Fe-periclase reactivity at Earth's lower mantle conditions: *ab-initio* geochemical modelling

Marcello Merli[1], Costanza Bonadiman[2], Valeria Diella[3], Luciana Sciascia[2], Alessandro Pavese[4]

[1] *Department of Earth and Marine Sciences, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy.*

[2] *Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy*

[3]*Consiglio Nazionale delle Ricerche, CNR-IDPA, Sezione di Milano, Via Botticelli 23, 20133 Milano, Italy*

[4] *Department of Earth Sciences "A. Desio", University of Milan, Via Botticelli 23, 20133 Milan, Italy*

Correspondence: Alessandro Pavese

e-mail: alessandro.pavese@unimi.it

key-words: MgO-FeO binary; pyrolitic geochemical model; lower mantle geochemical heterogeneities; subsolidus reaction modelling; mixing Gibbs energy

ABSTRACT

Intrinsic and extrinsic stability of the (Mg,Fe)O solid mixture in the Fe-Mg-Si-O system at high *P*,*T* conditions relevant to the Earth's mantle is investigated by the combination of quantum mechanical calculations (Hartree- 26 Fock/DFT hybrid scheme), cluster expansion techniques and statistical thermodynamics. Iron in the (Mg,Fe)O binary mixture is assumed to be either in the low spin (LS) or in the high spin (HS) state. Un-mixing at solid state is observed only for the LS condition in the 23-42 GPa pressure range, whereas HS does not give rise to un-mixing. LS (Mg,Fe)O un-mixings are shown to be able to incorporate iron by subsolidus reactions with a *reservoir* of a virtual bridgmanite composition, for a maximum *total* enrichment of ~0.22 FeO. At very high *P* (up to 130/3150 GPa/K), a predominant (~0.7 phase proportion), iron-rich Fe-periclase mixture $(Mg_{0.50}Fe_{0.50})O$ is formed, and it coexists, at constrained phase composition conditions, with two iron-poor assemblages [$(Mg_{0.90}Fe_{0.10})O$ and $(Mg_{0.825}Fe_{0.175})O$]. These theoretical results agree with the compositional variability and frequency of occurrence observed in lower mantle Fe-periclase from diamond inclusions and from H*P*-H*T* synthesis products. The density difference among the Fe-periclase phases increases up to ~10%, between 24 and 130 GPa. The calculated bulk Fe/Mg partitioning coefficient between the bridgmanite *reservoir* and Fe-periclase, Kd, is 0.64 at 24 GPa; it then drops to 0.19 at 80 GPa, and becomes quasi-invariant (0.18-0.16) in the lowermost portion of the Earth's mantle (~80-130 GPa). These Kd-values represent an approximate estimate for the Fe/Mg-partitioning between actual bridgmanite and Fe-periclase. Consequently, our Kd-values agree with experimental measurements and theoretical determinations, hinting that iron preferentially dissolves in periclase with respect to all the other iron-bearing phases of the lower mantle. The continuous change up to 80 GPa (~2000 km depth) of the products (compositions and phase proportions) over the MgO-FeO binary causes geochemical heterogeneities throughout the lower mantle, but it does not give rise to any sharp discontinuity. In this view, anomalies like the ULVZs, explained with a local and abrupt change of density, do not seem primarily ascribable to the mixing behavior and reactivity of (Mg,Fe)O at subsolidus.

47 **1. INTRODUCTION**

48

49 **1.1 (Mg,Fe)O-system**

50

51 The Earth's lower mantle is home to some of the most fascinating problems related to the interior of
52 our planet, ranging from sharp discontinuity to anisotropy and unresolved geochemical processes,
53 *i.e.* origins of mantle plumes, segregation of dense sub-ducted slab components, residual of core
54 formation processes and core/mantle chemical exchange (Albarede and vander Hilst, 2002).
55 All the Earth Reference models (*e.g.* PREM and AK135; Dziewonski and Anderson, 1981; Kennett
56 et al., 1995), which are designed to match whole Earth mechanical properties and astrophysical
57 data, agree to indicate Fe-periclase and (Mg,Fe)-perovskite (bridgmanite) as the main phases of the
58 lower mantle bulk phase-composition. Therefore, the reactions involving the subsolidus MgO-FeO
59 system (*i.e.* Fe-periclase phase) provide a relevant contribution to the general geochemical
60 behaviour of the lower mantle. Seismic anomalies are associated to geochemical discontinuities,
61 such as those of the D''-layer (Lay and Helmberger, 1983; Sidorin et al., 1999; Kaneshima and
62 Helffrich, 1999; Murakami et al. 2012) and ULVZs (McNamara et al., 2010), in the lowermost
63 portion of the Earth's mantle. Geochemical perturbations in this region are ascribed to diverse
64 possible causes, some of which are related to the Fe content and its distribution in the lower mantle
65 phases, *i.e*: (i) high-to-low spin state transition of iron in Fe-periclase (Dobson and Brodholt, 2005;
66 Mao et al., 2006; Lin et al., 2013; Zhang et al., 2016); (ii) appearance of new phases, *e.g.* a post-
67 perovskite, Fe-segregation in iron-bearing phases, Si-Mg-Fe melts and partially molten systems
68 (Trampet et al., 2004; Murakami et al. 2005, 2012; da Silva et al., 2000; Karki et al., 2001;
69 Wentzcovitch et al., 2004; Garnero, 2004; Lay et al., 2004; Nomura et al., 2011; Andrault et al.,
70 2011; Thorne et al., 2013, Zhang et al., 2016).
71 Although the (Mg,Fe)O solid mixture at high pressure and high temperature conditions (H*P*-H*T*)
72 has been largely investigated (*e.g.*: Vassiliou and Ahrens, 1982; Fei et al., 1992; Richet et al., 1989;

Dubrovinsky et al. 2000; 2001; Kung et al., 2002; Jacobsen et al., 2004; 2006; Zhang and Kostak, 2002; van Westrenen et al., 2005; Jackson et al., 2006; Lin et al, 2009), several questions are still open, *i.e*. the un-mixing process and the highest allowed Fe content in the lower mantle Fe-periclase. Some authors (*e.g*.: Lin et al., 2003; Ohta et al., 2014) do not observe un-mixing of (Mg,Fe)O in static compression experiments, whereas others (Dubrovinsky et al. 2000; 2001) report a gradual formation of magnesium-rich and iron-rich oxide phases from (Mg,Fe)O at *P* and *T* above 80 GPa and about 1000 K, respectively. In addition, Fe-periclase obtained by H*P*-H*T* Fe/Mg partitioning experiments from a starting material bearing 0.1-0.3 FeO (Auzende et al., 2008; Sinmyo et al., 2008, Nakajima et al., 2012; Prescher et al., 2014) shows a wide compositional range (0.088-0.487 FeO) with respect to the coexisting (Mg,Fe)-perovskite (0.026-0.161 FeO). These results are in keeping with observations of lower mantle Fe-periclase findings (~0.15-0.70 FeO) that occur as inclusions in diamonds (Kaminsky, 2012 and reference therein). It is worth noting that ~0.3-0.5 FeO natural compositions (Kaminski, 2012) have a relevant statistical occurrence (55 out of 230 samples), whereas Mg-wüstite (0.5-0.7 FeO) is rarely observed (6 out of 230 samples). Such a variety, in terms of Fe-periclase compositions, is difficult to be explained in the frame of the extant experimental works on un-mixing processes (*i.e*. Ohta et al., 2014 and reference therein). All this has led some authors (Javoy et al., 2010; Kaminsky, 2012) to ultimately invoke a different reference Earth model (enstatite/chondrite *versus* pyrolite) to account for the bulk lower mantle composition (Badro et al., 2003; Irifune et al. 2010; Mao et al. 2006; Matas et al, 2007).

In this work the miscibility of (Mg,Fe)O and possible disequilibrium reactions with a *reservoir*, which complements the Fe-periclase in the formation of the bulk lower mantle, are investigated and the results of our study are compared with observations.

The bulk lower mantle was split into two different geothermal regions: the lower mantle (LM) and the lowermost lower mantle (LLM). LM accounts for the mantle region well below the transition zone (>23 GPa; >700 Km) and above the perturbed D''-layer, and exhibits relatively smooth trends of seismic profiles. In this view, LM can be considered as a seismically and chemically

homogeneous lower mantle portion, along a given model geotherm. LLM, in turn, refers to the lowermost region of the Earth's mantle (>80 GPa; >2000 Km), where deviations in the seismic profiles suggest changes of the *P-T* regime and phase composition, with respect to LM's. LM and LLM are assumed to be undistinguishable in terms of bulk geochemical model.

1.2 Deviations from ideality

The present modelling aims to provide a global view of the Fe-periclase compositional trend that stabilises along a chosen geotherm. In order to achieve this, some simplifications were inevitably introduced.

First, the effects of plastic deformation were neglected. In the Fe-periclase/bridgmanite system, the former is supposed to accommodate most of the plastic deformation, which develops through dislocation creeps (Madi et al, 2005). However, much uncertainty still exists about the actual mechanism driving such a phenomenon, its relation to composition and its occurrence throughout the lower mantle (Reali et al, 2017; Girard et al, 2016; Cordier et al, 2012; Tommaseo et al, 2006). Van Orman et al. (2003) observed that the occurrence of dislocations in Al-doped MgO does not seem to extensively affect cation diffusion. This suggests that dislocations modestly influence the octahedral-site force field in periclase, which still preserves its crystal structure and is affected by plastic deformation processes (see the authors quoted above). An approximate estimate of the ratio between energy due to "dislocations" (*i.e.* $\frac{1}{2}\ G_{\text{shear modulus}} \times b_{\text{Burgers vector}}^2 \times \rho_{\text{dislocation density}} \times V$) and elastic energy of "hydrostatic deformation" (*i.e.* $P \times (V\text{-}V_0)$) gives a value of $\sim 10^{-3}$, using the periclase's elastic constants and dislocation density from Zha et al (2000) and Miyajima et al (2014), respectively. Given that the deformation energy is mostly due to its hydrostatic/elastic contribution we think it reasonable to neglect the dislocation effects.

Another important simplification was to ignore ferric iron. First of all, lower mantle ferric iron is experimentally predicted to preferentially enter bridgmanite (Frost and Myhill, 2016; Kurnosov et

al. (2017). In addition, Fe^{3+} is theoretically associated to the appearance of vacancies in non-stoichiometric wüstite and (Mg,Fe)O (Wdowik et al. 2015; Otsuka et al. 2010). Measured iron in Fe-periclase and bridgmanite, both coexisting as inclusions in lower-mantle diamonds (Kaminsky and Lin (2017), reveals that Fe^{3+} un-mixes from periclase lattice, giving rise to clusters of $(Mg_{1+x}Fe^{3+}_{2-x})O_{4-x/2}$. The iron related to Fe-periclase and un-mixed clusters is inferred to be $Fe^{3+}/\Sigma Fe$ 8-12 at%. Given that most iron content values in natural (Mg,Fe)O do not exceed 0.5 FeO (Harte, 2010; Kaminsly, 2012), the vacancy generation effect induced by ferric iron can therefore be assumed negligible in the present modelling.

Finally, the potential effects of metallization of iron were neglected since such a reaction is experimentally observed only in *quasi*-wüstite compositions (Otha et al. 2014).

