Contact overprinting of regional metamorphism, New York

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A goal of metamorphic petrology is to find evidence at outcrop or sample scale to provide direct constraints on orogen-scale tectonics. Pelitic schist from the contact aureole of a small mafic pluton in Westchester County, NY, exhibits evidence of a high-P (0.8 - 0.9 GPa) high-T contact overprint at 440 Ma of a Taconic Barrovian regional metamorphic assemblage formed at 465-470 Ma. In a key sample, euhedral grt up to 5mm is set in a matrix of qtz, plg, bt, sil, ilm, gr, with Zn-rich Al-spls scattered in the matrix. No kfs or mus are present. Nearby schists without contact overprinting have the assemblage qtz-plg-mus-bt-grt-st-sil-ilm-gr; in these assemblages, T = 620-640°C and P = 0.5-0.6 GPa, consistent with values of similar sil-ms-st grade rocks just to the N. X-ray maps for Ca and Mg in multiple grt show sharply delineated rim zones on both grt and matrix plg with enrichment in Ca; bt inclusions in grt interiors show significantly higher Mg than bt in either grt rim zones or matrix. Inclusions of qtz, plg, bt and sil allow determination of P (GASP) and T (Grt-Bt Mg-Fe exchange) within grt interiors, within rim zones and for grt rims against matrix. Grt interior contacts with bt and plg inclusions inside the boundary of the grt rim zone yield average T of 623°C and P of 0.52 GPa. Similar pairs in the modified rim zone yield an average T of 780 °C and P of 0.87 GPa. Grt equilibrated under Taconic regional conditions, then under-went reaction during the later contact event. Strong P increase following a regional event requires explanation. Taconic allochthons were emplaced during the waning stages of the Taconic orogenic event at ca. 450 Ma. Only in contact aureoles were regional metamorphic mineral compositions overprinted, reflecting the new shallow crustal P-T realities resulting from shallow crustal thickening following thrusting.

Ce anomalies in zircon vs. oxygen fugacity and melt composition

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A common feature among chondrite normalized rare earth element (REE) zircon profiles is that they display enriched Ce concentrations relative to La and Pr. An increase in the magnitude of the Ce anomaly is commonly attributed to an increase in Ce^{4+}/Ce^{3+} (Ce^{4+} is more compatible than Ce^{3+} in zircon), which is generally believed to be controlled by the oxygen fugacity of the crystallizing medium.

In order to gain some insight into the cause (s) and magnitude of Ce anomalies, we have synthesized zircons in a variety of siliceous melts (68-77% SiO_2) in a piston cylinder apparatus from 925-1100°C and 10 kbar, with the oxygen fugacity buffered at IW, FMQ, NNO, and HM. Melts contained 6-10 wt% H_2O, ranged in composition from peralkaline to peraluminous, and in some cases were silica saturated. Experiments were doped with ~3000-5000 ppm of La, Ce, and Pr. Bracketing LREEs were added in order to decouple changes in the partition coefficients ($D^{zrc/melt}$) caused by melt composition; Ce anomalies could then be correlated with melt composition and oxygen fugacity. Rare earth elements were analyzed by electron microprobe and Al was used as a proxy for secondary fluorescence (i.e. contribution) of REEs from zircons with the surrounding melt; in some cases, the quenched melts were dissolved in HF and zircons were remounted and analyzed.

Our results yield systematic variation of LREE partition coefficients with melt composition; for example, melts with higher SiO_2 content also have increased partition coefficients. In addition, data are consistent with early proposals that suggested positive Ce anomalies (or negative Eu anomalies) in zircon may not be controlled by the oxygen fugacity alone [1]. Thus, these experiments may yield information about the oxygen fugacity of zircons that reside in their host rocks, but in addition, experiments may give broad constraints on the nature of the melts from which detrital grains crystallized.

[1] Maas *et al*. (1992) *Geochim. Cosmochim. Acta*, **56**, 1281–1300