Iron partitioning in natural lower-mantle minerals:

Toward a chemically heterogeneous lower mantle

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Abstract

The concentrations of Fe, Al and Ni and their distributions were determined for all known natural assemblages of ferropericlase (fPer) and bridgmanite (Bridg), coexisting as inclusions in deep-mantle diamonds from Brazil, Canada, Guinea and South Australia. Based upon these data, it is likely that some areas within the deep lower mantle are iron-rich and differ markedly from a pyrolitic composition. In the lowermost lower mantle, Bridg is Al-rich and fPer is Ni-poor, witnessing the presence of a free metallic phase in the mineral-forming environment. The iron partitioning in the Bridg + fPer association (K\textsubscript{D}\textsuperscript{Bridg-fPer} = ([Fe/Mg]\textsuperscript{Bridg})/(Fe/Mg)\textsuperscript{fPer})\textsubscript{a}) in juvenile diamond inclusions is as low as 0.1-0.2. During ascent of the diamonds with their inclusions to the surface, the K\textsubscript{D}\textsuperscript{Bridg-fPer} eventually increases to values of 0.4-0.5 and even as high as 0.7.

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The details of the element partitioning between natural Bridg and fPer in the lower mantle are as follows: iron in Bridg is ferrous Fe\(^{2+}\) in the A site, substituting for Mg\(^{2+}\); almost all iron in fPer is ferrous Fe\(^{2+}\); the share of ferric Fe\(^{3+}\) iron in fPer is Fe\(^{3+}\)/ΣFe = 8-12 at%; iron concentrations in both Bridg and fPer increase with depth (pressure), reflecting the increasing Fe content in the lower part of the lower mantle, different from that of a pyrolitic model. Al in Bridg is mainly in the cation site B and partly in the cation site A, in both cases substituting for Si, Mg and Fe with vacancy formation; and in the case of Al positioning into both B and A sites, a charge-balanced reaction occurs.

The natural samples show very diverse \(K_D^{\text{Bridg-fPer}}\) values and elemental distribution that cannot be simply explained by our current understanding on alumina dissolution in Bridg and the spin transition of Fe\(^{2+}\) in fPer. These major differences between experimental results and observations in natural samples demonstrate the complex, inhomogeneous iron speciation and chemistry in the lower mantle.

Keywords: lower mantle, ferropericlase, bridgmanite, iron partitioning, pyrolite

Introduction

The Earth’s lower mantle, based on a pyrolite compositional model, is believed to comprise three major mineral species, bridgmanite \([(\text{Mg,Fe})(\text{Si,Al})\text{O}_3]\), ferropericlase \([(\text{Mg,Fe})\text{O}]\) and calcium silicate perovskite \([\text{CaSiO}_3]\), that are gravitationally compressed near adiabatically. It has been proposed that these minerals are distributed homogeneously and have constant compositions, for the most part through the lower mantle, and thus contribute to continuous
features of the observed, one-dimensional seismic model of density, compressional wave
velocity and shear wave velocity (Dziewonski and Anderson 1981; Kennett et al. 1995).
Bridgmanite (Bridg) and ferropericlase (fPer) contain significant amounts of iron, whose
complex chemical speciation and electronic spin transitions can affect a broad spectrum of the
physical and chemical properties of the two major phases of the lower mantle (e.g., Irifune et al.
2010; Lin et al. 2013).

High P-T experiments along an expected mantle geotherm for a pyrolitic composition
demonstrated that the iron index, \( f_e = \frac{Fe}{(Fe+Mg)}_{at} \), of the pyrolitic lower-mantle fPer should be
0.12-0.27 (e.g., Wood 2000; Lee et al. 2004) or even lower, at c. 0.10 (Kesson and Fitz Gerald
1991). These results suggest that the iron chemistry of lower-mantle fPer may not vary
significantly. However, although a majority of the studied natural lower-mantle fPer grains
hosted within deep-diamond inclusions have \( f_e = 0.10-0.20 \), more than 40% of them vary in a
‘forbidden’ range with up to \( f_e = 0.62 \), falling into the field of magnesiowüstite (e.g., Hutchison
1997; Kaminsky 2012); one of the analyzed samples has an iron index even as high as 0.9, which
is almost close to the end-member wüstite stoichiometry. Some Bridg grains, coexisting with
iron-rich fPer, also exhibit relatively high iron contents. The discovery of these iron-rich
ferropericlase and magnesiowüstite grains deviates from the traditional view of the pyrolitic
lower mantle composition that displays a homogenous iron chemistry and mineralogy, and points
to a much more complex chemistry of the lower mantle.