2. LOWER MANTLE GEOCHEMICAL FRAME

The pyrolite model provides one of the possible chemical compositions for the Earth's lower mantle. On the basis of phase equilibrium principles and known physical properties of H*P* minerals, the lower mantle turns out to be mainly constituted of $(Mg,Fe)SiO_3$ (bridgmanite), (Mg,Fe)O (Fe-periclase) and $CaSiO_3$ (Ca-perovskite), besides an ‘‘undefined H*P* Al-phase’’ (i.e. Miyajima et al., 2001; Pamato et al., 2014). Such phases occur in proportions that are a function of both geochemical and geophysical models. The former constrains the bulk chemical composition (McDonough and Sun, 1995; Lyubetskay and Korenaga, 2007; Stixrude and Lithgow-Bertelloni, 2007; Merli et al. 2016); the latter accounts for density-pressure-temperature profiles that are consistent with observations (*i.e.*: seismic velocities, density and bulk sound speed; Jackson 1998, Mattern et al. 2005; de Wit and Trampet, 2015).

Assuming the mantle to be representable by the CMASF system ($CaO-MgO-Al_2O_3-SiO_2-FeO$), the pyrolitic model’s phase composition of the lower mantle consists of ~75-78 wt% $(Mg,Fe)SiO_3$, ~6-10 wt% $CaSiO_3$, ~15 wt% (Mg,Fe)O and ~2 wt% high-pressure Al-rich phase (Ono and

151 Oganov, 2005; Mainprice, 2007; Merli et al., 2016). Given that Ca-perovskite and bridgmanite
152 exhibit similar thermoelastic responses at the reference lower mantle *P*-*T* conditions (Deschamps
153 and Trampert, 2004; Matas et al, 2007; Li et al. 2005), a simplified MgO-SiO_2-FeO system (MSF)
154 was used in the present work.
155 The conversion from CMASF to MSF consists in replacing Mg+Ca+Al/2 with Mg, and Si+Al/2
156 with Si. The resulting bulk chemical composition (Table 1) has a Mg/Si molar ratio of 1.20, which
157 is lower than the pyrolitic value (~ 1.27) but higher than the chondritic one (~ 1.1). Such a ratio is in
158 agreement with a lower bulk chemical composition slightly enriched in SiO_2 (and FeO) and
159 depleted of MgO, with respect to the pristine pyrolitic model (Deschamps and Trampert, 2004;
160 Matas et al., 2007; Merli et al., 2016). The fractions by weight of Fe-periclase and bridgmanite in
161 the lower mantle were estimated 0.13 and 0.87 (Table 1) respectively, by means of least-square
162 mass balance calculations (Paktunc, 1998; Kobayashi et al., 2005) under the constraint of the LM-
163 LLM bulk chemical composition.
164 A geotherm (Fig.1) with a potential temperature of 1920 K at 24 GPa and *T*-vertical-gradient
165 (*dT/dz*) of ~0.5 K/Km (Matas et al., 2007; Ono, 2008; Merli et al., 2016) was assumed for LM
166 (~700-1900 Km depth). A geotherm (>80 GPa; >2000 Km) with a potential temperature of 2615 K
167 at 96 GPa and a higher *T*-gradient than LM's, *i.e. dT/dz* ~0.85 K/Km (Deschamps and Trampert,
168 2004; de Koker, 2010; Wicks et al., 2010; de Wit and Trampert, 2015), was instead chosen for LLM
169 (Fig.1).
170
171 **3. THERMODYNAMIC APPROACH**
172
173 The mixing of the MgO and FeO components in the periclase structure was modelled by extending
174 to the H*P*-regime the formalism of Merli et al (2015) that uses discrete Chebychev polynomial
175 expansions (Barnard et al. 1998) and statistical thermodynamics (Sanchez et al, 1984). A Hartree-

176 Fock/DFT hybrid scheme was adopted to carry out quantum energy calculations (Dovesi et al.
177 2009) on super-cells.
178
179 **3.1 Gibbs energy of mixing at high-pressure and high-temperature**
180
181 A given Fe-periclase composition, expressed by x=Fe/(Fe+Mg) and (1-x)=Mg/(Fe+Mg), is
182 compatible with many Mg-Fe configurations (Λ), each one corresponding to a specific arrangement
183 of the magnesium and iron atoms. In the frame of the isothermal-isobaric ensemble a system is
184 composed of N particles at equilibrium with P and T (*i.e.* NPT-ensemble). For simplicity, we do not
185 take into account the explicit dependence on P and T of the thermodynamic potentials, except for
186 the functions $\Xi(P,T,x)$ and $\xi(P,T,x,)$, which are related to the NPT-ensemble.
187 $\Xi(P,T,x)$ is defined by Dill et al. (2003) as:
188 $$\Xi(P,T,x,) = \sum_{\Lambda=1,n} \exp[-H(x,\Lambda)/kT] = \sum_{\Lambda=1,n} \exp[-(U(x,\Lambda)_{st} + PV(x,\Lambda)_{st})/kT] \times Z(x,\Lambda)_{vib} \quad (1)$$
189 where n is the number of all the possible configurations.
190 The Gibbs function is related to $\Xi(P,T,x)$ in terms of
191 $$G(x) = -k \times T \times ln[\Xi(P,T,x)] \quad (2)$$
192 where: k=Boltzmann constant; st=lattice static contribution; vib=vibration contribution;
193 $Z(x,\Lambda)_{vib}$=partition function from harmonic approximation for a given Λ–configuration;
194 $H(x,\Lambda)$=enthalpy for a given Λ–configuration; $U(x,\Lambda)_{st}$= lattice static energy for a given Λ–
195 configuration. Numerical calculations show that $Z(x,\Lambda)_{vib}$ exhibits, on average, a moderate
196 dependence on the Mg/Fe configuration. Therefore $Z(x,\Lambda)_{vib}$ of eq.(1) can be replaced with $Z(x)_{vib}$,
197 namely $\langle Z(x,\Lambda)_{vib} \rangle_{\Lambda=1,n}$ (see Section 3.2). From eq.(2) the Gibbs free energy can be split into two
198 parts: $G(x) = G(x)_0 + G(x)_{vib}$, where $G(x)_0$ collects the static contributions and $G(x)_{vib} = -k \times T \times ln(Z(x)_{vib})$. Transferring all this to the Gibbs energy of mixing (Ottonello 1997), we obtain:
199
200 $$\Delta G(x)_{mixing} = \Delta G(x)_{0,mixing} + \Delta G(x)_{vib,mixing}.$$

where

$$\Delta G(x)_{0,mixing} = -k \times T \times ln\{\sum_{\Lambda=1,n} \exp[-(\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing})/ kT]\}. \quad (3)$$

Δ in eq.(3) means, for a generic thermodynamic "*A*" quantity of a mixing, the following difference:

$\Delta A(x)_{mixing} = A(x) - x \times A(\mathrm{FeO}) + (1-x) \times A(\mathrm{MgO})$.

According to Merli et al.(2015), the sum of eq.(3) can be approximated, so that

$$\Delta G(x)_{0,mixing} \approx -k \times T \times ln[\xi(P,T,x)] - \mathrm{R} \times T \times ln(\mathrm{N}(x)_{\mathrm{configurations}}), \quad (4)$$

where: R is the gas constant; $\mathrm{N}(x)_{\mathrm{configurations}} = \mathrm{N}_{\mathrm{Avogadro}}!/\{[x \times \mathrm{N}_{\mathrm{Avogadro}}]!\ [(1-x) \times \mathrm{N}_{\mathrm{Avogadro}})]!\}$;

$$\xi(P,T,x) = (1/\mathrm{N}_{\mathrm{sampled\ configurations}}) \times \sum_{\Lambda=1,\mathrm{sampled\ configurations}} \exp[-(\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing})/kT].$$

The subscript 'sampled configurations' means that the sum over *all* the possible configurations ($\approx 10^{23}$, for 1 mole) is replaced with a random sampling over an appropriately chosen number of different Fe/Mg arrangements for a given composition, *i.e.* $\mathrm{N}_{\mathrm{sampled\ configurations}}$.

3.2 Vibrational contributions to the Gibbs free energy of mixing

Semi-empirical potentials (Lewis and Catlow 1985; Merli et al., 2015), harmonic model and lattice dynamics (GULP code; Gale 1997) were used to calculate $\Delta G(x)_{vib,mixing}$, from random Mg-Fe configurations in 64 cation-sites super-cells over the subsolidus MgO-FeO binary. The range 30-70 GPa and 2000-3500 K was investigated for *x*-values strewn over the 0-1 interval, sampling up to 10^5 independent configurations. Attention was focussed on how mixing affects $\Delta G(x)_{vib,mixing}$. It was observed that the $G(x,\Lambda)_{vib}$-values oscillate, as a function of the random Λ-configurations, less than 0.1% around $G(x)_{vib}$, *i.e.* their Λ-average, which therefore provides a faithful estimate of the actual vibrational contribution to the Gibbs energy for a given *x*. $\Delta G(x)_{vib,mixing}$, calculated accordingly, amounts at most to about 2% of the configuration entropy contribution. Given that in the present case the harmonic $\Delta G(x)_{vib,mixing}$ contribution is very modest, then the anharmonic one is expected to

be negligible. Altogether, P seems to make the vibrational contribution to the Gibbs energy of mixing of marginal importance for (Mg,Fe)O. Neglecting $\Delta G(x)_{vib,mixing}$ at high pressure is in contrast to what observed at room conditions (Merli et al., 2015), where a small, but significant vibrational contribution (10-15%) participates in the Gibbs energy of mixing.

3.3 Cluster expansion

$\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing}$ was computationally modelled exploiting the formalism that relies upon the cluster-expansion (Yuge 2010) and discrete Chebyschev polynomials (Merli et al. 2015; Sanchez et al. 1984). Such an approach leads to the following expression for $\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing}$ of a given Λ-configuration:

$$\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing} \approx \Delta H(P)_0 + \Delta H(P)_1 \times x + x\times(1-x)\times[A(P)_0 + A(P)_{Fe}\times x] + \sum_{j=1,\text{number of clusters}} A(P)_{Fe\text{-}Mg,j}\times n(x,\Lambda)_{Fe\text{-}Mg,j}, \quad (5)$$

This equation accounts for a Vegard-like residue; $A(P)_0$ and $A(P)_{Fe}$ contribute to a composition dependent parabolic term; $A(P)_{Fe\text{-}Mg,j}$s weigh the number of Fe-Mg couples, *i.e.* $n(x,\Lambda)_{Fe\text{-}Mg,j}$, whose atoms are d_j apart from one another, and constitute the j^{th}-cluster. $\Delta H(P)_j$ and $A(P)_k$ are functions of the pressure and were modelled by polynomials like

$$\omega_j^{(0)} + \omega_j^{(1)}\times P^{\nu(j)} + \omega_j^{(2)}\times P^{\chi(j)} + \ldots\ldots \quad (6)$$

The χ, ν,….. exponents for each j-coefficient were determined by a trial-and-error approach, whereas the $\omega_j^{(0,1,2,\ldots..)}$-coefficients were obtained by fitting the expression given by eq.(5) to the values calculated by quantum-mechanics. Preliminary tests indicated that parabolic expansions are appropriate for eq.(6); adding higher order terms does not enhance the quality of the results. Eventually, using eq.(5) and (6), $\xi(P,T,x)$ of eq.(4) was calculated by sampling ~10^6-10^8 Λ-configurations (Merli et al. 2015), which guarantee negligible oscillations of the resulting $\Delta G(x)_{0,mixing}$.

