

## Petrologic implications of variations in metamorphic reaction affinity

David Pattison

Metamorphic reactions may be overstepped in temperature due to kinetic barriers to nucleation and growth. The extent to which these kinetic barriers delay the onset of reaction is related to the reaction affinity of each reaction, defined herein as the Gibbs free energy difference between the thermodynamically stable, but not-yet-crystallized, products and the metastable reactants.

Mineral reactions which release large quantities of H<sub>2</sub>O, such as chlorite-consuming reactions, have a higher entropy/volume change, and therefore a higher reaction affinity per unit of T/P overstep, than those which release little or no H<sub>2</sub>O, such as chlorite-free reactions. The former are expected to be overstepped in T or P less than the latter. In at least two natural settings (Bushveld regional aureole: Waters & Lovegrove 2002, JMG; Nelson contact aureole: Pattison & Tinkham 2009, JMG), contrasting degrees of reaction overstepping, as revealed by the distribution, textures and compositions of mineral assemblages, fit these predictions.

Some implications of the above include:

- (1) metamorphic reaction intervals are expected to be discrete rather than continuous, even (especially?) in broad multivariant domains in an equilibrium phase diagram across which smooth, continuous reaction is predicted;
- (2) reaction intervals may not correspond in a simple way to reaction boundaries and domains in an equilibrium phase diagram, and can involve metastable reactions;
- (3) overstepping can lead to a 'cascade effect', in which several stable and metastable reactions involving the same reactant phases proceed simultaneously;
- (4) fluid generation, and possibly fluid presence in general, is expected to be episodic rather than continuous, corresponding to discrete intervals of reaction;
- (5) fluid ingress to metastable fluid-deficient rocks dramatically lowers kinetic barriers to nucleation and growth, potentially resulting in infiltration-driven rather than thermally-driven reaction intervals;
- (6) thermobarometry based on combined use of phase diagram sections and mineral modes/compositions on the one hand, and classical thermobarometry methods on the other, may not agree even if the same thermodynamic data are used.

The extent to which these findings apply to regional metamorphism depends on several factors, a major one being enhanced deformation, which is expected to lower kinetic barriers to nucleation and growth. The simple fact of the metamorphic facies principle demonstrates that the above kinetic effects do not seriously compromise the equilibrium model of metamorphism, and are not the governing factors in the development of metamorphic mineral assemblages other than in exceptional circumstances. On the other hand, the petrologic interpretation of mineral textures with respect to reaction processes and P-T paths may be strongly influenced by kinetic effects.