To elucidate the lower-mantle chemistry in these minerals, we have analyzed Fe, Ni and Al
contents and their distribution in all the currently known fPer + Bridg assemblages coexisting as
inclusions in natural diamonds from Brazil, Canada, Guinea and South Australia.
Review of experimental data

A number of experimental works on iron partitioning between Bridg and fPer in a laser-heated diamond anvil cell, subjected to relevant lower-mantle conditions of up to approximately 120 GPa, were performed over the last two decades. Almost all experiments modelled the suggested pyrolitic model of the lower mantle with the iron index, \( f_e = \frac{\text{Fe}}{\text{Fe}+\text{Mg}}_{\text{at}} = 0.05-0.10 \). The only exception was the work performed by Tange et al. (2009) in a multianvil apparatus with sintered diamond anvils, in which the starting material was very different from pyrolitic and had \( f_e = 0.50 \); it resulted in highly iron-rich association, Bridg with \( f_e = 0.16-0.32 \) and fPer with \( f_e = 0.49-0.92 \). The other studies have shown disparate results for the distribution of Fe in the various minerals (Fig. 1A). For example, while some demonstrated a positive correlation of the iron index between Bridg and fPer (0.070-0.234) (Katsura and Ito 1996; Kesson et al. 2002; Kobayashi et al. 2005; Murakami et al. 2005; Sakai et al. 2009); others found the opposite, a negative correlation (Irifune 1994; Kesson et al. 1998; Wood 2000; Irifune et al. 2010) (Fig. 1A). At \( f_{e,fPer} = 0.05-0.20 \) for both trends, the positive correlation was obtained mainly in association with low-Fe Bridg (\( f_e = 0.010-0.103 \)), while the negative correlation was in association with high-Fe Bridg (\( f_e = 0.081-0.167 \)). There were, as well, experimental results showing variations in \( f_{e,Bridg} = 0.011-0.077 \) virtually independently of \( f_{e,fPer} \) (c. 0.10) (Auzende et al. 2008). The general trends (I and II) can be identified in a consolidated graph (Fig. 1A). The positive trend divides into two branches (trends Ia and Ib) with the same correlation but different values of \( f_{e,Bridg} \), which could be due to different pressure range examined. These experimental discrepancies remain unexplained.

Experimental evaluations of the partition coefficient of iron between fPer and Bridg
defined as $K_{D}^{\text{Bridg-fPer}} = ([\text{Fe/Mg}]^{\text{Bridg}})/([\text{Fe/Mg}]^{\text{fPer}})$, produce even more inconsistent results. The values of $K_{D}^{\text{Bridg-fPer}}$ vary from 0.04 to 0.9 (Fig. 1B). Some of the experiments have shown an increase of $K_{D}^{\text{Bridg-fPer}}$ with pressure (Irifune, 1994; Kobayashi et al. 2005; Sinmyo and Hirose, 2013), whereas others have demonstrated the reverse (Andrault 2001; Kesson et al. 2002; Murakami et al. 2005; Tange et al. 2009; Irifune et al. 2010), or have found no correlation between $K_{D}^{\text{Bridg-fPer}}$ and pressure (Guyot et al. 1988; Katsura and Ito 1996; Auzende et al. 2008).

Specifically, the concentration of Al$^{3+}$ in bridgmanite has been shown to significantly affect its iron partitioning and Fe$^{3+}$ content; it has been shown that the dissolution of Al$^{3+}$ in bridgmanite at the top lower-mantle conditions can significantly enhance the Fe$^{3+}$ occupancy in the A site of the lattice resulting in higher $K_{D}^{\text{Bridg-fPer}}$ (Irifune et al. 2010). The cause of these discrepancies may relate to dissimilar conditions under which the experiments were performed (great thermal gradients, pressure duration, chemical homogeneity, non-thermodynamic equilibrium, etc.) and/or in the compositions of starting materials, including different concentrations of Fe and Al used in the experiments.

The discovery of iron spin crossover in fPer led to the suggestion that $K_{D}^{\text{Bridg-fPer}}$ would behave differently in relevant high $P-T$ conditions found in the deep lower mantle, decreasing from the mid-lower mantle to bottom lower mantle conditions, such that most of the iron partitions into fPer leaving Bridg essentially iron-free (Badro et al. 2003; Speziale et al. 2005).

