

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

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Received and published: 22 January 2019

I truly appreciate the effort and the time that the reviewer(#2) has put into this manuscript.

It is also a fantastic opportunity to be able to respond in a public forum, thanks to Solid Earth and the open review policy of the journal.

General comments:

It is true that the physics of mechanical mixing in the mantle has been addressed for

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many years now in the "end-member idealization" (as referred by the reviewer) where two lithologies are forever impermeable to mass exchange (the early studies by Kellog, for example, are very interesting). However we know that some chemical exchange always takes place on a certain spatial scale (this end-member case is strictly correct only for contact-time = 0), but no effort has been put to quantify the approximation introduced by the end-member case, why?

The idea that chemical equilibration is too slow to be effective has been permeating the solid Earth community for over forty years. Unfortunately there are no modern published evidences that support such conclusion nor quantify it. The concept of chemical diffusion is also often used quite freely either to dismiss any further investigation or to make general assumptions. But which diffusion mechanism? what chemical elements? which minerals are affected and how much? what other processes are involved and how? The "simple answer" (quoting the reviewer) that diffusion is too slow for the problem in hand is really too simple.

The field of chemical kinetics is also much more than "diffusion", there are several excellent books describing the complexity of chemical processes, for example "Chemical Kinetics of Solids" by H. Schmalzried. Perhaps from a geophysics perspective an analogy can be made between the chemical equilibration processes and the processes in the deformation creep. Even for a monomineralic polycrystalline assemblage elemental volume diffusion (e.g. Si) does not entirely describe the various creep models. And when a two minerals assemblage is considered, the deformation can assume a large range of values depending on several factors (a couple of well known references are worth to mention: Karato's book, Deformation of Earth materials; and Takeda, Flow in rocks modelled as multiphase continua: application to polymineralic rocks. J. Struct. Geol., 1998). What about deformation for a 4-5 minerals assemblage?

Back to the chemical equilibration problem. The early work by Hofmann, which by the way was great for that time (1978), has been already discussed in the manuscript. I am not aware of further studies that substantiate and quantify experimentally or theoret-

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cally the extent and the nature of the chemical equilibration between two multiphase multicomponent assemblages (peridotite-eclogite or similar). How far the eclogite and peridotite equilibrate at 1300C, 50 kbar after 1 Myr? and after 1Byr? what about 80 kbar? what is the composition/mineralogy? Any reference would be greatly appreciated.

Comments on specific issues:

Perhaps there is a misunderstanding on what is the other end-member extreme that the reviewer refers as a "new homogeneous lithology". From a chemical perspective it does not happen. When the two sub-systems (lithologies) A and B are in chemical equilibrium they will not homogenize. They will preserve distinctive chemical and mineralogical features but different from those in the initial state (before equilibration). For a fixed proportion of A0 and B0, this is the other end-member state, it is not an intermediate state. Perhaps the easiest way to see this is by considering the reaction between qz and periclase to form forsterite(fo) and enstatite(en):



As shown for example by Gardes et al. (CMP, 161, 1-12, 2011), in complete equilibrium fo and en will not mix to form an homogeneous biminerale single layer but instead there will be two separate layers (A and B), one made of polycrystalline pure fo and the other by polycrystalline pure en.

The reviewer called the computation described in the manuscript a constrained minimization of the Gibbs free energy, I don't think it is correct, although I am not quite sure. Minimization of the Gibbs energy is applied to the whole system (W), without any constraint beside the usual mass balance. The standard procedure requires as input quantities P,T and bulk composition (computed from A0 + B0 in a predefined pro-

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portion). The output is the mineral phases composition and abundance for the whole system W. Clearly there are no info regarding the two sub-systems A,B. Using the analogy of the example with qz and periclase, the G minimization applied to the whole system (qz+MgO) will determine that en and fo will be formed in equilibrium and it will define their abundance. For completeness, for this simple example mass balance would have been sufficient to determine the abundance, but in any case, the key point is that no indication is provided regarding the spatial distribution of fo and en.

In the manuscript the constraints are applied in a subsequent step. The answer to the question on why do we need to impose chemical constraints, is quite simply actually, because we want to know what is the composition and mineralogy of A and B after they have been put together and they reached chemical equilibrium. Translating the task in the simple example above, the question would concern the spatial distribution of fo and en. As mentioned by the reviewer (I think), something similar has been done for an analogous simple system in the previous study (Tirone, 2015), that is the reaction $qz + fo \rightarrow en$. But we want to push things forward, right? The main problem here is that there are no experimental data to validate the procedure that defines A and B for much more complex systems (described by 9 oxides), like those considered in this manuscript.

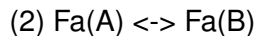
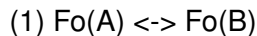
Now looking back at the way the constraints have been presented in the manuscript I am realizing that I could have done a better job. In particular making first a list of the constraints that are not based on any assumption, those are eqs. 1-4: eq.1) mass conservation, eq.2) equality of the chemical potentials for the same components (more on this later), relations similar to eq.3) to constrain the extent of certain reactions and eq.4) conservation of the total G. The last equation, eq.4, simply imposes that the sum of the Gibbs energy on the two sides (A and B) must be equal to the Gibbs energy of the whole system (W)

Unfortunately these relations are not sufficient to determine a unique set of compositions in A and B after equilibration, hence certain assumptions need to be made. For example olivine is initially present only in A0 but not in B0. After equilibration, in the

