Dramatic effects of stress on metamorphic reactions

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Wheeler (2014) claims that differential stress has a dramatic effect on metamorphic reaction, by computing the affinity for a “reaction pathway,” that he has unified the theories for the equilibrium assemblage in a hydrostatically stressed rock and for pressure solution; and that these processes are coupled. His conclusions would invalidate many of the inferences metamorphic petrologists have made about pressure-temperature relations prevailing in metamorphic terrains. Here, I show that Wheeler’s claims do not have a sound basis. In particular, the suggestion that one is free to choose a “reaction pathway” leads to contrived outcomes, and is contrary to the tenets of model formulation.

The notion of a reaction pathway is motivated by the observation that, in natural examples, reactant dissolution may only occur on interfaces ~ normal to the maximum compression and product precipitation only on interfaces ~ normal to the least compression (incongruent pressure solution, IPS). In (congruent) pressure solution, one phase dissolves and precipitates, with deformation but no reaction, and the dependence is on deviatoric stress alone. If IPS were the usual way metamorphic reactions took place, one might suggest that the rate of metamorphic reaction would also depend on deviatoric stress. A statement of Wheeler’s conceptual model, excerpting from his paper, is: (1) “...there are multiple reaction pathways and multiple affinities in stressed systems”, (2) “Which pathways are favored then depends on the kinetics of diffusion along grain boundaries and of attachment and detachment of chemicals at interfaces”, and (3) “The affinity does not dictate the details of reaction kinetics but its sign is a fundamental indication of whether a reaction can occur.” He considers a 2-D microstructure of cylindrical grains of rectangular cross section. Uniform normal stresses $\sigma_{xx}$ or $\sigma_{yy}$ act on their surfaces. A reaction pathway is specified, and conclusions are drawn from the affinity computed for it. Here, I single out the IPS reaction pathway.

However, a complete model for metamorphic reaction and pressure solution consists of: (1) conservation laws, as for mass; (2) constitutive laws, as for interfacial diffusion and reaction kinetics; and (3) initial- and boundary-conditions for its full domain, providing a mathematical model, closed in the sense of “N equations in N unknowns.” Consequences emerge as solutions or derived statements. To call a model a conceptual model is to imply it is incomplete. Here, conclusions are drawn from a complete 2-D model for metamorphic reaction and pressure solution. Its domain consists of a periodic array of square, cylindrical grains of side 2a, with faces aligned in the x- and y-directions. Normal stresses $\sigma_{xx}$ and $\sigma_{yy}$ are applied to the array. In a one-component system, initial grains of phase B undergo the reaction $B \rightarrow A$ by dissolution and precipitation. MacDonald (1957) also treated the effect of nonhydrostatic stress on mineral equilibria using a phase change—e.g., calcite-aragonite.

By symmetry, mass is conserved within each ¼ grain. If the combined local rates of dissolution or precipitation of B and A are uniform, grain contact does not require deformation. In the limited circumstance considered, layers of A on both interfaces are sufficiently thin that the B-A interface may be approximated by the initial grain outline. Ignore the mechanical constraint at face intercepts. Finally, let interfacial kinetics be rate-determining, in the fast-diffusion limit. Interfacial chemical potential, $\mu$, and stresses $\sigma_{xx}$ and $\sigma_{yy}$ are then uniform. This tractable model is chosen to clarify “theory,” not to fully mirror nature. Its statement consists of kinetics equations for A and B at the two interfaces, denoted $\perp x$ and $\parallel x$, expressed as rates of mass change per unit depth on ½ of each surface—e.g.,

$$\frac{dm_A}{dt} \perp x = \frac{aK_A}{V_A} \left( \mu - \mu_A^0 \right) (\mu - \mu_B^0 + \sigma_{xx}V_B^0)$$

$$\frac{dm_A}{dt} \parallel x = \frac{aK_A}{V_A} \left( \mu - \mu_B^0 + \sigma_{xx}V_B^0 \right)$$

and of mass conservation:

$$\frac{dm_A}{dt} \perp x + \frac{dm_A}{dt} \parallel x = 0 . \tag{1}$$

The solution is:

$$\frac{dm_A}{dt} \perp x = Q + aK_A \delta_{xx}, \quad \frac{dm_A}{dt} \parallel x = -Q - aK_A \delta_{xx}$$

$$Q = a \left( \frac{K_A}{V_A} \right) \left( \frac{K_A}{V_A} + \frac{K_B}{V_B} \right)^{-1} \left( \mu_A^0 - \mu_B^0 \right) + \sigma(V_A^0 - V_B^0) \right) , \tag{3}$$

where $\delta = 1/2(\sigma_{xx} + \sigma_{yy})$, $\delta_{xx} = 1/2(\sigma_{xx} - \sigma_{yy})$ are mean and deviatoric stress. Rate of production of A, $Q$, is independent of deviatoric stress. Terms $\delta_{xx}$ give rate of mass transfer by pressure solution. Reaction and pressure solution are uncoupled. These conclusions contradict those inferred by Wheeler.

For incoherent grains with dimensions $2a(x$ and $2b)y$, $\sigma(V_A^0 - V_B^0)$ is replaced by $\sigma_a(V_A^0 - V_M^0) = \sigma_a(V_A^0 - V_M^0) + \delta_{xx}(x_0^0 + y_0^0)$. Wheeler attributes the dramatic effect of stress on reaction to the last term. If the present procedure is applied to this reaction pathway:

$$\frac{dm_A}{dt} \perp x = a \left( \frac{K_A}{V_A} \right) \left( \frac{K_A}{V_A} + \frac{K_B}{V_B} \right)^{-1} A_{IPS}$$

$$A_{IPS} = (\mu_A^0 - \mu_B^0) + \sigma(V_A^0 - V_M^0) + \delta_{xx}(x_0^0 + y_0^0). \tag{4}$$

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seemingly in support of Wheeler’s conclusion. But the solution to the complete model is (3), and IPS can only be achieved if $K_e = K_B$, with IPS constraints yielding $\delta_{xx}(x_0^0 + y_0^0) = (\mu_A^0 - \mu_B^0) + \sigma(V_A^0 - V_M^0)$, and the rate dependence on $\delta_{xx}$ is removed.

I have shown that the concept of a reaction pathway, selecting both a set of interfaces and placing restrictions on dissolution or precipitation of phases on them, is inadmissible. The “existence” of such a pathway reduces to a special case arising, or not, for some combination of independent variables and model parameters. A complete model describing an example of IPS requires posing additional conditions, e.g., as on phase nucleation. In such a model, the same dependences would likely occur, with reaction and pressure solution uncoupled, and no dramatic effect of (deviatoric) stress on metamorphic reaction.

REFERENCES CITED