More recent theoretical and experimental studies on a pyrolite composition have found that $K_{D}^{\text{Bridg-fPer}}$ increases from approximately 0.5 at top-lower mantle conditions to 0.8-0.9, at about 800 km in depth due to the suggested coupled substitution of Al$^{3+}$ and Fe$^{3+}$ in Bridg, but then decreases to 0.4 or even lower due to the spin crossover of iron in fPer at mid-lower mantle conditions (Wood and Rubie 1996; Irifune et al. 2010; Vilella et al. 2015; Xu et al. 2016).
However, a high $P$-$T$ diamond anvil cell study, using a pyrolite composition, has shown that $K_{D}^{\text{Bridg-fPer}}$ increases to 0.9 at bottom-lower mantle conditions, suggested to be due to the spin transition of Fe$^{3+}$ in Bridg (Sinmyo and Hirose 2013). Recently, Fe-bearing bridgmanite has been reported to dissociate into Fe-rich phase, called H-Phase, and MgSiO$_3$-rich bridgmanite at deep lower mantle $P$-$T$ conditions (Zhang et al. 2014), which can challenge the aforementioned conventional view of the iron index in the lower-mantle mineral assemblage. However, this report remains to be verified experimentally and theoretically. Thus far, a consensus on the iron partition coefficient across the spin transition in the lower-mantle assemblage has not yet been reached, especially under natural compositional, oxygen fugacity, and $P$-$T$ environments.

**Results**

To date, a number of Bridg, fPer and other lower-mantle minerals have been identified as natural inclusions in diamonds, collected from Brazil, Canada, Guinea, Australia and some other countries, and subsequently analyzed (Kaminsky 2012 and references therein). The details of these finds and analytical procedures are presented elsewhere, including references to Tables 1 and 2 and Supplementary Table 1. Among them, are 19 Bridg $+$ fPer pairs, each of which coexist in the same diamond, sometimes in a close (‘touching’) association, i.e., formed under equilibrium conditions. This relationship permits studies of the distribution and partitioning of iron and other elements within the media where those minerals originated within the lower mantle (Supplementary Table 1). We should note that the Bridg samples in these assemblages may have retrograde transformation into enstatite under ambient conditions, but a number of
physical and chemical characteristics established in previous studies justified their deep lower mantle origin as Bridg (e.g., Harte et al. 1999; Kaminsky 2012).

Ferropericlase

Ferropericlase in the lower-mantle compositional model has been typically assumed to exhibit a composition with $f_{\text{e}} = 0.08-0.11$ and even more precisely, at c. 0.10 (Kesson and Fitz Gerald 1991). In the natural environment, however, $f_{\text{Per}}$ may be much more iron-rich, up to $f_{\text{e}} = 0.64$, and sometimes even up to 0.90; as such, this does not correspond to the pyrolitic composition of the formation media. Recently, Fe-rich magnesiowüstite has been observed to occur in melting of subducted slabs in the mantle at approximately 300-700 km in depth (Thompson et al. 2016), providing a mechanism for the formation of very Fe-rich $f_{\text{Per}}$ in the lower mantle. TEM studies with the use of EDX and EEL spectroscopy demonstrated that ferric iron in $f_{\text{Per}}$ grains is located in exsolved non-stoichiometric $\text{Fe}^{3+}$-enriched clusters ($\text{Mg}_{1+x}\text{Fe}^{3+}_{2-1-x}\text{O}_{4-x/2}$), varying in size from 1–2 nm to 10–15 nm and comprising ~3.6 vol.% of $f_{\text{Per}}$, while the remaining iron in $f_{\text{Per}}$ is in the ferrous, $\text{Fe}^{2+}$ state (Fig. 2A) (Kaminsky et al. 2015a). Recent work by Nestola et al. (2016) demonstrated a possibility for studying the internal structure of ferropericlase and distribution of ferric iron in it (including its exsolved phases) with the use of in situ synchrotron Mössbauer spectroscopy. As the host diamond ascended through the uppermost lower mantle, these iron-rich clusters experience falling pressure conditions which resulted in their release and formation of 10-50 nm-sized magnesioferrite $\text{MgFe}^{3+}_{2}\text{O}_{4}$ crystals, developing along dislocations in $f_{\text{Per}}$ with a precise orientation relationship between both phases: $(022)_{\text{mFer}} // (022)_{f_{\text{Per}}}$; $(11-1)_{\text{mFer}} // (11-1)_{f_{\text{Per}}}$ and the zone axis for both phases is [2 -11] (Fig. 2B) (Kaminsky et al. 2015b).
Bridgmanite

Bridgmanite is a member of the perovskite family with an orthorhombic distortion of the ideal cubic perovskite structure and a general formula, $\text{VIII}_{\text{A}}\text{VI}_{\text{B}}\text{II}_{\text{XII}}^{2+}\text{VI}^{4+}\text{O}^{2-}_3$ (where VI, VIII and XII are cation fold positions), in which A larger (mainly divalent) pseudo-dodecahedral (eight/twelve-fold) site cations mostly include Mg, Fe$^{2+}$, Mn, Ni, Ca and some other elements, and B smaller six-fold site cations are Si, Al and partly Fe$^{3+}$. The analyzed natural lower-mantle bridgmanite samples have cation compositions as presented in Table 1.

