

## From partly serpentinized peridotite to continental crust through weathering and recycling processes

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Partial melting of peridotite is a fundamental process in forming continental crust. However ultramafic material are also added to the crust through obduction of ophiolites and extrusion of komatiitic lavas. Such olivine rich rocks are highly reactive and so prone to weathering. In a tropical climate they are known to develop into a thick Ni-laterite zone, hosting some of the worlds largest Ni-deposits. In order to evaluate the role of weathered peridotites on the composition of both the continental crust and the oceans, we need to understand how weathering of peridotites can fractionate elements and how the various components involved are incorporated in continental sediments or alternatively transported to the oceans. That is, a knowledge of the mechanisms involved in weathering processes and element mobilization is essential for the understanding of the continuous redistribution of elements within the Earth.

We present microtextures and mineral and whole rock chemistry from a weathering profile through the Goliath laterite of the Archaean Agnew-Wiluna Greenstone belt of Western Australia, to show that the protolith was a strongly serpentinized peridotite and that weathering involved removal of Mg, leaving behind a 20 m thick residue of quartz hematite with high Ni/Mg and Cr/Mg ratios. Rocks with similar geochemical and textural signatures are also present in clast material from three studied Devonian sedimentary basins of S-Norway[1]. Weathering of peridotite to form quartz-hematite rocks may explain that the average Cr and Ni values of continental crust are higher than those of andesite and this deviation may be used to estimate that ca 5 % of the crust may have formed from weathered peridotite. Consequently the removed Mg may contribute to the Mg budget of the Oceans.

[1] Beinlich *et al.* (2010) *Geochim. Cosmochim. Acta.* **74**, 6935-6964.

## Zircon and baddeleyite solubility in alkaline aqueous fluids

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Field evidence and thermodynamic data at ambient conditions suggest that complexing of Zr with hydroxyl ions at high pH enhances the solubilities of Zr-bearing minerals. We tested this hypothesis by measuring the solubilities of baddeleyite (ZrO<sub>2</sub>) and the assemblages zircon (ZrSiO<sub>4</sub>) + baddeleyite (Z + B) and zircon + quartz (Z + Q) in neutral to alkaline fluids at 0.2 GPa. Measured solubilities expressed as molality (*m*) of Zr in the fluid are very low, close to procedure detection limits.

We measured the solubility of baddeleyite in alkaline fluid (0.1, 1*m* NaOH) at 600°C. Solubilities measured in 1*m* NaOH using the single crystal weight loss method were higher than double capsule values, possibly due to recrystallization in a temperature gradient. For double capsule measurements the average measured Zr concentration in equilibrium with baddeleyite was  $1.8 \times 10^{-5}m$  in 0.1*m* NaOH and  $5.8 \times 10^{-5}m$  in 1*m* NaOH, suggesting that baddeleyite solubility increases with increasing hydroxyl concentration in the fluid, presumably due to formation of the Zr(OH)<sub>5</sub><sup>-</sup> complex.

In neutral to alkaline fluids (0, 0.1, 1*m* NaOH) zircon dissolved incongruently in quartz-undersaturated fluids to form baddeleyite. At 450°C vlasovite (Na<sub>2</sub>ZrSi<sub>4</sub>O<sub>11</sub>) also precipitated from fluids saturated and undersaturated in quartz. We observed no significant dependence of solubility on temperature. Ion microprobe analysis showed that the oxygen isotope compositions of zircon grains in the starting material and run products were similar, indicating that zircon dissolution-reprecipitation did not occur during the experiments.

The solubility of zircon increases with increasing fluid silica concentration, suggesting that zirconium complexes with silica in the fluid. At 600°C linear regression of experiment results yielded:

$$\ln(\text{Zr}) = -3.9 + (1.9 * \ln(\text{Si}))$$

where terms in parentheses represent molal concentrations. Zircon solubility also seems to increase with increasing hydroxyl concentration in the fluid.

At low silica activities the solubility of Zr-minerals is enhanced at high pH through complexing of zirconium with hydroxyl. Alkaline fluids may therefore dissolve zirconium minerals such as baddeleyite and zircon and mobilize Zr. At high silica activity zircon solubility is enhanced by complexing of zirconium with silica, suggesting that zirconium may also be mobile in silica-rich fluids. Fluids without high concentrations of hydroxyl or silica are not responsible for the rare observed occurrences of Zr metasomatism, but they may still catalyze recrystallization of zircon grains because recrystallization does not require high solubility.