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The thermodynamic role of water in metamorphic reequilibration: Implications for interpreting the rock record

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Equilibrium mineral assemblages in metamorphic rocks are essential for constraining Earth's tectonic history, and many petrologic studies assume that rocks equilibrate under the conditions of interest and retain associated mineral assemblages during subsequent changes in pressure and temperature. However, as we continue to integrate textural information and geochronology to constrain multiple portions of rocks' pressure-temperature-time-deformation (*P-T-t-d*) histories, it becomes essential to quantitatively understand which parts of paths may be missing or only cryptically preserved. It is therefore necessary to evaluate under what circumstances metamorphic rocks reequilibrate.

Water has long been understood as a driver of metamorphic reequilibration, but it is unclear if its role is primarily thermodynamic or kinetic. We use thermodynamic models to calculate the Gibbs free energy of reaction associated with converting a metastable mineral assemblage to a stable mineral assemblage, conducting these calculations for several example systems. For a given bulk composition, the Gibbs free energies of reaction for the conversion of a metastable assemblage to an equilibrium assemblage at a given *P-T* point are very similar for dry recrystallization or hydration reactions in the presence of water. This implies that the thermodynamic driving force for dry recrystallization is similar to that of hydration, and that the role of water is primarily kinetic. Our results also suggest that the buildup of Gibbs free energy is strongly dependent on the specific *P-T* path as well as major mineralogical changes, which may include but are not limited to devolatilization reactions.

These results have several implications for interpreting the metamorphic rock record. Rocks that may have undergone multiple phases of metamorphism should be evaluated carefully, as they may not record portions of the *P-T* path during which they were dry. This is particularly relevant for methods such as diffusion modeling and thermochronology, which may be affected by thermal pulses that leave little to no mineralogical evidence in the absence of fluid ingress but would enhance intracrystalline diffusion rates.