3.4 Ab- initio calculations

Static enthalpy calculations and structure relaxation were carried out at a given 0 K pressure by the HF/DFT-CRYSTAL14 program (Dovesi el al. 2009), which implements "A*b-initio* Linear-Combination-of-Atomic-Orbitals" in the case of periodic systems. Pressure was corrected for zero point and thermal contribution following Merli et al (2016). A Hamiltonian based on the WC1LYP functional (Scanavino et al. 2012; Scanavino and Prencipe 2013) was used in the present work, along with the flexible HF-DFT hybrid scheme earlier discussed and adopted for (Mg,Fe)O at room pressure by Merli el al. (2015). It relies upon mixing HF and DFT exchange energy contributions, in terms of a Hartree-Fock fraction ($\Im_x$) given by $\Im_x=(1-x)\times\Im_{MgO}+x\times\Im_{FeO}+x\times(1-x)\times\Im_{MgO}\times\Im_{FeO}$ (hybridization, tuning of functional and delocalization error: Autschbach and Srebro, 2014; Alfredsson et al. 2004). For the end-members the following hybridization rates were used: $\Im_{FeO}$=0.16 (HS; calibration on the band gap) and 0.24 (LS; calibration on the HS to LS transition at 40 GPa, for x=0.2); $\Im_{MgO}$=0.2 (calibration on the band gap). Such an approach has proven effective to yield mixing energies that are weakly sensitive to change of the end members' hybridization rate. Tests performed at room pressure show that shifts even by 30-35% of $\Im_{MgO\text{-}FeO}$ lead to mixing enthalpy average changes within 5-10%. The following values were used for the tolerance governing the accuracy of the integrals of the self-consistent-field-cycles: 10^{-6} for coulomb overlap, 10^{-6} for coulomb penetration, 10^{-6} for exchange overlap, 10^{-6} for exchange pseudo-overlap in direct space, 10^{-12} for exchange pseudo-overlap in reciprocal space and 10^{-9} a.u. threshold for SCF-cycles' convergence. The Mg basis set from Causà et al. (1986) was extended by the addition of diffuse *sp* and *d* shells (85-11G* contraction). The O basis set of Ottonello et al. (2010) was used, modified by the introduction of a *d* shell (84-11G* contraction) according to Belmonte et al. (2014). The Fe basis set is from Valerio et al. (1995). The ability to reproduce physical observables of MgO and FeO using the present computing set-up is discussed by Merli et al. (2015-2016).

The static contributions to the Gibbs free energy of the substance at 4-6 independent Λ–configurations were calculated using super-cells of 16 cation sites to obtain multiplicity-weighted average $\Delta U+P\Delta V$'s for each LS-composition of x~0.125-0.25-0.375-0.5-0.625-0.75-0.875, at 24-40-70-90-110-128 GPa. The HS-state was treated alike, but restricting calculations to x~0.125-0.375-0.50-0.75-0.875, at 24-60-80-110 GPa. The approach of Merli et al. (2015) was followed to model a HS-paramagnet, by resorting to disordered up and down spin configurations such as yield a total residual spin of zero.

The average $(\Delta U+P\Delta V)$-values were then fitted by polynomials in x to get by interpolation additional $(\Delta U+P\Delta V)$-values, strewn over the 0-1 x-range, at every explored P. Eq.(5-6) were eventually fitted to the obtained set, using average $n(x)_{\text{Fe-Mg,j}}=\langle n(x,\Lambda)_{\text{Fe-Mg,j}}\rangle_{\Lambda}$ calculated over 10^5-configurations for each given x. A cut-off of 10 Å was chosen after tests to fix up the size of the clusters of expansion (5). By means of the $\Delta H(P)_k$ and $A(P)_j$ coefficients, the static term $\Delta U(x,\Lambda)_{st,mixing} + P\Delta V(x,\Lambda)_{st,mixing}$ was calculated for super-cells of 1024 Fe/Mg-atoms, and thereby $\Delta G(x)_{0,mixing}$ was determined according to eq.(4).

Given the fact that the vibrational contributions are negligible, we introduce the following approximation: $\Delta G(x)_{mixing} \approx \Delta G(x)_{0,mixing}$ and hereafter use $\Delta G(P,T,x)_{mixing}$ to indicate the bulk Gibbs free energy of mixing at P-T conditions and x FeO, calculated accordingly.

3.5 Reaction model

Once $\Delta G(P,T,x)_{mixing}$ is determined, it can be used to investigate the (Mg,Fe)O mixture at subsolidus and its interactions with the *reservoir* through irreversible disequilibrium reactions, implying an exchange of matter between *reservoir* and Fe-periclase.

We start from the basic reaction:

$$(Mg_{1-x0}Fe_{x0})O \Leftrightarrow y1\ (Mg_{1-x1}Fe_{x1})O + y2\ (Mg_{1-x2}Fe_{x2})O \qquad (7)$$

where xi is the ith FeO fraction, and yi is the ith phase fraction related to the Fe-periclase having xi FeO. To fulfil the mass conservation principle, $y1$ and $y2$ of eq.(7) result in (see Appendix I, for derivation):

$$y1=(x0-x2)/(x1-x2) \quad (8.a)$$

$$y2=1-y1. \quad (8.b)$$

Reaction (7) is dealt with from two points of view: one related to a *closed system*, and another to an *open system*.

A *closed system* is modelled in terms of a given (Mg,Fe)O-phase that can un-mix into two more stable compositions, according to the MgO-FeO binodal/spinodal curves (Ottonello 1997; for application to the MgO-FeO system at room pressure see Merli et al 2015). Un-mixing is intimately linked to the Gibbs energy minimization under the constraint of equality of chemical potentials. The consolute temperature, T_C, defines the upward limit of a miscibility gap in a *T-X* Schreinemaker projection, *i.e.* the temperature above which un-mixing processes do not occur, for a given *P*, and solid mixings are stable.

Alternatively, an *open system* is modelled, treating eq.(7) in terms of forward and backward reactions, in which the left- and right-hand side members act both as reagents and products and equilibrium is achieved when forward and backward rates are equal to one another. Eq.(7) is a simplification of the possible more complex natural reactions involving a larger number of reactants and products. $x0$ is a 'reference pivot-composition', which is supposed to exist at any *P-T* point of both LM and LLM geotherms, along with the compositions given by $x1$ and $x2$ (Appendix II). The $x0$-value can be taken over the interval 0.15-0.20 FeO, since: (i) this range includes the average FeO content of Fe-periclase inferred by the geochemical model (Table 1); (ii) it accounts for the most frequent Fe-periclase's compositions observed both in natural findings from lower mantle samples (Harte, 2010; Kaminsky, 2012) and in Fe/Mg partitioning experiments (Auzende et al., 2008; Nakajima et al., 2012; Prescher et al., 2014). In this model, the (Mg,Fe)O-system achieves *P-T-X* equilibrium with a thermodynamic matter *reservoir*, which behaves as an ideal Fe/Mg exchanger

(see Appendix II and III for a description of the disequilibrium-to-equilibrium process, involving Fe-periclase and *reservoir*). Such a matter *reservoir* is the portion of lower mantle other than Fe-periclase and can be likened, in terms of *bare* MSF-composition, to a ‘’virtual’’ (Mg,Fe)-perovskite (Table 1).

The phase proportions of the solid mixings that correspond to the $x0$-, $x1$- and $x2$-compositions are addressed here by means of $\lambda 0$, $\lambda 1$ and $\lambda 2$, respectively. Note that

$$\lambda 0+\lambda 1+\lambda 2=1. \quad (8.c)$$

The equilibrium constant of the reaction (7) is

$$K(P,T,x0,x1,x2)= \exp[-(\Delta G(P,T,x0)_{mixing}- y1\times\Delta G(P,T,x1)_{mixing}- y2\times\Delta G(P,T,x2)_{mixing})/RT] \approx$$

$$\lambda 0/(\lambda 1^{y1}\times\lambda 2^{y2}), \quad (9)$$

where the activity coefficient is approximated by unity.

For each $\{x0\text{-}x1\text{-}x2\}$-set we seek for the $\{\lambda 0, \lambda 1, \lambda 2\}$-set that minimises the function

$$\Delta G(P,T,x0,x1,x2)_{\text{Total}mixing}=\lambda 0\times\Delta G(P,T,x0)_{mixing}+$$

$$\lambda 1\times\Delta G(P,T,x1)_{mixing}+\lambda 2\times\Delta G(P,T,x2)_{mixing}, \quad (10)$$

under the constraints given by eq.(8.a-b-c and 9).

Such an approach implies that:

(i) an exchange of FeO/MgO between (Mg,Fe)O-system and lower mantle *reservoir* takes place *via* $\lambda 0\text{-}\lambda 1\text{-}\lambda 2$ under the sole constraint that the global bulk (FeO+MgO) content must be preserved, so that Fe-periclase gives Δx-moles of FeO(MgO) to the *reservoir* and takes as many moles of MgO(FeO) from it;

(ii) the point above requires that the incorporation of FeO/MgO into the *reservoir* causes variations of its Gibbs energy that are assumed of the same order of magnitude of the oscillations occurring because of the many reactions in the lower mantle (Appendix III). Such an assumption is equivalent to taking Fe-periclase as the pivot-exchanger for iron/magnesium in the deep interior of the Earth. This is consistent with that the Fe/Mg partitioning coefficient between bridgmanite (the other main

mineral competitor for incorporation of Fe) and Fe-periclase is observed to be significantly smaller than 1, *i.e.* (Mg,Fe)O is the main host of iron.

The λj-values, determined according to eq.(9-10), depend on $x0$, $x1$, $x2$, P and T, so that λj($x0$, $x1$, $x2$), dropping for brevity P and T. Given that we are interested in average values, mean phase proportions, <λj>, were obtained by a numerical integration over the allowed $x0$, $x1$ and $x2$ ranges (note that $x2<x0<x1$, due to that $0<y1<1$), that is:

$$< \lambda j >= C \int_{x0-inf}^{x0-sup} dx0 \int_{x0}^{1} dx1 \int_{0}^{x0} \lambda j(x0, x1, x2) dx2 \quad (11)$$

where C is a normalization factor, $x0$-*sup*=0.20 and $x0$-*inf*=0.15.

<$x0$>, <$x1$> and <$x2$> are calculated as <λj×xj>/<λj>. This way, <λ0,1,2> and <$x1$,2> depend on P-T only, and show how the (Mg,Fe)O-system changes along a pressure-temperature path in terms of Mg-Fe-solid mixings. Note that eq.(7) and integration $x0$-interval imply that <$x0$> is equal to 0.175.

In the ensuing discussions, the notations xj (jth-phase's composition) and λj (jth-phase proportion) will be used in place of <xj> and <λj> from eq. (11), for simplicity.

3.6 Spin state and excess Gibbs energy of mixing

LS-HS mixed states, which affect the physical properties of the (Mg,Fe)O-phases, are often accounted for in a solid mixing by a linear combination of the pure LS and HS systems (Lyubutin et al., 2009; Wentzcovitch et al. 2009; Muir and Brodholt, 2015; Vilella et al., 2015). It is straightforward to prove that in a HS-LS-(FeO-MgO) system (x^{LS-HS}-x^{LS}-x^{HS} being x- FeO in mixed HS-LS state, pure LS or HS state, respectively) the exact mixing energy is expressible as

$$\Delta G(P,T,x^{LS-HS})_{mixing} = \eta \times \Delta G(P,T,x^{LS})_{mixing} + (1-\eta) \times \Delta G(P,T,x^{HS})_{mixing} + \{G(P,T,x^{LS-HS}) - \eta \times G(P,T,x^{LS}) - (1-\eta) \times G(P,T,x^{HS})\}, \quad (12)$$

where $\eta = 1/(1+\exp((G^{LS}-G^{HS})/xRT)$. In principle, it is possible to calculate the quantity $G(x^{LS-HS},P,T)$, but in practice it is difficult, because of the exceedingly large super-cell size required in order to achieve statistical representativeness and faithfulness, and of the many configurations to explore. However, if we assume that the third term of the right-hand side member of the eq.(12) is negligible, then the equilibrium constant, *i.e.* eq.(9), becomes:

$$K(P,T,x0,x1,x2)=\exp[-\eta\times\Delta G(P,T,x0,x1,x2)^{LS}_{mixing}/RT]\times\exp[-(1-\eta)\times\Delta G(P,T,x0,x1,x2)^{HS}_{mixing}/RT]\approx$$

$$[K(P,T,x0,x1,x2)^{LS}]^{\eta}\times[K(P,T,x0,x1,x2)^{HS}]^{(1-\eta)} =$$

$$\{[\lambda0/(\lambda1^{y1}\times\lambda2^{y2})]^{LS}\}^{\eta}\times\{[\lambda0/(\lambda1^{y1}\times\lambda2^{y2})]^{HS}\}^{(1-\eta)} \quad (13)$$

where two sets of ‘‘virtual’’ phase proportions of the x0-1-2-phases are defined, *i.e.* $[\lambda0,\lambda1,\lambda2]^{LS}$ and $[\lambda0,\lambda1,\lambda2]^{HS}$. LS and HS can be treated as decoupled states, with respect to the constraint given by eq.(13). Although such approximation provides an ‘‘extreme’’ depiction, as only pure spin states are involved, it gives a general view of how far either spin state affects the reactivity of the (Mg,Fe)O-system and guarantees the required precision to treat small and complex quantities such as mixing energy.

