Using Sm-Nd garnet geochronology to date mid-to lower-crustal partial melting: An example from Fiordland, New Zealand

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Trace element compositional zoning and Sm and Nd isotope data provide information on the nature, timing, and duration of partial melting in the Cretaceous magmatic arc exposed in Fiordland. Mid-to lower-crustal meta-igneous rocks display evidence for intrusion followed by high-pressure metamorphism and partial melting. These high Sr/Y melts may have facilitated large-scale extension of the crust.

We present ages for peritectic garnet in high Sr/Y trondhjemite leucosomes that constrain the timing of partial melting in the Western Fiordland Orthogneiss (WFO) in the Doubtful Sound area. Garnet compositions were determined by EPMA and LA-ICPMS in order to identify compositional zoning and inclusion phases. HREE: Yb (20-100 ppm), Lu, Y, and Cr show cyclic zoning with sharp boundaries. LREE: Sm (6-8 ppm) and Nd are unzoned, and Tb displays little or no zoning. These patterns are compatible with either cyclic availability of HREE during garnet growth or slow diffusion of HREE and faster diffusion of LREE. Single phase inclusions are: rutile –random and -lattice controlled orientations, apatite, sphene, ilmenite, zircon, clinopyroxene, and plagioclase. Biotite is restricted to garnet that shows retrograde alteration along fractures. Albite, potassium feldspar, and quartz only occur as polyphase inclusions in garnet and are interpreted as melt that was trapped during incongruent melting of the host diorite gneiss. Garnet isotope ratios may be strongly affected by inclusions of REE-rich accessory phases; therefore, inclusions were removed by hand-picking followed by HF leaching which increased garnet Sm/Nd ratios. In one example, multiple splits of a single garnet crystal resulted in an increase from 0.8254 to 1.1867 as inclusions were removed.

Garnet isochron ages indicate that partial melting occurred at 109.8±1.3 Ma (4 pts.) in Crooked Arm, below the Doubtful Sound Shear Zone. U-Pb zircon ages from these rocks date intrusion of the WFO between 115.6±2.4 Ma and 114±2.2 Ma [1] indicating a brief interval between emplacement and partial melting. Additional garnet ages of 111.9±3.0 Ma (6 pts.), 115.5±3.0 Ma (5 pts.), and 113.6±2.5 Ma (5 pts.) from E to W along Doubtful Sound require widespread near synchronous partial melting.

[1] Hollis *et al*. (2004) *J. Meta. Geol*., **22**, 607-627.

Catalytic mechanism of Hg-C bond cleavage by the organomercurial lyase MerB

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The bacterial organomercurial lyase, MerB, catalyzes the cleavage of Hg-C bonds in organomercurial species such as methylmercury ($[CH_3Hg\ (II)]^+$). Two cysteines (Cys196 and Cys159) and an aspartic acid (Asp99) are known to be required for catalysis, but the detailed reaction mechanism has not yet been determined conclusively. We have performed hybrid density functional theory calculations on an active-site model of MerB derived from an X-ray crystal structure of the Hg (II)-bound product complex. Stationary point structures and energies were computed for two mechanisms that have been proposed in the literature. The calculations favor a two-step mechanism in which Asp99 first abstracts a proton from one of the two cysteines and subsequently protonates the organic leaving group. We show that coordination of organomercurials by two cysteine thiolates is sufficient to activate Hg-C bonds. Natural Population Analysis reveals that MerB lowers the activation energy of the Hg-C bond cleavage reaction by redistributing electronic charge into the leaving group and away from the catalytic proton.