrSiO_4) is an accessory mineral that is used widely in U–Pb geochronology. It may incorporate significant amounts of the radioactive actinides U and Th. The U–Th–Pb isotope system may, however, be disturbed, as for instance caused by the secondary loss of radiogenic Pb. The recognition of such alteration is crucial for the sound interpretation of geochronology results.

The secondary ion mass spectrometry (SIMS) technique has various advantages, when compared with other analytical methods, for the investigation of “normal” zircon, but a number of problems may arise when using this technique for dating zircon with exceptionally high U concentrations exceeding 0.5 wt%. In such cases, chemical electron probe micro-analyser (EPMA) dating may be a more appropriate approach, in comparison to isotope dating, for determining the sample’s geological age. In the present project (Zamyatin et al., 2017) we have studied partially altered, high-U zircon from a granite pegmatite from the Aduiskii Massif, Middle Urals (Russia) using analytical techniques with spatial resolutions on the micrometre range.

Methods. The structural and chemical heterogeneity of samples was characterised by means of an EPMA (Cameca SX100), including joint probability distribution (JPD) analysis (Votyakov et al., 2014) of back-scattered electrons (BSE), cathodoluminescence (CL) and U M_β images, and by Raman and photoluminescence (PL) spectroscopy (Horiba LabRAM HR Evolution). Analyses of the chemical composition including direct oxygen analysis (the O K_α line was measured) were carried out for a number of points. Chemical U–Th–total Pb dating based on the measured U, Th and Pb concentrations was performed according to Suzuki and Adachi (1991) and Montel et al. (1996).

Results. A high-U interior region (U up to 11.4 wt%) without any obvious indication of post-growth chemical alteration was found (zone 1 in Fig. 1a). This domain has stoichiometric chemical composition, and its Raman spectrum corresponds to that of amorphous ZrSiO_4 (Fig. 1d). It is surrounded by two zones (zones 2 and 3 in Fig. 1a) that we interpret as high-U zircon that was formed by fluid-driven alteration reactions under the influence of aqueous fluids. Zone 2 was formed by diffusion-reaction processes whereas zone 3 is a result of coupled dissolution-reprecipitation processes. Both of these chemically altered zones are somewhat depleted in U when compared to the un-altered zone 1 (Fig. 1b) and have non-stoichiometric chemical composition; they contain non-formula elements such as Ca (Fig. 1c), Al, Fe and H_2O up to several wt%. Raman spectra obtained in these regions yielded a band near $760\text{--}810\text{ cm}^{-1}$ which is not related to any ZrSiO_4 vibration (Fig. 1 d); we assign it tentatively to the symmetric stretching of $(\text{UO}_2)^{2+}$ groups. This assignment is supported by the observation of a fairly intense PL phenomenon whose spectral position and vibrational-coupling structure strongly indicates a uranyl-related emission.

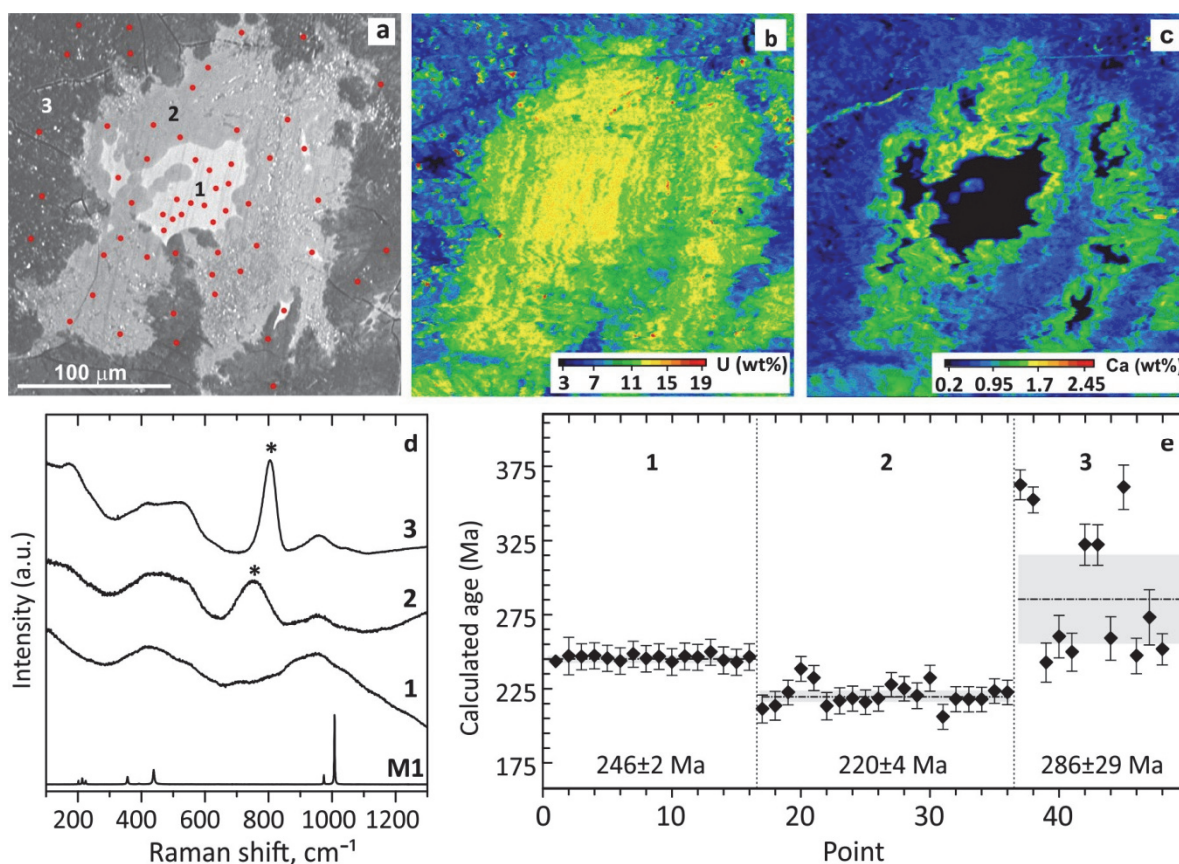


Fig. 1. Heterogeneous high-U zircon from the Aduiskii Massif (modified from Zamyatin et al., 2017). (a) BSE-image; red spots mark EPMA analysis points. (b, c) U and Ca distribution patterns. (d) Raman spectra obtained in zones 1 (high-U, stoichiometric), 2 (altered), 3 (altered), and from reference zircon M1. (e) Histogram showing the variations of calculated EPMA U–Th–total Pb ages in zones 1–3. Dash-dot lines visualize the weighted mean ages and grey bars their 2σ uncertainties

It was found that the variations of BSE and CL intensities in amorphous high-U zircon are controlled by the sample's chemical composition and the presence of H₂O and (UO₂)²⁺ groups. Diffusion-controlled alteration has caused preferred loss of radiogenic Pb, compared to the rather moderate losses of U and Th, which results in calculated ages that are apparently too young (Fig. 1e). Fluid-driven coupled dissolution-reprecipitation, in contrast, has caused higher losses of U, compared to Pb losses, leading to too old calculated ages (Fig. 1e). A weighted mean EPMA age of 246 ± 2 Ma was determined for the primary, unaltered zone 1, which agrees reasonably well with previous dating results for the Aduiskii Massif.

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