Using the cluster expansion technique (see section *3.3*), we generated $\Delta G(P,T,x)_{mixing}$ data for either iron state and interpolated them by Redlich-Kister-type expressions (Stølen and Grande 2004), which model the mixing Gibbs energy as

$$\Delta G(P,T,x)_{mixing} = x\times(1-x)\times h(P,T,x) + R\times T\times[x\times ln(x)+(1-x)\times ln(1-x)],$$

where the first term of the right-hand side member gives the excess enthalpy, and

$$h(P,T,x)=\sum_{l=0,L;m=0,M;n=0,N} p_{lmn}\times P^{l}\times T^{m}\times x^{n}$$

The p_{lmn}-parameters of the expansion above for LS and HS (interval: x=0-1, T=1900-4000 K, P=24-140 GPa) are reported in Table 2.

4. RESULTS

4.1 Un-mixing processes in closed (Mg,Fe)O-system

Our calculations predict that at lower mantle *P*-*T* conditions, HS never gives rise to un-mixing reactions in the MgO-FeO system at subsolidus, as $T_C < T_{geotherms}$ (Fig.1). LS, too, yields T_C values that are smaller than the temperatures of both LM and LLM geotherms (Fig.1), but for the shallowest portions of the lower mantle (~23-42 GPa). Pure LS gives un-mixings between 0.24 and 0.84 FeO (Fig.2), at the base of the immiscibility region (T_C =1920 K, *P*=24 GPa), and between 0.50 and 0.65 FeO, at its top (T_C =2174 K, *P*=42 GPa). Given that for reference Fe-periclase composition, HS on average prevails up to ~40 GPa (Fei et al. 2007; Lin et al. 2007) and stabilizes solid mixings (Fig.1), it is unlikely that the un-mixed products due to LS can provide an important contribution in nature below ~40 GPa.

It is important to note that almost all the experiments agree to exclude that Fe-periclase un-mixes at lower mantle conditions. Lin et al. (2003) and Ohta et al. (2014), who explored the compositional range from 0.61 to 0.95 FeO, did not observe any disproportionation, except for *quasi*-wüstite compositions (140 GPa-2580 K). Conversely, Dubrovinsky et al. (2000; 2001) report un-mixing of (Mg,Fe)O, with *x* up to about 0.5 FeO, into Mg-rich and Fe-rich periclase like phases, but at conditions far from lower mantle's (86 GPa and 1000 K). However, the relevant variety of Fe-periclase compositions observed in the lower mantle diamond inclusions (Kaminsky, 2012 and reference therein) and in the samples from Fe/Mg bridgmanite/Fe-periclase partitioning experiments (Auzende et al., 2008; Nakajima et al., 2012; Prescher et al., 2014) has to be explained.

4.2 Extension to the MgO - FeO - SiO2 system

The wide range of Fe-periclase compositions (the statistically most relevant interval is ~0.3-0.5 FeO) observed both in natural findings and in H*P*-H*T* syntheses suggests that the (Mg,Fe)O-system

426 can be modelled by reactions according to eq. (7), which imply forward-backward transformations
427 and may include exchange of matter with the surroundings.
428 Fig. 3a and 3b show xj and λj as function of P, along the lower mantle geotherms, for LS and HS.
429 All the compositions exhibit slight changes (not graphically appreciable) in the case of HS over the
430 explored P range (Fig.3a), whereas a significant enrichment in Fe occurs in the x1-phase for LS.
431 The phase proportions of the x0-, x1- and x2-phases (Fig. 3b) remarkably vary along the geotherms
432 in the case of LS, only.
433 $<K(P,T)>$ as function of P (Fig.4a), namely the average equilibrium constant obtained by an
434 integration over the allowed x0-x1-x2 ranges of eq.(7), provides a partial explanation for the
435 insensitivity to P-T of the HS's λ-values (Fig.3b). In fact, LS exhibits a significantly steeper trend
436 than HS, along the LM-LLM-paths ($\partial<K(P,T)/\partial P>\approx 9\ 10^{-4}$ and $2\ 10^{-4}$ GPa^{-1}, for LS and HS,
437 respectively), suggesting that different mixing behaviours take place as a function of the spin state.
438 The average equilibrium constant for HS is, in practice, *quasi*-invariant over the LM and LLM
439 mantle regions (Fig. 4a). In addition, the LS-HS excess enthalpy functions (ΔH_{excess}), at 24/1900-
440 107/2910 GPa/K, show relevant differences (Fig. 4b). LS has larger absolute ΔH_{excess} and
441 $d\Delta H_{mixing}/dx$ values than HS; this underlies that the LS (Mg,Fe)O-system is more sensitive to P-T in
442 terms of equilibrium constant than HS. LS and HS exhibit excess enthalpy curves similar in shape
443 at 24 GPa, but they remarkably change at 107 GPa, in such a way that the two spin states yield
444 opposite trends (Fig.4b).
445
446 **5. DISCUSSION**
447
448 On the basis of these results, LS can be consider the main booster of phase changes in the
449 (Mg,Fe)O-system over most of the LM and LLM regions. Therefore, we focus on the results of the
450 LS-state only.

451 The *x*2-phase (FeO ~ 0.10, at 24 GPa) mimics the *x*0-phase (FeO ~ 0.175 as inferred by the bulk
452 geochemical model), showing slight changes in composition along the geotherms (Fig. 3a). This
453 implies that both *x*2=$Mg_{90}Fe_{10}$-phase and, obviously, *x*0=$Mg_{82}Fe_{18}$-reference-phase are products in
454 the (Mg,Fe)O-system, which occur at any *P*-*T* of the lower mantle regions.
455 Conversely, the *x*1-phase [$(Mg_{0.61}Fe_{0.39})O$ at 24 GPa] remarkably changes in composition with
456 respect to both *x*0 and *x*2, increasing over the entire LM region (up to ~ 80 GPa) its Fe-content up
457 to 0.49 (Fig. 3a). This leads to an enrichment of 0.1 FeO from 24 to 80 GPa; at higher pressure
458 (LLM region), the *x*1-phase stabilises at ~0.5 FeO content (Fig. 3a).
459 At 24 GPa, the *x*0-*x*1-*x*2-phases occur in proportions of $\lambda 0 \approx 0.34$, $\lambda 1 \approx 0.23$ and $\lambda 2 \approx 0.43$ (Fig.3b),
460 respectively. The iron rich *x*1-phase is the least abundant in the uppermost part of the lower mantle,
461 but rapidly increases exceeding *x*0- and *x*2-phases at some 30 GPa, along the LM geotherm. At 80
462 GPa (~ 2000 Km depth), the *x*1-phase, $(Fe_{0.5}Mg_{0.5})O$, reaches the proportion of ~0.67. Deeper, in
463 the region of the LLM geotherm (80-130 GPa), the iron rich *x*1-phase keeps on being the most
464 abundant reaction product in the (Mg,Fe)O-system (Fig.3b). This suggests that the modelled
465 possible products of the (Mg,Fe)O-system in the LLM region are highly stable, invariant in
466 composition and proportion.
467 Moreover, we observe that the *x*1-phase is the major exchanger with the *reservoir*; this is consistent
468 with the fact that the *x*1-composition is the most distant among *x*0-1-2-phases' from *reservoir*'s,
469 thus suggesting the occurrence of elemental concentration gradients that promote flow of matter. In
470 turn, the *x*2-phase's comparatively low amount might be related to a high activation energy to
471 achieve the critical size of nucleation that triggers then crystal growth.
472 As expected, the density (ρ) of the *x*0-*x*1-*x*2-phases progressively increases as function of *P* (Fig.5).
473 At 24 GPa, the most dense *x*1-phase [$(Fe_{0.39}Mg_{0.61})O$; ρ_{x1}=5.3 g/cm^3] is also the least abundant
474 (Fig.3b), whereas the *x*0- and *x*2-phases, which share almost equal density values (4.6 and 4.3
475 g/cm^3, respectively), together account for ~0.80 phase proportion in the (Mg,Fe)O-system (Fig.3b;
476 Fig.5). Consequently, the average density of the (Mg,Fe)O-system in the shallow part of the lower

mantle (~700 Km) is controlled by iron poor phases (~4.5 g/cm^3). It is worth noting that the density of the *x*1-phase increases linearly in the LLM region, even if the *x*1-phase ceases to incorporate additional iron from the *reservoir* at about 80-90 GPa. This implies that below ~2000 Km depth, the bulk density of the (Mg,Fe)O-system (6.5 g/cm^3, using the LLM geotherm), primarily depends on the pure physical properties of the involved phases, which are invariant in composition and phase fractions from ~90 GPa to the core-mantle boundary. Moreover, if the (Mg,Fe)O-system is considered as constituted by *x*1 and (*x*0+*x*2) only, then they yield a net change in terms of differential density, *i.e.* $\Delta\rho=[\rho_{x1} -(\rho_{x0} +\rho_{x2})\times 0.5]$, from 0.8, at 24 GPa, to 1.4, at 130 GPa. This corresponds altogether to a mean $\Delta\rho$-increase of approximately 10%, in keeping with the results of Rost et al. (2005) and McNamara et al. (2010).

On the whole, the lower mantle (Mg,Fe)O-system with the pyrolitic reference composition 0.175 FeO (Table 1) tends to acquire iron from the *reservoir* upon increasing pressure, for a maximum *total* enrichment of ~0.22 FeO and by effect of LS only (Fig.6).

Following the suggestion of iron-rich starting material used in a few Fe/Mg periclase/bridgamite partitioning experiments (Nakajima et al., 2012), a fictitious 'not-pyrolitic' lower mantle (Fe,Mg)O-system with a reference composition *x*0=0.3 FeO was also modelled, in order to test the sensitivity of eq.(7) to *x*0 in the case of LS. This system results in a weaker exchanger with the *reservoir* ($\leq$0.09 Fe at ~130 GPa) in comparison with the pyrolitic model, and the compositions of the resulting phases scarcely change along both the LM and LLM *P-T* paths. The Fe-rich phase occurs with ~0.55 FeO at 24 GPa, ~0.51 FeO at 48 GPa and then slightly increases its iron content to ~0.52 FeO at ~130 GPa. These data reflect an iron-saturation effect in the (Mg,Fe)O-system, owing to an unduly large *x*0-value for the reference composition with respect to the pyrolitic model (Table 1, Fig. 3).

