

# High-Pressure phase transitions of zircon: phase relations based on thermodynamic measurements and application to the mantle

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ZrSiO<sub>4</sub> zircon is an important accessory mineral in igneous, sedimentary and metamorphic rocks as the host of radiogenic U and Th, and is used for U-Pb age dating. Zircon is also useful to investigate the P-T history of various rocks by using mineral inclusions. Previous high-pressure experimental studies reported that zircon first transforms at ~12 GPa and ~900 °C to reidite, a scheelite-type polymorph which is 11 % denser than zircon, and that reidite further dissociates into stishovite + cotunnite(cot)-type ZrO<sub>2</sub> at ~22 GPa and ~1000 °C. Natural occurrences of reidite have been reported in impact ejecta layers in marine sediments and shock-metamorphosed craters. However, high-pressure high-temperature phase relations in ZrSiO<sub>4</sub> have not yet been fully examined. In this study we measured enthalpies and entropies of the above phase transitions of zircon, and calculated the transition boundaries. The results were applied to clarify stability depth ranges of zircon, reidite and the dissociation phases, and also to evaluate pressure conditions of some shocked zircon crystals.

The drop-solution enthalpies of synthetic zircon, reidite and ZrO<sub>2</sub> (cot) were measured by high-temperature oxide melt calorimetry method. The entropies of reidite and ZrO<sub>2</sub> (cot) were determined by low-temperature heat capacity measurements. The obtained enthalpies for the zircon-reidite transition and the dissociation to stishovite + ZrO<sub>2</sub> (cot) were 27.5±3.3 and 50.3±3.0 kJ/mol, respectively, and the entropies of these phase changes were -6.7±1.3 and -4.2±0.1 J/molK, respectively. Based on the measured enthalpy and entropy data with available other thermodynamic data, the equilibrium transition boundaries were calculated.

The results indicate that the calculated zircon-reidite transition boundary is consistent within the errors with that determined with in-situ X-ray diffraction study by Ono et al. (2004). However, the calculated dissociation boundary of reidite has a much shallower slope than that determined with high P-T quench experiments by Tange and Takahashi (2004). Our calculated transition boundaries suggest that zircon transforms to reidite at 330-km depth and reidite dissociates to stishovite + ZrO<sub>2</sub> (cot) at 610-km depth, assuming the normal mantle geotherm.

Recently, reidite crystals containing lamellae of ZrO<sub>2</sub> baddeleyite and amorphous SiO<sub>2</sub> were found in shocked zircon crystals in Stac Fada impactite in Scotland. Based on our calculated boundaries, it is suggested that the lamellae minerals were formed under shock pressure of at least ~16-20 GPa.

キーワード : zircon、 reidite、 thermodynamics、 high pressure 、 mantle、 shock event

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