

One migmatite, three ages: Metamorphic zircon growth during and after partial melting?

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Zircon is the most robust of the single-mineral geochronometers, with single crystals recording multiple events during the Earth's evolution. SIMS dating of zircon *in situ* allows zircon behavior during metamorphism to be understood in terms of mineral equilibria. Zircon in thin sections were analysed from a migmatite locality near Kodaikkanal, southern India, which formed during ultrahigh-temperature metamorphism (950-1000°C; 7-8kbar), with a clockwise prograde *P-T-t* path and multistage exhumation [1]. Surprisingly, three associated samples from migmatite contain metamorphic zircon grown at different times: *ca.* 564 Ma in leucosome; *ca.* 529 Ma in Si-undersaturated restite; and *ca.* 514 Ma in Si-saturated restite.

Zircon growth in leucosome is limited to minor thin U-rich rims on detrital cores. Rims are absent from zircon inclusions in garnet porphyroblasts that formed during incongruent melting involving biotite. Zircon growth at *ca.* 564Ma is attributed to crystallisation from anatectic melt.

In Si-undersaturated restite, detrital zircon grains have thin but abundant metamorphic rims in equilibrium with spinel and ilmenite, grown during peak metamorphism and incongruent melting at 529Ma. Subsequent breakdown of garnet, spinel, ilmenite and zircon, along with cordierite growth, indicate retrograde cooling, but where does the Zr and Ti go?

Adjacent cordierite-rich, quartz+biotite bearing restite contains neoblastic clusters of relatively coarse, low-U zircon, grown at *ca.* 514Ma. We suggest that Zr and Ti released from zircon, garnet and ilmenite breakdown in Si-undersaturated restite was transferred to silica-saturated domains by post-anatectic fluids or fluid-rich melt.

The model proposed suggests that zircon growth at multiple stages during anatexis can occur, not only from melt as a function of Zr saturation [2] but also in restite, during both melt formation and retrograde hydration.

[1] Sajeev *et al.* (2006) *Lithos* **92**, 465–483. [2] Kelsey *et al.* (2008) *J Metamorph. Geol* **26**, 199–212.

Nanoscale process in the alteration of bentonite-iron system under the hyper alkaline conditions

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Because of the use of cementitious materials in geological repositories for nuclear waste disposal, hyper alkaline solutions derived from dissolution of the cementitious materials are likely to alter the bentonite buffer material, resulting in deterioration of its capability as an engineered barrier. Iron derived from degradation of steel overpack also affects the bentonite alteration. In order to understand nanoscale mechanisms in the bentonite alteration, we have demonstrated a laboratory experiment under ambient P_{O2} condition, in which compacted bentonite (~1 MPa) was reacted with selected aqueous solutions; (i.) a solution saturated with Ca (OH)₂, (ii.) a 1 mol/l NaOH solution, (iii.) a simulated groundwater saturated with Ca (OH)₂, or (iv.) a 1 mol/l FeCl₂ solution, for the period of 2-14 days at 130 °C. The pHs of the solutions (i)~(iii) were 12.5-13.5 during the reaction. The pH of the solution (iv) was kept almost constant within 4-5. The solid specimens were characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The solution analysis reveals a gradual increase in Na and K concentrations in the solutions (i), indicating montmorillonite dissolution. Both Ca and Si concentrations are nearly constant for the period of reaction. The thermodynamic calculation using Geochemists' Workbench reveals that the Ca concentration is constrained by the Ca (OH)₂ (s) solubility and the Si concentration is supersaturated with respect to calcium-silicate-hydrate (CSH). The SEM images of the cleaved samples show the occurrence of montmorillonite, spherical silica particles, BaSO₄ that is initially included in bentonite, and CSH between montmorillonite grains. Further, in the all specimens reacted with the solution (vi), numerous iron nanoparticles at the size of 5 to 20 nm occurred homogeneously in the bentonite, suggesting that Fe nanoparticles derived from overpack degradation can become a mobile carrier of hazardous radionuclides and potentially enhance their migration under oxic condition.