For the sake of completeness, it is worth pointing out that a simultaneous occurrence of LS and HS depicts the most likely Earth's lower mantle iron state (Lin et al., 2013). We approximately estimated the LS-HS effects by linearly combining the results from one spin state with those of the

other using the η-weighting function (see eq.13). In so doing and leaving aside any claim of precision, the composition of the *x*1-mixed-states-phase achieves the same ''saturation'' value as for pure LS of 0.5 FeO upon *P*, at about 100 GPa. The general trends of the phases' compositions and phase proportions in mixed spin states as a function of the geotherms are preserved with respect to pure LS's, although they are shifted by ~20 GPa to higher *P*-values. Despite the level of approximation we have to accept in view of the complexity of the reactions occurring in the lower mantle, altogether our results corroborate that $(Fe_{0.5}Mg_{0.5})O$-phase is expected to be the likeliest Fe-rich periclase composition in the LLM region (from 80-100 GPa), independently of the *x*0-reference composition. This is in agreement with the results of multicomponent experiments that, using as starting material the San-Carlos olivine (0.3 FeO), yield Fe-periclase whose highest iron content is 0.487 FeO (Nakajima et al., 2012). We are aware that a direct comparison between theoretical and experimental results has to be taken with due care. In fact, H*P*-H*T* experimental set-up, reaction kinetics and compositional constraints significantly affect the results, causing deviations from expectations (*i.e*. high temperature effects on transformations, occurrence of gradients, meta-stability, complex REDOX-reactions).

5.1 Fe/Mg partitioning between reservoir and Fe-periclase

Using the *reservoir*'s composition (likened to a "virtual" bridgmanite's; Table 1) and the predicted (Mg,Fe)O-phases, the bulk Fe/Mg partitioning between *reservoir* and Fe-periclase $[Kd=(Fe/Mg)^{reservoir}/(Fe/Mg)^{Fe\text{-}periclase}]$ was calculated. In this view, Kd may be considered as an approximate estimate of the actual partitioning between bridgmanite and Fe-periclase, yet taking into account that we are neglecting the *reservoir*'s energetics and therefore we assume that the Fe/Mg exchange/equilibration is driven by the (Mg,Fe)O-system only, as already stated. Kd is determined weighting the Fe-periclase *x*0-*x*1-*x*2-phases by their proportions.

In the LM region, when the LS state drives the degree of iron reactivity, a continuous decrease of Kd from 0.64 to 0.19 can be observed. At higher pressures, in the LLM region, where the (Mg,Fe)O-system's phases do not significantly change, neither in composition nor in proportion, the bulk Fe/Mg-Kd is almost constant (Kd=0.18-0.16 between ~80 and 130 GPa). If the Fe/Mg partitioning between *reservoir* and Fe-periclase is calculated treating each *x*j-phase as independent of the others, then Kd-intervals of 0.5-0.3, 0.18-0.06 and 1-0.5, for *x*0, *x*1 and *x*2, respectively, are obtained. This means that the (Mg,Fe)O-phases exhibit diverse attitudes to iron hosting.

In addition, if a mixed spin state of ferrous iron was taken into account, the Kd-values would increase because of the HS contribution. However, using the compositions and phase proportions obtained from HS-LS linear combination, the Fe-Mg partitioning trend does not change with respect to LS's, with Kd-values as large as 0.19-0.16 in LLM region.

Our results of Fe/Mg partitioning between *reservoir* and Fe-periclase agree with experimental and theoretical studies on pyrolitic and Al-free systems, which give Kd, for bridgmanite/Fe-periclase, ranging from 0.6 to 0.06 (*i.e.* Deschamps and Trampert, 2004; Kobayashi et al., 2005; Sakai et al., 2009; Auzende et al., 2008; Nakajima et al., 2012; Presher et al., 2014; Miur and Brodhlt, 2016). In particular, H*P*-H*T* experiments carried out between 30-130 GPa and 1760–2500 K (Presher et al. 2014; Sinmyo et al. 2008, 2013; Narigyna et al., 2011) yield Kd-estimates showing a trend flattening at LLM pressures like our predictions, although in a restricted range of values (0.35-0.16 *versus* 0.69-0.16). Taking into account that we modelled the Fe/Mg exchange/equilibration neglecting the *reservoir*'s energetics, the general consistency between the present results and previous determinations suggests that iron always prefers Fe-periclase in comparison to all the other iron-bearing phases of the lower mantle.

6. CONCLUSIONS

To our knowledge, this is the first investigation which uses Gibbs energy of mixing, forward-backward transformations and treats the (Mg,Fe)O system as an open exchanger of matter with the lower mantle surroundings.

Un-mixings over the closed MgO-FeO binary at lower mantle *P*-*T* conditions are predicted to occur between 23 and 42 GPa in the case of LS, only. Taking into account that HS is the preferred spin state of iron up to ~40 GPa and that it excludes occurrence of disproportionation at any pressure, un-mixing processes are therefore unlikely. In this light, it is difficult to ascribe to un-mixing phenomena the observed compositional variability of lower mantle Fe-periclase in diamond inclusions and in H*P*-H*T* synthesis products.

In turn, using a geochemically open model and equilibrium reactions formalism, we show that the (Mg,Fe)O-system is able to continuously exchange iron with the lower mantle *reservoir* (*i.e.* MSF-system) and provides the phases *x*0 (reference average; 0.175 FeO), *x*1 and *x*2. *x*1 increases progressively in phase proportion, becoming richer and richer in iron up to 0.5 FeO at ~80 GPa (~2000 km depth). *x*2, 0.10 FeO, is *quasi*-invariant in composition and occurs with phase proportion values that decrease as a function of *P*, similarly to *x*0's. Above ~80 GPa, such phases change neither in composition nor in phase proportion, and the Fe-rich phase becomes the most abundant in the LLM region, in terms of 0.7 phase proportion.

The resulting phases yield a larger and larger density inhomogeneity, estimated by $\Delta\rho=[\rho_{x1}-(\rho_{x0}+\rho_{x2})\times0.5]$. $\Delta\rho$ changes from 0.8, at 24 GPa, to 1.4, at 130 GPa, and corresponds altogether to a mean increase of approximately 10%.

The Fe/Mg partitioning between *reservoir* (roughly approximated by a "virtual" bridgmanite chemical composition) and Fe-periclase, *i.e.* Kd, decreases in LM following its geotherm, but it becomes *quasi*-constant in LLM. In fact, Kd varies from 0.64, at 24 GPa, to 0.19, at 80 GPa and from 0.18, at ~90 GPa, to 0.16, at 130 GPa, in general agreement with previous theoretical and experimental determinations in the case of actual bridgmanite and Fe-periclase. This suggests that iron prefers Fe-periclase in comparison to all the other iron-bearing phases of the lower mantle.

In summary:

- the obtained results indicate the (Mg,Fe)O-system stabilises phases that ultimately give rise to geochemical heterogeneities as a function of the *P-T* paths in LM and LLM. Such heterogeneities are due to changes of the (Mg,Fe)O-phases in (i) composition, (ii) phase proportions, (iii) density and (iv) Fe/Mg partitioning coefficients between *reservoir* and Fe-periclase. These changes, which rapidly occur across LM, become significantly more modest in LLM, where a steady Fe-rich–phase is dominant (~0.7 phase proportion);
- Fe-periclase behaves as the main "pivot" in the Fe/Mg-exchange processes with respect to the lower mantle *reservoir*;
- (Mg,Fe)O is a source of geochemical heterogeneities (the average compositions from 24 to 130 GPa are strewn over the interval 0.19-0.40 FeO), but it does not give rise to any sharp discontinuity. In this view, anomalies, like the ultra-low velocity zones (ULVZs), interpreted as due to local abrupt change of density, do not seem primarily associated to the mixing behaviour of Fe-periclase.

ACKNOWLEDGEMENTS

The present research was funded by the Italian University and Research Ministry (MIUR) /PRIN2015_ project (CB). The authors are thankful to three anonymous reviewers and the Associate Editor for their useful suggestions and remarks, which relevantly improved the original manuscript.

APPENDIX I

Derivation of equations (8.a) and (8.b)

Starting from eq.(7), we require that the conservation of mass principle is fulfilled between right-hand side and left-hand side members. Therefore, we have

$x0 = y1 \times x1 + y2 \times x2$ (I.1.a)

$1-x0 = y1 \times (1-x1) + y2 \times (1-x2)$ (I.1.b).

Summing (I.1.a) and (I.1.b), we obtain

$y1 + y2 = 1$ (I.2)

Expressing $y2$ in (I.1.a) by (I.2), we determine $y1$ as a function of $x1$ and $x2$, *i.e.* equation (8.a). Eq. (8.b) is a consequence of (I.2).

APPENDIX II

Open *system* and constrained phase assemblages

With μ_j^{α} and n_j^{α} we represent the chemical potential and number of moles of the j^{th}-component with respect to the α-phase, respectively. We assume the existence of one *independent* and *known* phase, "^{0}phase". Its composition is fixed and expressed by n_j^0; ξ stands for the number of moles of the ^{0}phase. The introduction of the ^{0}phase is needed when the complexity of a system is so high that a further constraint on the nature of the involved phases can help addressing the problem. For instance, such a situation is met when transformation kinetics is low, or impaired, and leads to the persistence of one or more phases, which constrain the phase composition of the resulting assemblage. Phases other than the ^{0}phase (they are here addressed to as *dependent* phases) are in total p; c indicates the number of components.

The Gibbs energy of such a system is

$$G = \sum_{\alpha=1,p} \sum_{j=1,c} n_j^{\alpha} \mu_j^{\alpha} + \xi \sum_{j=1,c} n_j^0 \mu_j^0.$$

At given P-T conditions we have

$$dG = \sum_{\alpha=1,p} \sum_{j=1,c} \mu_j^{\alpha} dn_j^{\alpha} + \sum_{j=1,c} n_j^0 \mu_j^0 \, d\xi, \quad \text{(II.1)}$$

and at equilibrium dG=0. If we assume the conservation of mass principle for components, *i.e.* closed system, then c-constraints are required to be fulfilled, *i.e.*

$$\sum_{\alpha=1,p} dn_j^{\alpha} + n_j^{0}\, d\xi = 0. \qquad \text{(II.2)}$$

Using the Lagrange multipliers (ψ_j) method, we combine (II.1) and (II.2), so that

$$\sum_{\alpha=1,p} \sum_{j=1,c} \mu_j^{\alpha}\, dn_j^{\alpha} + \sum_{j=1,c} n_j^{0}\, \mu_j^{0}\, d\xi + \sum_{j=1,c} \psi_j \left(\sum_{\alpha=1,p} dn_j^{\alpha} + n_j^{0}\, d\xi\right) = 0.$$

Rearranging the terms of the equation above, we can write

$$\sum_{j=1,c}\left[\sum_{\alpha=1,p}(\mu_j^{\alpha}+\psi_j)\, dn_j^{\alpha} + (\mu_j^{0}+\psi_j)\, n_j^{0}\, d\xi\right] = 0. \qquad \text{(II.3)}$$

(II.3) requires that

$$\mu_1^{1} = \mu_1^{2} = \ldots\ldots = -\psi_1 = \mu_1^{0} \qquad \text{(II.4)}$$

……

$$\mu_c^{1} = \mu_c^{2} = \ldots\ldots = -\psi_c = \mu_c^{0}$$

The set of equations (II.4) leads to the well understood equality between chemical potentials of the same component in different phases.

