

## ***Interactive comment on “Chemical Heterogeneities in the Mantle: Progress Towards a General Quantitative Description” by Massimiliano Tirone***

**Anonymous Referee #2**

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Review of Tirone, Chemical Heterogeneities in the Mantle. . .

I do not recommend publication of this paper.

This paper addresses an important problem in geophysics. Given a lithologically heterogeneous portion of the mantle consisting of two lithologies ( $A_0$ ,  $B_0$ ) with length scale (thickness) large compared with grain sizes, what is the nature and extent of chemical exchange between the two lithologies? The simplest answer, based on the inefficiency of chemical diffusion, is that the two lithologies do not chemically interact at all, maintaining their chemical compositions unchanged for geologically long periods of time, or at least until mantle convection has thinned them to such an extent that chem-

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ical diffusion can operate. This end-member idealization has been widely explored in geophysics.

At the other extreme, assuming diffusion is sped up (perhaps by fluids) or the lithological thickness is sufficiently small for chemical diffusion to operate, the two lithologies may completely equilibrate, forming a new homogeneous lithology,  $W$ . This new homogeneous lithology is uniquely defined by equilibrium thermodynamics: given the compositions and relative amounts of  $A_0$  and  $B_0$ , there is a unique equilibrium state  $W$  that results from minimization of the global Gibbs free energy.

The author explores something in between these two extremes. He allows for some, limited, reaction between  $A_0$  and  $B_0$ , such that the two lithologies end up with altered, but still distinctive compositions, ( $A$  and  $B$ ). This state is NOT uniquely given by equilibrium thermodynamics. It results from a CONSTRAINED minimization of the global Gibbs free energy. Depending on what one assumes for the nature of these constraints, one can achieve a whole host of non-equilibrium assemblages  $A, B$ .

Why would you impose constraints? It is unclear what the author's answer to this question might be. I might impose constraints because I might believe that a) chemical diffusion is limited but not zero and that b) some components might diffuse faster than others. Whether this is what the author has in mind or not is unclear.

We can examine the form of his constraints. These seem either to be thermodynamically unrealistic or ad hoc or both. Let's examine them in detail:

Aside from (trivial) mass conservation (Eq. 1), we come first to Eq. 2, which states that the chemical potentials of all components in  $A$  and  $B$  should be the same as they are in  $W$ . This makes no sense to me. How do the partially equilibrated lithologies  $A$  and  $B$  “know” about the chemical potentials in the true thermodynamic equilibrium state  $W$ ? Consider an example:

$A_0$ :  $(1-f)$  moles of forsterite  $B_0$ :  $f$  moles of fayalite  $W$ : olivine:  $f_0(1-f)f_a$   $A$ : ?  $B$ : ?

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The chemical potentials of  $f_o$  and  $f_a$  in A and B cannot be equal to those in W UNLESS,  $A=W$  and  $B=W$ . In other words, the constrained minimization in this case does provide an answer that differs from the unconstrained minimization. For any limited equilibration between  $A_0$  and  $B_0$ , the chemical potential must differ.

The next paragraph (pg. 5 ll. 15-28) proposes another constraint based on inspection of phase assemblages in  $A_0$ ,  $B_0$ , and W. In this case, one phase (olivine) is proposed to end up entirely in A with none in B, because this avoids the formation of a “new mineral” in B. But why should this be a constraint? I suppose there is some relationship here to minimizing mass exchange. But the formulation seems ad hoc. Such restrictions have consequences for other mineral exchange reactions and this seems to be the focus of the following paragraph (pg. 5 ll. 29-pg. 6 l. 6).

The next constraint is stated in Eq. 4. There is a potentially interesting notion behind this constraint that is not made explicit. It is in some way an attempt to minimize a generalized chemical driving force between the two lithologies, by minimizing the difference in Gibbs free energy between them. This is intriguing, although why one should focus on minimizing the chemical driving force, rather than minimizing the mass exchange is not clear to me. It is worth pointing out that while the left-hand side of Eq. 4 can be minimized, the equation as written cannot be satisfied, even in simple systems, as the author showed in his previous study (2016).

The last constraint, Eq. 5, seems to derive from the arguments already presented (ca. Eq. 5). Not sure why an additional constraint is needed here.

The author then goes on to consider time-dependent problems, for which Eq. 6 seems to be the basis. This is obviously a diffusion equation and S clearly plays the role of a diffusivity. So why insist that S is dimensionless? Some more physical motivation is needed here. By the way, I do not understand the “\*” notation. Is the composition  $A^*=A$ ? If so, wouldn't  $G^*(A)$  be better notation than  $G(A^*)$  for the normalized Gibbs free energy? Also, what is the normalized Gibbs free energy? I do not see it defined.

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A final comment. The paper is completely untethered to observations, either from experiment or the field. Rocks consisting of finely interlayer eclogite/peridotite are well studied. Surely there is some opportunity for comparison? I note that the previous paper (Tirone et al., 2016) made some comparison with the experiments of Milke et al. (2007), although that study emphasized the importance of the relative diffusion rates of different chemical components, which Tirone does not seem to consider, or perhaps only in an indirect way via Eq. 6.

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Interactive comment on Solid Earth Discuss., <https://doi.org/10.5194/se-2018-67>, 2018.

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