Improved crustal *PTtD* evolution constraints using TitaniQ thermobarometry

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Applications of the Ti-in-quartz (TitaniQ) thermobarometer provide insight into the conditions, timing, mechanisms and rates of metamorphism and deformation. Our work on Vermont metapelites has documented quartz growth with respect to microstructural contexts as resulting from (a) early prograde growth; (b) quartz-producing metamorphic reactions; (c) precipitation from deforming micaceous domains; and (d) retrograde Si-charged fluid influx. In each case, the TitaniQ thermobarometer (with known pressures and activity estimates) reveals temperatures for these events, which all resulted in new quartz growth. However measurements of dynamically recrystallized quartz (notably through subgrain rotation) from Vermont and the Sutlej Valley (NW India) show that new subgrains usually exhibit [Ti] much lower than expected for the temperatures at which deformation occurred. This is an artifact of the mechanisms driving recrystallization in an attempt to minimize internal lattice strain. Defects aligned into subgrain boundaries may provide pathways for Ti to leave the crystal during formation of nearly strain-free subgrains. Increased lattice strain from Ti substitution may be reflected in the systematic increase in uncertainties of lattice refinements with single crystal X-ray diffraction measurements with increasing [Ti]. Therefore application to quartzites where only scarce weak interconnected phases are present to accommodate strain is problematic.

Ti diffusion from garnet porphyroblasts into quartz inclusions has recently been shown to be an effective technique for constraining metamorphic time scales [1]. In Vermont, this diffusion modeling suggests heating after encapsulation and cooling to 450 °C must have occurred in a short amount of time (<1.2 Myrs). Preliminary application to the Sutlej Valley suggests very similar time scales for metamorphic evolution. Coupled growth and diffusion modeling of large (*ca.* 4–5 mm diameter) garnets attaining low peak temperatures (<600 °C) have been unable to effectively discriminate *T-t* histories at the resolution of Ti-in-quartz diffusion modeling.

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Thermodynamics of melts from shock wave experiments and a simplified speciation model

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Although the thermodynamics of melts nominally falls outside the boundaries of a "thermodynamics of minerals" session, the subjects are intertwined by melting and crystallization and by the critical planetary dynamics that arise from differences between the physical, thermochemical, and transport properties of solids and liquids.

An extensive campaign of shock wave experiments on liquid compositions in the CaO-MgO-Al_2O_3-SiO_2-FeO system now provides constraints on the equations of state (EOS) of multicomponent melts at all terrestrial mantle pressures. The results can be compared to *ab initio* and empirical molecular dynamics (MD) simulations, static experiments, and geophysical observations. Key material property conclusions that have emerged include: (1) a negative temperature dependence to the sound speed, at least for Mg_2SiO_4 melt; (2) clear composition dependence to the effective partial molar volume of the FeO component, presumably related to composition-dependent coordination or spin states; and (3) universal behavior of the Grüneisen parameter, increasing upon compression at a near-uniform rate. Earth science conclusions at this stage include: (4) an absence of cases where mid-mantle magma ocean crystallization can give rise to a neutrally buoyant solid assemblage, at least initially near the liquidus; and (5) the near impossibility of finding a bulk composition in MgO-SiO_2-FeO and an extent of partial melting consistent with phase equilibrium and geophysical constraints for partially molten ultra-low velocity zones at the core-mantle boundary.

Given the expense and limitations of current MD methods for the study of silicate liquids and the challenge of linking microscopic data (e.g. spectroscopy) to mesoscopic data (e.g. EOS) or macroscopic observations (i.e., geophysics), it is helpful to develop simplified models that capture certain key aspects of melt behavior. We have extended the hard-sphere model into a coordination-number dependent, predictive model of speciation and equation of state for silicate liquids, *CHASM*. Currently the model has been calibrated on solid structures for SiO_2, MgO, and MgO-SiO_2 binary systems. It reproduces the pressure-dependence of coordination statistics from MD and allows insight into the natural origins of phenomena (1), (2), and (3) above.