In the general approach, there is not any imposed ^{0}phase, hence we set it aside for the moment. A set of $c \times p$ unknown $\{x_j^{\alpha}\}$-values, *i.e.* component fractions on which the chemical potentials depend, must be determined. In this way, the problem of the absolute amount of each component can be avoided. However, component fractions require more p-constraints of normalization, *i.e.* $\sum_{j=1,c} x_j^{\alpha}=1$, in addition to the $c\times(p\text{-}1)$ constraints due to (II.4). Hence, at given P and T, the classic relationship: $f_{\text{degrees of freedom}} = (p\times c)\text{-}c\times(p\text{-}1)\text{-}p = c\text{-}p$ is obtained.

In the case of the presence of an *independent* ^{0}phase, the constraining equations of (II.4)-type are $p\times c$, given that the lagrangian multipliers are determined by by μ_j^{0}, *i.e.* $-\psi_j=\mu_j^{0}$. We now assume the system to be off equilibrium but, in order to evolve towards the equilibrium state, it exchanges matter with a *reservoir* according to an irreversible transformation, dG_{irrev}<0, which, once reached, fulfills (II.4) and dG=0. Hence, the *p dependent* phases behave as an "*open system*" in the

equilibration process. Relaxing the constraint of conservation of mass, we have to seek for $c \times p$ unknown $\{n_j^{\alpha}\}$-values, $n_j^{\alpha} \geq 0$, to fulfill the $c \times p$ constraint equations of (II.4)-type. In this view, the problem is solvable and the solution is unique, there being as many variables as constraints, and the independent ^{0}phase pivots equilibration of the *p dependent* phases.

We now aim to introduce more than one *independent* phase: p_{indep}-phases. First, they must be at equilibrium with each other at *P*-*T*, namely they must satisfy the constraints of the Gibbs rule, *i.e.* $p_{indep} \leq c$ and the equality of the chemical potentials. The ψ_i's, determined by the chemical potentials of the *independent* phases accordingly, lead to the $c \times p$ constraining equations. The $\{n_j^{\alpha}\}$-values that determine the *p dependent* phases are obtained by exploiting an exchange of matter with the *reservoir*, as in the case of the ^{0}phase.

It is worth noting that the obtained assemblage represents the least Gibbs energy system compatible with p_{indep} *independent* ($p_{indep} \leq c$) and *p dependent* phases. The assemblage of *dependent* phases, in turn, must be as physically consistent as possible with the conditions following a relaxation of the constraints of the imposed *independent* phases. In this view, $p \leq c$, for the *dependent* phases, too.

The application discussed in the text for Fe-periclase can be likened to the case in which the ubiquitous *x*0-phase acts as an *independent* ^{0}phase, whereas *x*1 and *x*2 are two *dependent* phases. In other words, the *system* is divided into two sub-*systems* (either fully consistent with the Gibbs rule) one of which exchanges matter with a *reservoir* and in this way equilibration is achieved.

APPENDIX III

System (Fe-periclase) and *reservoir*

The *reservoir* provides a simplified description of that portion of the lower mantle other than (Mg,Fe)O. Let us suppose that at given *P*-*T*-conditions, *reservoir* and (Mg,Fe)O, with compositions $X_{reservoir}$ and $X_{(MgFe)O}$, respectively, interact and exchange matter. If *P* and *T* are kept constant, the *system* and the *reservoir* undergo an irreversible transformation towards a Gibbs energy minimum.

If the *reservoir* is *compositionally* likened to a fictitious "bridgmanite", $(Mg,Fe)SiO_3$, we can envisage an exchange of matter between it and the *system* through the following reaction:

$(Mg_{1-x}Fe_x)O + (Mg_{1-y}Fe_y)SiO_3 \Leftrightarrow (Mg_{1-x-\chi}Fe_{x+\chi})O + (Mg_{1-y+\chi}Fe_{y-\chi})SiO_3$,

in which χ FeO is transferred from the *reservoir* to the Fe-periclase, and χ MgO does the opposite. The Gibbs energy of the *reservoir* at *P-T* conditions composed by *N*-moles of a given chemical component, is represented by $G_R(P,T,N) \pm\Delta_f$; where Δ_f is the *reservoir*'s fluctuation that accounts for the energy, complex transformations, reactions, and flows of matter that take place in the lower mantle. For simplicity, we restrict to one chemical component our analysis and use

$g_{Sys}(P,T,n)$

to refer to the "instantaneous" Gibbs energy of a *system* (Fe-periclase), in which *n* defines a generic reference composition at *P-T*. "Instantaneous" Gibbs energy means the Gibbs energy of the *system* frozen off equilibrium. We take $G_R(P,T,N) >> g_{Sys}(P,T,n)$ and their total Gibbs energy is

$$G_{tot}(P,T,N,n) = g_{Sys}(P,T,n) + G_R(P,T,N) \pm\Delta_f. \quad \text{(III.1)}$$

At a given time, *system* and *reservoir* start to interact and exchange matter. The exchange of matter leads to

$G_R(P,T, N-\chi) \pm\Delta_f$

and

$g_{Sys}(P,T, n+\chi)$.

From eq.(III.1), we aim at minimizing the following quantity, with respect to χ,

$$\Delta_{tot}=G_{tot}(P,T,N-\chi,n+\chi)-G_{tot}(P,T,N,n) \pm\Delta_f, \quad \text{(III.2)}$$

in which *system+reservoir* evolve through an irreversible change towards an equilibrium state. Given that $|G_R(P,T, N-\chi)- G_R(P,T, N)|<<\Delta_f$, owing to $\chi<<N$ and, from statistical mechanics, $\Delta_f \propto N^{1/2}$, then we can neglect the change of the *reservoir*'s Gibbs energy due to an exchange of matter with the *system* with respect to the fluctuations' contribution.

In this light, eq.(III.2) becomes

$$\Delta_{tot} \approx [\pm\Delta_f]_{reservoir} + [-\mu(P,T,n+\chi)_{Sys}\cdot\chi + O_{Sys}(\chi^2)]_{system}, \quad \text{(III.3)}$$

Eq.(III.3) shows that if a super-*system* composed by *reservoir*+*system* is considered, then the *system* alone can be considered, if its size is significantly smaller than the *resorvoir*'s. Therefore, exchanges of matter are mainly governed by the *system*, given that they do not affect the *reservoir* more than its fluctuations do.

REFERENCES

Albarede, F., van der Hilst, R.D., 2002. Zoned mantle convection. Philos. Trans. R. Soc. Lond. Ser.A, Math.Phys. Eng. Sci.360, 2569–2592. http://dx.doi.org/10.1098/rsta.2002.1081.

Alfredsson, M., Price, G.D., Catlow, C.R.A., Parker, S.C., Orlando, R. Brodholt, J.P., 2004. Electronic structure of the antiferromagnetic B1-structured FeO. *Phys. Rev*. B **70**, 165111-165116.

Andrault, D., Bolfan-Casanova, N., Lo Nigro,G., Bouhifd, M.A., Garbarino, G., Mezouar, M., 2011. Solidus and liquidus profiles of chondritic mantle: Implication for melting of the Earth across its history. Earth Planet. Sci. Lett., 304, 251-259.

Autschbach, J., Srebro, M., 2014. Delocalization Error and "Functional Tuning" in Kohn–Sham Calculations of Molecular PropertiesAcc. Chem. Res., 2014, 47 (8), 2592–2602

Auzende, A.-L., Badro, J., Ryerson, F.J., Weber, P., Fallon, S., Addad, A., Siebert, J., Fi-quet, G., 2008. Element partitioning between magnesium silicate perovskite and ferropericlase: new insights into bulk lower-mantle geochemistry. Earth Planet. Sci. Lett.269, 164–174.

Badro, J., Fiquet, G., Guyot, F., Rueff, J., Struzhkin, V.V., Vankò, G., Monaco, G., 2003. Iron Partitioning in Earth's Mantle: Toward a Deep Lower Mantle Discontinuity. Science, 300, 789-791

Barnard , R. W., Dahlquist ,G., Pearce, K., Reichel, L., Richards K. C., 1998. Gram Polynomials and the Kummer Function. *J. Approx. Theory*94, 128–143.

Belmonte, D., Ottonello, G., and Vetuschi Zuccolini, M., 2014. Ab initio thermodynamic and thermophysical properties of sapphirine end-members in the join $Mg_4Al_8Si_2O_{20}$ – $Mg_3Al_{10}SiO_{20}$.American Mineralogist 99, 1449-1461.

Causà, M., Dovesi, R., Pisani, C., Roetti, C., 1986. Electronic structure and stability of different crystal phases of magnesium oxide. Physical Review B, 33, 1308-1316.

733 Cordier, P., Amodeo, J., Carrez, P. (2012) Modelling the rheology of MgO under Earth's mantle
734 pressure, temperature and strain rates. *Nature*, 481, 177-180.
735 da Silva, C.R.S., Wentzcovitch, R.M., Patel, A., Price, G.D., Karato, S.I., 2000. The composition
736 and geotherm of the lower mantle: constraints from the elasticity of silicate perovskite. Phys.
737 Earth Planet. Int. 103-109.
738 de Koker, N., 2010. Thermal conductivity of MgO periclase at high pressure: Implications for the
739 D″ region. Earth Planet. Sci. Lett., 292, 392-398
740 de Wit, R.W.L., Trampert, J., 2015. Robust constraints on average radial lower mantle anisotropy
741 and consequences for composition and texture. Earth Planet. Sci. Lett., 429, 101-109.
742 Deschamps, F., Trampert, J., 2004. Towards a lower mantle reference temperature and composition.
743 Earth Planet. Sci. Lett. 222, 161–175. http://dx.doi.org/10.1016/j.epsl.2004.02.024.
744 Dill, K.A., Bromberg, S., Stigter, D., 2003. Molecular Driving Forces: Statistical Thermodynamics
745 in Chemistry and Biology.. (1st edition). pp 665. New York: Garland Science.
746 Dobson, D.P., Brodholt, J.P., 2005. Subducted banded iron formations as a source of ultralow-
747 velocity zones at the core–mantle boundary. Nature434, 371–374.
748 Dovesi, R., Saunders, V.R., Roetti, C., Orlando, R., Zicovich-Wilson, C.M., Pascale, F., Civalleri,
749 B., Doll, K., Harrison, N.M., Bush, I.J., D'Arco, P., Llunell, M. 2009. CRYSTAL09 user's
750 manual. University of Torino, IT, Torino
751 Dubrovinsky, L. S., Dubrovinskaia, N. A., Saxena, S. K. , Annersten, H. , Hålenius, E. , H.
752 Harryson, Tutti, F., Rekhi, S., Le Bihan, T. 2000. Stability of ferropericlase in the lower
753 mantle. Science 289, 430– 432
754 Dubrovinsky, L. S., Dubrovinskaia, N. A., Annersten, H., Hålenius, E. , Harryson, H. 2001.
755 Stability of magnesiowüstites $(Mg_{0.50}Fe_{0.50})O$ and $(Mg_{0.80}Fe_{0.20})O$ in the lower mantle. Eur. J.
756 Miner. 113, 857-861.
757 Dziewonski, A., Anderson, D.L., 1981. Preliminary earth reference model. Phys. Earth Planet.
758 Inter.25, 297–356.