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whole assemblage a certain amount of olivine must be present (see last column of the tables). Where would this olivine be located? As a first approximation the assumption is that the various reactions will change the composition of the preexisting olivine in A while no new olivine will be formed on the B side. As mentioned previously and also in the manuscript, only new experimental data can validate this type of assumptions.

if I understand correctly, the reviewer question is the following: why in phases described by the same components the chemical potential of the components must be equal when the system is in chemical equilibrium? This is one of those fundamental principles discussed in many books on chemical thermodynamics, my favorite are the classics (e.g Chemical Thermodynamics, Prigogine & Defay; The Principles of Chemical Equilibrium, Denbigh). The following simple explanation is based on material I used for teaching a while ago. Let's say we have two systems, A,B each made only of olivine but with different compositions Ol(A) made of two components, Fo(A), Fa(A) and Ol(B) made of Fo(B), Fa(B). When they are put together to form a larger system (A+B), two and only two independent reactions can be used to describe the chemical equilibrium (see for example the book: Chemical Reaction Equilibrium Analysis by Smith & Missen). The choice of the two reactions is arbitrary (for other combinations the conclusion will be the same), let's pick the simplest reactions:



based on the stoichiometry of the reactions it is obvious the changes of the moles "dn" are related:

$$dn_{\text{Fo(A)}} = -dn_{\text{Fo(B)}}$$

and

$$dn_{\text{Fa(A)}} = -dn_{\text{Fa(B)}}$$

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Let's now recall the well known differential relation for G:

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

where the sum is over the moles of the "i" independent components describing the system, and μ_i is the chemical potential of these components.

Therefore for the large system (A+B) at constant T, and P we have:

$$dG_{(A+B)} = \mu_{Fo(A)} dn_{Fo(A)} - \mu_{Fo(B)} dn_{Fo(A)} + \mu_{Fa(A)} dn_{Fa(A)} - \mu_{Fa(B)} dn_{Fa(A)}$$

The minimum of the Gibbs energy defining the equilibrium condition is given by two relations:

$$dG_{(A+B)}/dn_{Fo(A)} = 0 = \mu_{Fo(A)} - \mu_{Fo(B)}$$

and

$$dG_{(A+B)}/dn_{Fa(A)} = 0 = \mu_{Fa(A)} - \mu_{Fa(B)}$$

It is trivial to show that $\mu_{Fo(A)} - \mu_{Fo(B)} = 0$ can be reduced to $n_{Fo(A)} = n_{Fo(B)}$ (and similarly for Fa) when olivine is described by an ideal mixing model. The equal number of moles condition was valid in the previous study, but not in this manuscript because this study relies on the thermo database by Ghiorso (and Berman).

The idea of using the extensive function G to describe the chemical changes in the 2 sub-systems over time and space is a mean to simplify a problem that otherwise becomes intractable for complex systems. However the choice is not a complete abstraction, it is based on the consideration that the mass exchange is not governed by the compositional gradient but by the differences in the chemical potential of the various components in the various phases (the book by Denbigh has a nice discussion about this topic).

Quoting from <Deformation Mechanism Maps> (Frost & Ashby, 1982, Ch.1): "Both the equations in the following sections, and the maps constructed from them, must be regarded as a first approximation only. The maps are no better (and no worse) than the equations and data used to construct them."

Regarding the dynamic models: the reviewer is correct that the parameter "S" in eq.6 and eq.9 serves the same purpose of the thermal or chemical diffusivity terms in the heat conduction eq and Fick's laws. The parameter S is dimensionless because the problem is dimensionless, no units are used for spatial and temporal variations. Once again, we don't have the experimental data to put real dimensions to these numbers.

About $G(A^*)$: the definition of A^* and B^* was introduced on pag. 7 line 7, as the mineralogical composition and abundance of the assemblages in A and B normalized to oxide bulk abundance = 100. But I agree that it should have been presented more clearly in the main text, including the relation with $G(A^*)$, $G(B^*)$ and the more general G^* , S^* .

As I mentioned also in the reply to review#1 the comparison with field observations is premature. There are no experimental data to validate the model and to constrain the extent of chemical equilibration. That's also why the title of this manuscript "Progress towards...". It is just a mere step forward not the end of the story.

If (huge IF) a project related to this problem will get funded (ERC-2019-SyG, ERC Synergy Program, "GEO-DIVE: Experimenting and Modeling Chemical GEO-DIVERsities in the Solid Earth"), we will finally acquire the first experimental data for the peridotite-eclogite equilibration and we will be able to apply the model to some real geological problems. Those mentioned in the ERC proposal are the evolution of cratons and

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thermochemical plumes.

Incidentally it also seems that I am the only one who has the data of the the first successful experiment of this kind on a peridotite-dunite couple, no melt or fluid involved (many thanks to Stephan Buhre at the IG in Mainz who carried out the exp). The preliminary (unpublished) results have been included in the ERC funding proposal.

Final Remark: I am strongly convinced that the manuscript is worth publishing since progress on such important topic in solid Earth has been stagnant for way too long.

I will make the necessary changes to the manuscript that, if the editor agrees, will be resubmitted.

In the meantime, assuming the online interacting forum will stay open, it would be really helpful to receive comments, requests for clarification, questions etc. (in alternative I'll gladly respond by email).

max

p.s. One may wonder why not doing the experiments first and then develop all the models and applications later. In a perfect world it would make sense. Unfortunately I already tried to get funds for the experimental work, twice, both attempts failed. The aforementioned ERC project is my last shot.

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

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