

Effects of reaction kinetics on mixed volatile (CO₂-H₂O) decarbonation reactions in contact aureoles

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One-dimensional models of heat and mass (CO₂-H₂O) transport are used to evaluate the roles of fluid flux, diffusion, and reaction rate during infiltration-driven metamorphism by modeling the reaction: calcite + quartz = wollastonite + CO₂. Incorporation of reaction kinetics (rate constants based on experimental data) produces little change in the rate of advance of a reaction front in up-T flow, but causes reductions of ≤ 20 to 25% in the rate of advance of a reaction front in down-T flow. In contrast, diffusion has no significant impact on the rate of advance or width of a reaction zone in either up- or down-T flow at significant fluid flux (10^{-9} m³ m⁻² sec⁻¹) and for limited timescales ($\leq 50,000$ yrs) of flow and reaction. A significant impact of reaction kinetics in down-temperature flow is to expand reaction fronts to reaction zones. At reaction rates based on experimental studies, reaction zones of > 40 m are quickly developed at significant fluid flux (10^{-9} m³ m⁻² sec⁻¹) and high porosity ($\phi = 0.1$). If fluid flux decreases by decreasing porosity, the width of the reaction zone narrows considerably; at low porosity ($\phi \leq 0.001$) reaction zones are less than 5 m in width. However if reaction rates in contact metamorphic environments are one to two orders of magnitude less than experimental results, then reaction zones of significant width (> 8 -10 m) could be developed in contact aureoles at porosity of ≥ 0.001 and fluid flux $\geq 10^{-11}$ m³ m⁻² sec⁻¹.

Isograds formed in contact aureoles during down-T flow are typically narrow ($\ll 10$ m; many $\ll 1$ m). Our modeling results indicate that these narrow reaction zones require significant fluid infiltration rates ($\geq 1 \times 10^{-8}$ m sec⁻¹), and either reaction rates faster than experimental values or low porosity (≤ 0.001). Rapid reaction rates appear at odds with an increasing number of reported occurrences of mineralogic and oxygen isotope disequilibrium in metamorphic systems. Alternatively, the narrow reaction zones may indicate that infiltration-driven metamorphism occurs at low porosity (≤ 0.001). If so, the modeling results indicate that equilibrium reaction surfaces may be significantly overstepped for both up- and down-T flow. Such overstepping leads to the possibility that index minerals could be produced in contact aureoles by metastable reactions.

Unreactivity of garnet in low pressure metapelites

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Garnet is one of the most widespread and petrologically important metamorphic minerals in metapelites. Several lines of evidence suggest, however, that in low pressure metamorphism at least, garnet forms at low grade but may not participate modally in subsequent mineral reactions until considerably higher grade is reached: even though it is physically present, it is to a large degree chemically inert due to sluggish kinetics of reaction. The evidence includes: distribution of garnet in individual rocks that is independent of the distribution of later-formed porphyroblasts; euhedral shape of garnet in rocks in which phase equilibrium considerations suggest it should have dissolved significantly (e.g. staurolite-bearing rocks); chemical zoning patterns of garnet in such rocks that show no evidence for reaction; and phase equilibrium systematics of low pressure metapelites that work fine when garnet is ignored.

To test the implications of these observations, we have performed phase equilibrium modelling for isobaric low pressure (3.8 kbar) prograde metamorphism of average metapelite for two end member situations: perfect equilibrium crystallization and perfect fractional crystallization with regard to garnet. The predicted sequence and position of reaction isograds is immaterially different between the two situations, possibly accounting for the success of low pressure phase equilibrium systematics that ignore garnet. These results show that care is required in using garnet in mineral assemblage-based petrogenetic grids, such as for bathozone determinations. Staurolite appears to show some of the same behaviour as garnet, which we have also modelled.