759 Fei W., Zhang L., Corgna A., Watson H., Ricolleau A., Meng Y., Prakapenka V., 2007, Spin
760 transition and equation of state of (Mg,Fe)O solid solutions. Geophys. Res. Lett. 34, L17307.
761 Fei, Y., Mao, H.-K., Shu, J., Hu, J., 1992. P-V-T equation of state of magnesiowüstite
762 ($Mg_{0.6}Fe_{0.4}$)O. Phys. Chem. Miner. 18, 416– 422.
763 Frost, D.J, Myhill, R. (2016) Chemistry of the lower mantle. In: Deep Earth: Physics and Chemistry
764 of the lower mantle and core, Geophysical Monograph 217. Edited by Teresaki H. and Fischer
765 R.A. American Geophysical Union. John Wiley and Sons, Inc.
766 Gale J. D., 1997, GULP-a computer program for the symmetry adapted simulation of solids. *JCS*
767 *Faraday Trans*. **93**, 629-637.
768 Garnero, E. J., 2004, A new paradigm for Earth's core-mantle boundary, Science, 304, 834–836,
769 doi:10.1126/science.1097849.
770 Girard, J., Amulele, G., Farla, R., Mohiuddin, A., Karato, S. (2016) Shear deformation of
771 bridgmanite and magnesiowüstite aggregates at lower mantle conditions. Science, 351, 144-
772 147.
773 Harte B. (2010) Diamond formation in the deep mantle; the record of mineral inclusions and their
774 distribution in relation to mantle dehydration zones. Mineralogical Magazine, 189–215.
775 http://dx.doi.org/10.1180/minmag.2010.074.2.189.
776 Irifune, T., Shinmei, T., McCammon, C. A., Miyajima, N., Rubie D. C., Frost D. J., 2010. Iron
777 Partitioning and Density Changes of Pyrolite in Earth's Lower Mantle. Science **327,** 193-195.
778 Jackson I., 1998. Elasticity, composition and the temperature of the Earth's lower mantle: a
779 reappraisal, Geophys. J. Int. 134, 291–311.
780 Jackson, J M., Sinogeikin, S. V., Jacobsen, S.D. , Reichmann, H. J., Mackwell, S.J. Bass, J. D.
781 2006. Single-crystal elasticity and sound velocities of ($Mg_{0.94}Fe_{0.06}$)O ferropericlase to 20 GPa.
782 Journal of Geophysical Research 111, B09203

783 Jacobsen, S. D., Spetzler, H., Reichmann, H.-J., Smyth, J. R., 2004. Shear waves in the diamond-
784 anvil cell reveal pressure-induced instability in (Mg,Fe)O. Proceedings of the National
785 Academy of Sciences of the United States of America, 101, 5867– 5871
786 Javoy M., Kaminski E., Guyot F., Andrault D., Sanlou J. R., Moreira M., Labrosse S., Jambon A.,
787 Agrinier P., Davaille A., Jaupart C., 2010. The chemical composition of the Earth: Enstatite
788 chondrite models. Earth Planet. Sci. Lett. 293, 259-268.
789 Kaminsky, F., Lin, J-F. (2017) Iron partitioning in natural lower-mantle minerals: toward a
790 chemically heterogeneous lower mantle. Am. Miner., DOI: http://dx.doi.org/10.2138/am-2017-
791 5949.
792 Kaminsky, F., 2012, Mineralogy of the lower mantle: A review of 'super-deep' mineral inclusions
793 in diamond. Earth-Science Reviews, 110, 127–147
794 Kaneshima, S., Helffrich G., 1999. Dipping low-velocity layer in the mid-lower mantle: evidence
795 for geochemical heterogeneity. Science, 283, 1888–1891.
796 Karki, B. B., Wentzcovitch, R. M., de Gironcoli, S., Baroni, 2001. First principles thermoelasticity
797 of MgSiO3-perovskite: consequences for the inferred properties of the lower Mantle. Geophys.
798 Res. Lett. 28, 2699-3702.
799 Kennett, B.L, Engdahl , E.R., Buland. R.,1995. Constraints on seismic velocities in the earth from
800 travel times. Geophys.J. Int. 122:108-124.
801 Kobayashi, Y., T. Kondo, E. Ohtani, N. Hirao, N. Miyajima, T. Yagi,T. Nagase, and T. Kikegawa
802 (2005), Fe-Mg partitioning between (Mg, Fe)SiO3 post-perovskite, perovskite, and
803 magnesiowüstite in the Earth's lower mantle. Geophys. Res. Lett., 32, L19301, doi:10.1029/
804 2005GL023257.
805 Kung, J., Li, B., Weidner, D. J., Zhang, J., Liebermann, R. C., 2002. Elasticity of $(Mg_{0.83},Fe_{0.17})O$
806 ferropericlase at high pressure: Ultrasonic measurements in conjunction with X-radiation
807 techniques. Earth Planet. Sci. Lett., 203, 557–566.

Kurnosov, A., Marquardt, H., Frost, D.J., Boffa Ballaran, T., Ziberna, L. (2017) Evidence for a F3+-rich pyrolytic lower mantle from (Al,Fe)-bearing bridgmanite elasticity data. Nature, 543, 543-546.

Lay T., Helmberger D.V., 1983.A shear velocity discontinuity in the lower mantle. Geoph.Res. Lett. 10, 63-66.

Lay, T., Garnero, E.J., Williams, Q., 2004. Partial melting in a thermo-chemical boundary layer at the base of the mantle. Phys. Earth Planet. Inter. 146, 441–467.

Lewis, G. V., Catlow, C. R. A.,1985. Potential models for ionic oxides. J. Phys. C: Solid State Phys. 18, 1149-1162.

Li, L., Brodholt, J.P., Stackhouse, S., Weidner, D.J., Alfredsson, M., Price, G.D., 2005. Elasticity of (Mg,Fe)(Si,Al)O_3 perovskite a high pressure. Earth Planet. Sci. Lett. 240, 529–536. http://dx.doi.org/10.1016/j.epsl.2005.09.030.

Lin, J. F., Speziale, S., Mao, Z., Marquardt, H., 2013. Effects of the Electronic Spin Transitions of Iron in Lower Mantle Minerals: Implications for Deep Mantle Geophysics and Geochemistry. Rev. Geophys. 51, 244-275.

Lin, J. F., Wenk, H. R., Voltolini, M., Speziale, S., Shu, J., Duffy, T. S., 2009. Deformation of lower-mantle ferropericlase (Mg,Fe)O across the electronic spin transition. Phys. Chem. Miner.36, 585–592.

Lin, J.F., Vankò, G., Jacobsen, S.D., Iota, V., Struzhkin, V.V., Prakapenka, V. B., Kuznetsov, A., Yoo, C.S. (2007) Spin transition zone in Earth's lower mantle. Science, 317, 1740-1743.

Lin, J.F., Heinz, D.L., Mao, H., Hemley, R.J., Devine, J.M., Li, J. and Shen, G. 2003. Stability of magnesiowüstite in Earth's lower mantle. PNAS, 100, 4405-4408.

Lyubetskaya T., Korenaga J., 2007. Chemical composition of Earth's primitive mantle and its variance: 1. method and results. J. Geophys. Res. 112, B03211. doi:10.1029/2005JB004223

832 Lyubutin, S., Gavriliuk, A. G., Frolov, K. V., Lin, J. F., Troyan , I. A., 2009. High_Spin–Low_Spin
833 Transition in Magnesiowüstite ($Mg_{0.75}$,$Fe_{0.25}$)O at High Pressures under Hydrostatic
834 Conditions. J. of Experim. Theoret. Phys. Lett., 90, 617–622
835 Madi, K., Forest, S., Cordier, P., Boussuge, M. (2005) Numerical study of creep in two-phase
836 aggregates with a large rheology contrast: implications for the lower mantle. Earth Planet. Sci.
837 Lett., 237, 223-238.
838 Mainprice, D., 2007. Seismic anisotropy of the deep Earth from a mineral and rock physics
839 perspective, Treatise Geophys., 2, 437–491
840 Mao, W.L., Mao, H.K., Sturhahn, W., Zhao, J.Y., Prakapenka, V.B., Meng, Y., Shu, J.F., Fei,
841 Y.W., Hemley, R.J., 2006. Iron-rich post-perovskite and the origin of ultralow-velocity zones.
842 Science, 312, 564–565.
843 Matas J., Bass J., Ricard Y., Mattern E. and. Bukowinski M. S. T. , 2007. On the bulk composition
844 of the lower mantle: predictions and limitations from generalized inversion of radial seismic
845 profiles. Geophys. J. Int. 170, 764–780.
846 Mattern, E., Matas, J., Ricard, Y., Bass J.D., 2005. Lower mantle composition and temperature
847 from mineral physics and thermodynamic modelling, Geophys. J. Int., 160, 973–990.
848 McDonough W.F., Sun S., 1995. The composition of the Earth. Chem. Geol. 120, 223–
849 253.doi:10.1016/0009-2541(94)00140-4.
850 McNamara, A.K., Garnero, E.J., Rost, S., 2010. Tracking deep mantle reservoirs with ultra-low
851 velocity zones. Earth Planet. Sci. Lett. 299, 1–9.http://dx. doi.: 10.1016/j.epsl.2010.07.042.
852 Merli, M., Sciascia, L., Pavese, A., Diella, V., 2015. Modelling of thermo-chemical properties over
853 the subsolidus MgO–FeO binary, as a function of iron spin configuration,composition and
854 temperature. Phys. Chem. Min. 42, 347-362.
855 Merli, M., Bonadiman, C., Diella, V., Pavese, A. 2016. Lower mantle hydrogen partitioning
856 between periclase and perovskite: A quantum chemical modelling. Geoch,. Cosmochim. Acta
857 173, 304-318.

858 Miyajima, Y., Ueda, T., Adachi, H., Fujii, T., Onaka, S., Kato, M. (2014) Dislocation density of
859 FCC metals processed by ARB. 6th International Conference on nanomaterials by severe plastic
860 deformation. IOP Conf. Series: materials Science and Engineering, 63, 012138,
861 doi:10.1088/1757-899X/63/1/012138.
862 Miyajima, N., Yagi, T., Hirose, K., Kondo, T., Kiyoshi Fujino, K., Miura, H. 2001. Potential host
863 phase of aluminum and potassium in the Earth's lower mantle. Am. Mineral., 86, 740-746.
864 Muir, J., Brodholt, J. 2015. Elastic properties of ferropericlase at lower mantle conditions and its
865 relevance to ULVZs. Earth Planet. Sci. Lett., 417, 40-48.
866 Murakami, M., Hirose, K., Sata, N., Ohishi, Y., 2005. Post - perovskite phase transition and
867 mineral chemistry in the pyrolitic lowermost mantle. Geophys. Res. Lett., 32, L03304,
868 doi:10.1029/2004GL021956.
869 Murakami, M., Ohishi, Y., Hirao, N., Hirose, K., 2012. A perovskitic lower mantle inferred from
870 high-pressure, high-temperature sound velocity data. Nature 485, 90–94.
871 http://dx.doi.org/10.1038/nature11004.
872 Nakajima, Y, Frost D.J., Rubie, D.C., 2012. Ferrous iron partitioning between magnesium silicate
873 perovskite and ferropericlase and the composition of perovskite in the Earth's lower mantle. J
874 Geophys. Res. 117:B08201.
875 Narygina, O., Dubrovinsky, L., Samuel, H., McCammon, C., Kantor, I., Glazyrin, I., Pascarelli, S.,
876 Aquilanti, G., Prakapenka, V., 2011. Chemically homogeneous spin transition zone in Earth's
877 lower mantle. Phys. Earth Planet. Inter. 185, 107–111.
878 Nomura, R., Ozawa, H., Tateno, S., Hirose, K., Hernlund, J., Muto, S., Ishii, H., Hiraoka, N., 2011.
879 Spin crossover and iron-rich silicate melt in the Earth's deep mantle. Nature473, 199–202.
880 Oganov, A., Dorogokupets, P.I., 2003. All-electrons and pseudopotential study of MgO: equation of
881 state, anharmonicity and stability. Phys. Rev. B 67, 224110-1/11.

