



# Chemical heterogeneities in the mantle: The equilibrium thermodynamic approach



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## ABSTRACT

This study attempts to answer a simple and yet fundamental question in relation to our understanding of the chemical evolution of deep Earth and planetary interiors. Given two initially separate assemblages (lithologies) in chemical equilibrium can we predict the chemical and mineralogical compositions of the two assemblages when they are put together to form a new equilibrated system? Perhaps a common perception is that given sufficient time, the two assemblages will homogenize chemically and mineralogically, however from a chemical thermodynamic point of view, this is not the case. Certain petrological differences in terms of bulk composition, mineralogy and mineral abundance remain unless other processes, like melting or mechanical mixing come into play. While there is not a standard procedure to address this problem, in this study it is shown that by applying chemical thermodynamic principles and some reasonable assumptions, it is possible to determine the equilibrium composition of each of the two assemblages. Some examples that consider typical mantle rocks, peridotite, lherzolite, dunite and eclogite described by simplified chemical systems are used to illustrate the general approach.

A preliminary application to evaluate the effect of melting a heterogeneous mantle in complete chemical equilibrium using a thermodynamic formulation coupled with a two-phase geodynamic model shows that major element composition of the melt product generated by different peridotites is very similar. This may explain the relative homogeneity of major elements of MORBs which could be the product of melting a relatively uniform mantle, as commonly accepted, or alternatively a peridotitic mantle with different compositions but in chemical equilibrium.

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## 1. Introduction

One of the fundamental challenges in solid Earth sciences is understanding the chemical evolution of the Earth's deep interior. A great debate has been carried on for several decades over the nature of the chemical heterogeneities in the mantle, how these chemical variations evolve and over what period of time (e.g. Carlson, 2006; Dobson and Brodholt, 2005; Gurnis and Davies, 1986; Helffrich, 2006; Morgan and Morgan, 1999; Poirier, 2000; Schubert et al., 2001; Tackley and Xie, 2002; Tolstikhin et al., 2006; Trampert et al., 2004; van Keken et al., 2002; Zhong, 2006). Geophysical evidence (e.g. van der Hilst et al., 1997) and numerical models (e.g. Christensen and Hofmann, 1994) followed by several studies afterwards provided indications that lithospheric material compositionally different from the surroundings may subduct in the lower asthenospheric mantle. Furthermore experimental studies (Kawazoe and Ohtani, 2006; Ozawa et al., 2009; Sakai et al., 2006) and arguments based on geophysical data (Garnero, 2004;

Garnero and McNamara, 2008) indicated that at the core–mantle boundary some chemical exchange may take place between the outer core and the lower mantle. Thermo-chemical erosion of cratonic roots and ancient lithosphere may also contribute to compositional variations of the asthenospheric mantle (Foley, 2008; Xu, 2001).

The arguments in support or against the persistent presence of large chemical variations in the mantle through the Earth's history are largely based on indirect evidence from geophysical and geochemical observations. Understanding the chemical evolution of the mantle has also potential implications for the convective structure of the mantle that in the two most accepted hypotheses involves the whole mantle or a layered structure (Butler, 2009; Peltier and Jarvis, 1982; van der Hilst et al., 1997; van Keken and Ballentine, 1998). The need for a better insight to the problem comes also from the consideration that trace elements and isotopic studies provide useful but not unequivocal information regarding chemical heterogeneities and mantle chemical evolution and these studies often ignore the complexity of the processes involved.

Chemical homogenization in the mantle is most effectively the result of the combined action of chemical and mechanical mixing (Kellogg, 1992; Kellogg and Turcotte, 1987). Mechanical mixing has been investigated using numerical models, while chemical mixing has been often

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ignored based on the argument that chemical diffusion is extremely slow and ineffective over large distance (Hofmann and Hart, 1978; Kellogg and Turcotte, 1987; Kogiso et al., 2004).

Equilibration of two lithologies has been addressed on a different scale by several studies in metamorphic petrology using the irreversible thermodynamic approach (Fisher, 1973; Joesten, 1977; Markl et al., 1998; Nishiyama, 1983), which can be applied, with some limitations, to describe chemically reactive systems involving diffusion controlled reactions between different lithologies. In general a critical point that needs to be considered is the scale of the problem (Knapp, 1989; Zhu and Anderson, 2002). In metamorphic petrology detailed observations on a scale ranging from mm to m demand a description of the physico-chemical processes involved at the same detailed scale. Numerical transport models often in hydrogeology and always in geodynamics assume local thermodynamic equilibrium on a spatial and temporal scale defined by the conditions imposed in the numerical model. The true scale of equilibration depends on the kinetic of the processes involved, however practical considerations on the objective of the modeling and the observational evidence that are used to validate the model (if any) should be taken into account. For instance detailed mineralogical description of the processes at the interface of two rock assemblages is marginally important in a mantle dynamic model in which the spatial grid is on the order of km and the observations are based on seismological data or global petrological data. However if the temporal scale of the model spans several hundreds of Myrs or more, then the extent of equilibration between two lithologies may have an influence on the outcome of the simulation at the spatial scale of the model and should not be ignored. Commonly this type of chemical interactions is not considered in geodynamic models, in other words if the model includes two lithologies, these lithologies are never modified, regardless of the timescale. In fact it is commonly assumed either complete disequilibrium (fixed compositions, e.g. subducting slab, lithospheric mantle, and crust) or complete equilibrium (defined by one composition for the whole mantle) where only melt can alter a predefined composition. These end-member scenarios are essentially correct at time zero or infinite time from the creation of the heterogeneity (the latter only under certain conditions briefly discussed in the Conclusions). Mass transfer induced by melting sometimes is approximately accounted for using particle tracers (Balmer et al., 2011; Brandenburg et al., 2008; Christensen and Hofmann, 1994; Huang and Davies, 2007; Balmer et al., 2009; Walzer and Hendel, 1999). A better representation, although restricted to mass and chemical exchange between solid and melt, is offered by two-phase flow models under the assumption of local equilibrium between the melt and the residual solid.

