Heterogeneous distribution of trace elements in zircon

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Zircon can structurally accommodate a range of trace elements including U, Th, Ti, and rare earth elements (REEs). Radioactive parents and their decay products (e.g., Pb-isotopes, ^{4}He, and intermediates in the decay chain) are used for "traditional" U-Th-Pb geochronology, ^{230}Th/^{232}Th vs. ^{238}U/^{232}Th isochrons to reveal timescales of crystallization in the thousands of years, and (U-Th)/He themochonology. The distribution of these elements in accessory minerals is of key importance; the concentrations are believed to be influenced at least by temperature and melt composition, but are typically assumed to reflect equilibrium lattice-melt partitioning. Here, we explore heterogeneous uptake of trace elements (U, Th, and rare earth elements) in sector-zoned zircons by experiment and analysis of natural samples.

Sector-zoned zircons were produced in the presence of U and Th (REEs were added to reveal growth sectors by CL[1]) and were analyzed by electron microprobe and LA-ICP-MS. When growth bands are followed across sectors, U and Th concentrations change by a factor of ~1.5 to 3.5, suggesting growth-face dependent decoupling of U and Th in the near surface of the growing crystal. Contemporaneous growth regions of different sectors also yield different Th/U ratios. Such variations have implications for ^{230}Th/^{232}Th vs. ^{238}U/^{232}Th geochronology in sector-zoned crystals, and may also provide useful information for (U-Th)/He themochonology models because: (i) these crystals could obtain a heterogeneous distribution of He resulting from sectoral variation of Th and U; and (ii) He diffusion in zircon is anisotropic[2].

Other systems also exhibit sector zoning; for example, while Ce L_{III} XANES spectroscopy of Bishop Tuff zircons reveal systematic core to rim increases in Ce^{4+}/Ce^{3+} (analytical "spot" size = 2x4 μm), grains also exhibit differences in Ce^{4+}/Ce^{3+} among sectors. If coupled with high precision ages, Ce valence may enable a direct assessment of secular changes in magma oxidation state over small time intervals, once the equilibrium and kinetic factors that influence the Ce^{4+}/Ce^{3+} in zircon are understood.

[1] Hanchar, J.M. *et al* (2001) *Am. Min* **86**, 667-680 [2] Cherniak, D.J. *et al* (2009) *Chem. Geol.* **268** 155-166