882 Ono, S., 2008. Experimental constraints on the temperature profile in the lower mantle. Phys.
883 Earth Planet. Inter., 170, 267–273, doi:10.1016/j.pepi.2008.06.033.
884 Ono, S., and A. R. Oganov (2005), In situ observations of phase transition between perovskite and
885 $CaIrO_3$-type phase in MgSiO3 and pyrolitic mantle composition, Earth Planet. Sci. Lett, 236,
886 914-932.
887 Ohta, K., Fujino, K., Y. Kuwayama, Y., Kondo, T., Shimizu, K. and Ohishi Y. (2014) Highly
888 conductive iron-rich (Mg,Fe)O magnesiowüstite and its stability in the Earth's lower mantle, J.
889 Geophys. Res. Solid Earth, 119, 4656–4665, doi:10.1002/ 2014JB010972.
890 Otsuka, K., McCammon, C.A., Karato, S. (2010) Tetrahedral occupancy of ferric iron in (Mg,Fe)O:
891 Implications for point defects in the Earth's lower mantle. Phys. Earth Plan. Int., 180, 179-188.
892 Ottonello, G., Civalleri, B., Ganguly, J., Perger, W.F., Belmonte, D., Vetuschi Zuccolini, M., 2010.
893 Thermo-chemical and thermo-physical properties of the high pressure phase Anhydrous B
894 ($Mg_{14}Si_5O_{24}$): an ab initio all-electron investigation. Am. Mineral.95, 563–573.
895 Ottonello G. (1997) Principles of Geochemistry, Columbia University Press, New York, 897 pp.
896 Pamato, M.G, Kurnosov, A., Boffa Ballaran, T., Trots, D.M., Caracas, R. Frost, D.J. 2014.
897 Chemistry and Mineralogy of Earth's Mantle. Hexagonal
898 Na0.41[Na0.125Mg0.79Al0.085]2[Al0.79Si0.21]6O12 (NAL phase): Crystal structure
899 refinement and elasticity. Am. Mineral., 99, 1562-1569.
900 Paktunc, A.D., 1998. MODAN: An interactive computer program for estimating mineral quantities
901 based on bulk composition. Comput. Geosci.-UK, 22(5), 425-431.
902 Prescher, C., Langenhorst, F., Dubrovinsky, L., Prakapenka, V., Miyajima, N., 2014. The effect of
903 Fe spin crossovers on its partitioning behavior and oxidation state in a pyrolitic Earth's lower
904 mantle system. Earth Planet. Sci. Lett.399, 86–91.
905 Reali, R., Boioli, F., Gouriet, K., Carrez, P., Devincre, B., Cordier, P. (2017) Modelling plasticity of
906 MgO by 2.5D dislocation dynamics simulations. Mat. Sciences and Engin., 690, 52-61.

907 Richet, P., Mao, H.-K., Bell, P. M., 1989. Bulk moduli of magnesiowüstites from static
908 compression experiments. J. Geoph. Res., 94, 3037–3045.
909 Rost, S., Garnero, E.J., Williams, Q., Manga, M., 2005. Seismological constraints on apossible
910 plume root at the core–mantle boundary. Nature 435 (7042), 666–669.
911 Sakai, T., Ohtani, E., Terasaki, H., Sawada, N., Kobayashi, Y., Miyahara, M., Nishijima, M., Hirao,
912 N., Ohishi, Y., Kikegawa, T., 2009, Fe–Mg partitioning between perovskite and ferropericlase
913 in the lower mantle. Am. Mineral., 94, 921–925.
914 Sanchez, J. M., Ducastelle, F. Gratias, D. 1984. Generalized cluster description of multicomponent
915 systems. Phys. A. 128, 334-350.
916 Scanavino, I., Prencipe, M., 2013, Ab-initio determination of high-pressure and high-temperature
917 thermoelastic and thermodynamic properties of low-spin (Mg1–xFex)O ferropericlase with x in the
918 range [0.06, 0.59]. American Mineralogist, Volume 98, 1270–1278.
919 Scanavino, I., Belousov, R., Prencipe M., 2012. Ab initio quantum-mechanical study of the effects
920 of the inclusion of iron on thermoelastic and thermodynamic properties of periclase (MgO).
921 Phys. Chem. Miner., 39, 649–663.
922 Sidorin, I., Gurnis,M., Helmberger, D. V., 1999. Evidence for a ubiquitous seismic discontinuity at
923 the base of the mantle. Science, 286, 1326–1331, doi:10.1126/science.286.5443.1326.
924 Sinmyo, R., Hirose, K., 2013. Iron partitioning in pyrolitic lower mantle. Phys. Chem. Miner.40,
925 107–113.
926 Sinmyo, R., Hirose, K., Nishio-Hamane, D., Seto, Y., Fujino, K., Sata, N., Ohishi, Y., 2008.
927 Partitioning of iron between perovskite/postperovskite and ferropericlase in the lower mantle. J.
928 Geoph. Res., 113, B11204, doi:10.1029/2008JB005730
929 Stølen S., Grande, T., 2004. Chemical Thermodynamics of Materials: Macroscopic and
930 Microscopic Aspects. John Wiley and Sons Ltd.
931 Stixrude, L., Lithgow-Bertelloni, C., 2007. Influence of phase transformations on lateral
932 heterogeneity and dynamics in Earth's mantle. Earth Planet. Sci. Lett. 263, 45–55.

933 Thorne, M.S., Garnero, E.J., Jahnke, G., Igel, H., McNamara, A.K., 2013. Mega ultra-low velocity
934 zone and mantle flow. Earth Planet. Sci. Lett. 364, 59–67.
935 http://dx.doi.org/10.1016/j.epsl.2012.12.034.
936 Tommaseo, C.E., Devive, J., Merkel, S., Speziale, S., Wenk, H.R. (2006) Texture development and
937 elastic stresses in magnesiowüstite at high pressure. Phys. Chem. Min., 33, 84-97.
938 Trampert, J., Deschamps,F., Resovsky, J. S., Yuen, D. A. , 2004. Probabilistic tomography maps
939 chemical heterogeneities throughout the lower mantle. Science, 306, 853–856,
940 doi:10.1126/science.1101996.
941 Tsuchiya, T., Wentzcovitch, R.M., da Silva, C.R.S., de Gironcoli, S., 2006.Spin transition in
942 magnesiowüstite in Earth's lower mantle. Physic. Rev. Lett., 96, 198501.
943 Valerio, G. , Catti, M., Dovesi, R., Orlando, R., 1995. Ab initio study of antiferromagnetic rutile-
944 type FeF_2. Phys. Rev. B, 52, 2422-2427.
945 van Orman, J.A., Fei, Y., Hauri, E.H., Wang, J. (2003) Diffusion in MgO at high pressures:
946 constraints on deformation mechanisms and chemical transport at the core-mantle boundary. J.
947 Geophys. Res., 30, 1056.
948 van Westrenen, W., Li, J., Fei, J., Frank, M.R., Hellwig, H., Komabayashi, T., Mibef, K.,
949 Minarik, W.G., Van Orman, J.A., Watson, H.C., Funakoshi, K., Schmidt. M.W., 2005.
950 Thermoelastic properties of $(Mg_{0.64}Fe_{0.36})O$ ferropericlase based on in situ X-ray diffraction to
951 26.7 GPa and 2173 K. Phys. Earth Planet. Int., 151, 163–176
952 Vassiliou, M. S., Ahrens, T. J., 1982. The equation of state of $Mg_{0.6}Fe_{0.4}O$ to 200 GPa. Geoph.
953 Res.Lett., 9, 127–130.
954 Vilella K.,Shim S-H., Farnetani C.G., Badro, J. 2015.Spin state transition and partitioning of iron:
955 Effects on mantle dynamics. Earth and Planet. Sci. Lett., 417, 57-66.
956 Wang, X., Tsuchya, T., Hase, A. (2015) Computational support for a pyrolitic lower mantle
957 containing ferric iron. Nature geoscience Letters, 8, 556-560.

Wdowik, U.D., Piekarz, P., Jochym, P.T., Parlinski, K., Olés, A.M. (2015) Influence of isolated and clustered defects on electronic and dielectric properties of wüstite. Phys. Rev. B, 91, 195111-1/10.

Wentzcovitch, R. M., Karki, B. B., Cococcioni, M. , de Gironcoli, S., 2004. Thermoelastic properties of MgSiO3-perovskite: insights on the nature of the Earth's lower mantle. Phys.Rev. Lett. 92, 018501

Wentzcovitch, R. M., Justo, J.F., Wu, Z., da Silva, C.R.S., Yuen, D., Kohlstedt, D., 2009. Anomalous compressibility of ferropericlase throughout the iron spin cross-over. Proc. the Nat. Acad. Sci.106, 8447–8452.

Wicks, J.K., Jackson, A., Sturhahn, W., 2010. Very low sound velocities in iron-rich (Mg,Fe)O: implications for the core–mantle boundary region. Geophys. Res. Lett.37, L153041 (5 pp).

Yuge, K., 2010. Cluster expansion approach for transmutative lattice systems. J. Phys Cond. Matter, **22**, 125402 (9pp).

Zha, C.S., Mao, H., Hemley, R.J. (2000) Elasticity of MgO and a primary pressure scale up to 55 GPa. PNAS, 97, 13494-13499.

Zhang, J., Kostak, P., 2002. Thermal equation of state of magnesiowüstite ($Mg_{0.6}Fe_{0.4}$)O. Phys. Earth Planet. Inter., 129, 301– 311

Zhang, *S.*, Cottaar, S., Liu, T., Stackhouse, S., Militzer, B., 2016. High-pressure, temperature elasticity of Fe- and Al-bearing MgSiO3: Implications for the Earth's lower mantle. Earth Planet. Sci. Lett. 343, 264-273.

CAPTIONS TO THE FIGURES

Figure 1. Geotherms used in the present work, for LM and LLM. LM-geotherm with a potential temperature of 1920 K at 24 GPa and a *T*-gradient (*dT/dz*) in the range of ~0.5 K/Km, is applied to the mantle region of ~24-80 GPa (solid blue line). LLM-geotherm, with a potential temperature of 2615 K at 96 GPa and d*T*/dz of ~0.85 K/Km, is considered in the mantle region of ~80-130 GPa (solid red line). The consolute temperature curves, T_C calculated for LS (solid black line) and HS (dashed black line) state of iron as a function of *P* are also shown. Miscibility gap ($T_C > T_{geotherm}$) occurs between 23 and 42 GPa for LS only.

Figure 2. Predicted miscibility gap for LS in the MgO–FeO binary system, as a function of pressure and temperature. *P*-*T* values from the geotherms here used. The pyrolitic Fe-periclase reference *x*0-composition (*x*=0.175 FeO) is also reported.

Figure 3. LS: blue; HS: red. **(a)** Compositions of the *x*0-, *x*1- and *x*2-phases (solid, dashed and dotted lines, respectively) in terms of FeO fractions; (**b**) phase proportions λ0, λ1 and λ2 (solid, dashed and dotted lines, respectively) of *x*0-, *x*1- and *x*2-mixings, respectively.

Figure 4. LS: blue; HS: red. (**a**) The average equilibrium constant, $<K(P,T)>$, is plotted according to eq.(7-11) in the text, along the LM-LLM-paths; (**b**) static excess enthalpy (ΔH_{excess}) determined at 24/1900-107/2910 GPa/K, as an example of the LM and LLM mantle regions, respectively.

Figure 5. Density (g cm^{-3}) of the *x*0-, *x*1- and *x*2-phases (solid, dashed and dotted lines, respectively) in the case of LS (blue) and HS (red).

Figure 6. LS: blue; HS: red. FeO-fraction excess with respect to the reference *x*0-composition due to exchange between Fe-periclase and *reservoir*, in open (Mg,Fe)O-system.