Dramatic effects of stress on metamorphic reactions: Reply

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I thank Fletcher for his stimulating Comment (Fletcher, 2015) on my paper (Wheeler, 2014). I agree with every aspect of his philosophy on how a complete model should be constructed and I agree with his mathematics and the assumptions behind it. But it is inappropriate to say that I am wrong, first because his model is not of the incongruent pressure solution (IPS) pathway, second because it actually contains confirmation of some of my claims, and thirdly because it is extremely restricted in scope.

First, Fletcher asserts his model is equivalent to my IPS pathway, but in fact his model is an interesting combination of pathways. In IPS some phases dissolve and different phases precipitate. In Fletcher’s model, A and B might both dissolve and precipitate; there is a single chemical component being redistributed among four types of interface (two phases, two orientations) which involves six pathways, and hence it is not surprising that some kind of intermediate behavior results. Instead of $A_{IPS}$ we should define, after Fletcher’s equation 3,

$$A_{MP} = \Delta F + (V^A - V^B)W,$$

where MP stands for “multiple pathways” and (noting that Fletcher has envisaged grain shapes evolving so that $A \rightarrow B$ can reverse direction so that $B \rightarrow A$ (a very restricted case). One can envisage grain shapes evolving so that $A_{MP}$ changes sign as grain shape evolves; the reaction $B \rightarrow A$ reverses direction so that $A \rightarrow B$. One might also expect a variety of grain shapes at one time, so we might find reactions $B \rightarrow A$ and $A \rightarrow B$ running simultaneously in different microstructural settings. All of this confirms my assertion that there is in general no equilibrium in a stress ed system. For elongate grains, microstructural settings. All of this confirms my assertion that there is in general no equilibrium in a stress ed system. For elongate grains, microstructural settings. All of this confirms my assertion that there is in general no equilibrium in a stress ed system.

Secondly note that in the (incorrect) assumption by others that mean compressive stress can replace pressure in thermodynamic calculations, the “mean” is defined as the average of the principal stresses. But $W$ is not equal to the mean stress unless $a = b$ (a very restricted case). One can envisage grain shapes evolving so that $A_{MP}$ changes sign as grain shape evolves; the reaction $B \rightarrow A$ reverses direction so that $A \rightarrow B$. One might also expect a variety of grain shapes at one time, so we might find reactions $B \rightarrow A$ and $A \rightarrow B$ running simultaneously in different microstructural settings. All of this confirms my assertion that there is in general no equilibrium in a stressed system. For elongate grains, $W$ can approach $\sigma_{xx}$ or $\sigma_{yy}$ in value and so a single principal stress may dominate reaction progress if Fletcher’s equation 3 applies. Experiments on polymorphic transformations in stressed systems confirm that $\sigma_{xx}$, not mean stress, has a direct effect on transformation, for example, coesite forming from quartz (Hirth and Tullis, 1994) and spinel forming from olivine (Vaughan et al., 1984); in the latter case, a mathematical treatment akin to Fletcher’s explained the main observations and is entirely in accord with my equation 2 (Wheeler, 2014).

Thirdly, note the very restricted assumptions in Fletcher’s model.

(1) Polymorphic transformation. Most phase transformations in the Earth are not polymorphic, so this model does not allow us to understand a more general situation in which chemical transport over long distances of the order of grain size or more is essential. Experiments on more complicated reactions do not indicate that mean stress controls reaction—instead, the dominant control may be, for example, fluid pressure (Llana-Fuñez et al., 2012).

(2) No other phases. With other phases present, the microstructural settings of A and B are unlikely to be the same; the stresses they support are, in contrast to Fletcher’s model, unlikely to be identical.

(3) An instantaneous response of a highly idealized microstructure (viewed in 2-D, a square array of A and B with no other phases). While all models must idealize nature, a square array of grains can give very misleading results. Every grain boundary junction in such a model is quadruple, not triple. Whatever happens is likely to change the topology and decompose these quadruple junctions into triple junctions. Hence, as Fletcher himself says, he looks only at the instantaneous response. The microstructure will retain quadruple junctions only if the polymorphs have the same molar volumes, but in this case the reaction rate $Q$ is independent of stress altogether (Fletcher’s equation 3) and the model is not very informative. The topology of grain boundary networks is very important in such models, as my own work on diffusion creep illustrates.

If one considers a “chessboard” arrangement of two phases, then a flow law for this two-phase composite in diffusion creep can be derived (Wheeler, 1992), but as, figure 5 in that paper shows, the topology will evolve. An attempt to derive a more general flow law for a more realistic microstructure with triple junctions shows that there are fundamental (and unsolved) mathematical problems (Ford and Wheeler, 2004). This shows how misleading oversimplified models might be.

(4) A limiting case where diffusion is fast and only interface kinetics matter. In general, the attachment and detachment of atoms at interfaces is important in reaction but so is diffusion. Fletcher assumes interfacial kinetics is rate-determining, which is correct in the fast-diffusion limit. He says “For finite rate of diffusion, the condition of no mismatch between grains results in a problem not easily solved. Ignoring it, …”. He may well have rediscovered the sorts of problems described above (Ford and Wheeler, 2004) but by ignoring these he reduces the value of his assertion that “For finite $\xi$ [that is, when diffusion matters], the present conclusions are retained.” Does diffusion matter in metamorphism? Yes for reaction—as shown by the common occurrence of reaction coronas and spatial association of reactants and products in natural rocks. Yes for diffusion creep—as shown by numerous flow laws that have stress proportional to the third power of grain size (Hirth and Kohlstedt, 1995). Interfacial kinetics matter as well; faceted porphyroblasts such as garnet show that attachment of atoms during growth is important, although not necessarily rate controlling. A complete theory for metamorphism must include both diffusion and interfacial kinetics.

In summary, Fletcher’s model is too restricted in scope to undermine my conclusions: we agree that a more general model is required. I challenge him and other interested readers (including myself) to construct such a model, which would be of great benefit to understanding how metamorphism and deformation interact.

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REFERENCES CITED


