Magmatic zoisite from high-pressure pegmatites, Münchberg Massif, Germany: A potential P,T,t,x indicator

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Epidote minerals are important minor constituents in igneous rocks. They carry significant amounts of U, Th, Pb, Sr, and rare earths that are the basis for age determination and their phase relations are sufficiently known to derive *P-T* data. Here we report new data on zoisite bearing high-pressure pegmatites of tonalitic to trondhjeimitic composition from the Münchberg Massif, Germany. These pegmatites formed by decompressional dehydration melting with accessory zoisite as solidus phase. The zoisite crystals are up to 10 cm in length and are inhomogeneously distributed within the pegmatites. Their modal content is < 1 vol%. The zoisite crystals display distinct major element zoning that records three stages of magmatic evolution. Zoisite cores of stage I are iron rich with $X_{Fe} = 0.17$ [$X_{Fe} = Fe/(Fe+Al-2)$]. Inner and outer iron poor rims with $X_{Fe} = 0.12$ and $X_{Fe} = 0.10$ represent stages II and III. Calculated minimum *P-T* conditions, based on the experimentally determined maximum iron content in zoisite as function of *P* and *T*, are: Stage I > 2.0 to 2.5 GPa/700 to 750°C, stage II 1.5 to 2.0 GPa/> 650 °C, and stage III > 1.0 GPa/650 °C. Trace element concentrations in the three growth zones are almost identical and suggest constant composition of the melt throughout the entire magmatic evolution. Chondrite normalized REE patterns of zoisite are LREE enriched with $La_N = 390$ to 770, $Lu_N = 9.3$ to 16, $(La/Lu)_N = 24$ to 54 and $(Nd/Lu)_N = 25$ to 62. The individual LREE are almost unfractionated with $(La/Nd)_N = 0.96$ to 1.06. The calculated REE pattern of the melt, based on experimentally derived $D_{REE}^{zo/melt}$, is straight, slightly LREE enriched with $La_N = 130$, $Yb_N = 18$, $(La/Yb)_N = 7.5$, and $(Nd/Yb)_N = 5.7$. With $(La/Nd)_N = 1.3$ the individual LREE are slightly more fractionated in the melt than in zoisite. Lu/Hf data of zoisite are evaluated for their use as geochronometer.

Zircon aqueous solubility and partitioning systematics

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The mineral zircon ($ZrSiO_4$) grows by solid state reaction (metamorphic) or precipitation from melts (magmatic) or fluids (hydrothermal), complicating interpretation of zircon U-Pb ages. Zircon has also been shown to be susceptible to alteration and dissolution - precipitation in alkaline hydrothermal fluids (Dubinska et al., 2004), suggesting that zircon solubility may be enhanced at high pH by reactions such as:

$$ZrSiO_4 + 5\ H_2O = Zr(OH)_5^- + H^+ + H_4SiO_4,$$

$$\log [Zr(OH)_5^-] = -\log [H_4SiO_4] + pH + \log K_{eq}$$

If zircon dissolves this way in alkaline fluids then zircon solubility will ↑ with ↑ pH and ↓ $[H_4SiO_4]$. Preliminary double-capsule zircon solubility-partitioning experiments run for 25 days at 600°C, fO_2 near NNO and 1 molal NaOH in cold seal pressure vessels show that zircon solubility does ↑ with ↓ $[H_4SiO_4]$. Dissolution of the contents of the outer capsule and analysis by solution ICPMS show that the assemblage zircon + baddeleyite (ZrO_2) yielded a fluid concentration of Zr of 2.1×10^{-5} molal, comparable to our measured baddeleyite solubility of $3.8 \pm 1.8 \times 10^{-5}$ molal, while the assemblage zircon + quartz yielded a significantly lower Zr concentration of 7.9×10^{-6} molal. We will present additional data to test the hypothesis that zircon solubility is enhanced in alkaline fluids.

Investigators have used zircon Th/U to distinguish magmatic (> 0.5) from metamorphic and hydrothermal zircons (often < 0.01) without knowing the causes for the variations (or that the classification rules are often violated) (Möller et al., 2003). Starting materials were doped with 100 ppm U and Th, allowing us to measure concentrations of U and Th in the quenched solutes and calculate $D_{zircon/fluid}$ values by mass balance. In the zircon experiment $D_U = 340$ and $D_{Th} = 160$, while similar values of $D_U = 230$ and $D_{Th} = 190$ were obtained from the quartz-saturated experiment. By varying experimental parameters such as oxygen fugacity we hope to identify the conditions that promote fractionation of Th and U and lead to the development of low Th/U in hydrothermal zircons.

References

Dubinska E. et al. (2004) *Chem. Geol.* **203**(3-4), 183-203.
Möller A. et al. (2003) In Geol. Soc. Spec. Pub. Vol. 220, pp. 65-81.