The condition of thermal and mechanical disequilibrium has been discussed from a thermodynamic standpoint by Bina and Kumazawa (1993). It should be also possible to apply the thermodynamic approach to study chemical heterogeneities in the Earth's interior and eventually extends it to the evolution of dynamic systems by considering a sequence of local states in thermodynamic equilibrium. The same assumption applies to the fundamental description of transport of physico-chemical properties in a continuous medium (Bird et al., 2002).

This study begins to tackle the problem of understanding the evolution of chemical heterogeneities in the solid mantle from a different perspective, that is by developing a procedure to describe chemical equilibration between two lithologies. Here this procedure is discussed in some details with the help of some examples in which the composition of two mantle assemblages in equilibrium has been determined. A preliminary application to mid-ocean ridges shows the results of melting a heterogeneous mantle in complete chemical equilibrium using a thermodynamic formulation combined with a two-phase dynamic model.

A step forward towards addressing the timescale of chemical evolution of the mantle using geodynamic and petrological numerical studies will require to combine the procedure discussed in this study with a proper formulation that models experimental data on the kinetics of the chemical processes driving the systems towards equilibrium.

## 2. Outline of the problem and study cases

The problem addressed in this study is illustrated in Fig. 1. Two separate assemblages with different bulk compositions defined by the oxides abundance are independently in chemical equilibrium at the same given pressure and temperature (P,T) conditions. Once the two assemblages are put together at the same conditions, the new system is defined by the bulk composition of the two assemblages in some predefined proportion (gray box in Fig. 1). For simplicity in the following sections, it is only considered a combined system in which the proportion of the two assemblages is 1:1, i.e. the new whole system is made of the sum of the oxide molar abundance of the two assemblages. Assuming that the new system is in complete chemical equilibrium, the objective is to find the composition and mineralogy of the two sub-systems or in other words find the compositional and mineralogical changes that took place in the two sub-assemblages after they have been brought together. A standard procedure to solve this problem is not available. However in the next sections few cases of different complexity are used to show how an approximate solution can be found and to illustrate the procedure to overcome certain difficulties inherent to each case. One of the thermodynamic tools applied to this problem is the Gibbs free energy minimization which determines the equilibrium assemblage in terms of mineral composition and abundance given a certain bulk composition and P,T conditions (Eriksson, 1971; Eriksson, 1975; Eriksson and Rosén, 1973; Smith and Missen, 1991; van Zeggeren and Storey, 1970). The essential prerequisite is the knowledge or definition of the thermodynamic properties of the considered phase components in a particular compositional system. The thermodynamic database applied here, which is reasonably acceptable to describe certain ultramafic rocks in the compositional system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (or related sub-systems), can be found in Tirone et al. (2012). Name of the minerals, abbreviations and formulas are listed in Table 1.

The exclusion of minor components from the model greatly simplifies the thermodynamic treatment. The effect of these components is to stabilize accessory minerals that most likely have a relatively small influence on the major element composition of the most abundant minerals and in general limited effect on the average physical properties of the rock assemblage. However the incorporation of minor components in the bulk composition could potentially shift the P,T stability conditions of the predominant mineral phases (Ganguly, 2008).

The pressure and temperature at which equilibration is assumed for all cases discussed in this study are 30 kbar and 1100 °C. The above conditions are not a limitation, in fact the method discussed here can be easily applied to other chemical systems at much higher pressure using the appropriate thermodynamic database.

No fluid phase is involved or is considered in the present model. The main reason is the fluid mobility and the transient state associated to the presence of a fluid. If equilibrium between two lithologies and a fluid is imposed, then it must be assumed that the fluid is available for the entire duration of the equilibration process and fluid transport in and out of the whole system should be taken into consideration. Because of the difficulties of the modeling approach, in particular for large scale problems, and the uncertainty on determining the geological setting in which the assumption of long term fluid circulation is applicable, in the following treatment all thermodynamic systems are assumed under dry conditions.

### 2.1. Case 1: peridotite–eclogite, system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , two assemblages with partially different mineralogy

The system  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  is considered in this section to describe the approximate composition of a peridotite and eclogite initially defined as ( $A_0$ ) and ( $B_0$ ). Bulk compositions in weight % (wt.%) and moles are given in Table 2. The eclogite bulk composition was

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