Most of the grains have compositions close to stoichiometric Bridg. Some deficit in both cation groups is likely caused by the presence of other, non-analyzed cations, such as P and REE, which are characteristic for this group of minerals. Judging by crystal-chemical calculations (Table 1), all iron substitutes for Mg$^{2+}$ in the A site and, most likely, is in the divalent form, Fe$^{2+}$, although McCammon et al. (1997), based on Mössbauer spectroscopy, suggested a significant portion of iron to be Fe$^{3+}$. There is no evidence for the presence of Fe$^{3+}$ in the B site in natural Bridg. The three most Al-rich specimens (##BZ210; BZ241 and BZ242, all from Brazil) show excess in alumina in the amounts of 0.069-0.185. These amounts balance the deficit in cation site A of these specimens, implying the location of this portion of Al to be in the eight/twelve-fold pseudo-octahedral coordination position.

Partition coefficient of iron in natural bridgmanite – ferropericlase assemblages

The analysis of the iron index $f_e$ in co-existing $f_{Per}$ and $f_{Bridg}$ grains and the partition
coefficient of iron $K_{D}^{\text{Bridg-fPer}}$ in all $\text{Bridg + fPer}$ assemblages shows that two groups of
assemblages can be distinguished (Table 2; Fig. 3A). The first group (Group A; 84 % of all
pairs) forms an elongated cloud illustrating a general positive correlation between $fe_{\text{Bridg}} = 0.032-0.138$ and $fe_{\text{fPer}} = 0.116-0.363$. The correlation trend is close to trend Ia from the experimental
data, confirming the regularity in Fe exchange between the two major lower-mantle minerals.
The second group (Group B; 16 % of all grains) is composed of three specimens with almost
constant $fe_{\text{fPer}} = 0.173-0.193$ and relatively high $fe_{\text{Bridg}}$, varying from 0.088 to 0.120; all
specimens are high-Al varieties. This group lies outside of any experimental trends. The increase
in $fe$ of both natural $f\text{Per}$ and $\text{Bridg}$ from Group A is independent of the $K_{D}^{\text{Bridg-fPer}}$ values (0.169-
0.479), while Group B, which has $fe$ values in the same range as Group A, has elevated values of
$K_{D}^{\text{Bridg-fPer}} = 0.433-0.657$ (Fig. 3B).

Such variations in the iron indices and the bulk iron contents in the co-existing, major
lower-mantle minerals differs drastically from what was expected for a pyrolytic lower mantle
with a homogeneous distribution of iron in $f\text{Per}$ and $\text{Bridg}$ (Kesson and Fitz Gerald 1991; Wood
2000; Lee et al. 2004). According to the experimental and theoretical data for a bulk pyrolytic
composition, where the total iron content in the system was fixed at $fe = 0.09-0.15$ (Irifune et al.
2010; Vilella et al. 2015; Xu et al. 2016), we should expect a decrease of the iron content in
$\text{Bridg}$ with an increase of the iron content in $f\text{Per}$. In reality, it is not the case, however, as both
$f\text{Per}$ and $\text{Bridg}$ demonstrate the simultaneous, well-correlated increase of $fe$ values (Figs. 3A-D).

Both groups of assemblages are characterized by similar concentrations of Ni in $f\text{Per}$,
mainly corresponding to the bulk Ni contents in the mantle (6,052-11,212 ppm from Group A
and 9,982-11,711 ppm from Group B) (Fig. 3C). However, one of the analyzed samples (#3-5
from Brazil) has a low concentration of Ni = 2437 ppm, and there are a number of low-Ni $f\text{Per}$
inclusions in diamond (Fig. 4A). Analysis of the Ni content in \( f\)Per as a function of the iron index shows that the \( f\)Per grains with \( fe \) of approximately 0.2 in deep-diamond inclusions (circled in Fig. 4B) have Ni contents close to the estimates of 8,000-12,000 ppm for the bulk pyrolytic composition; however, the Ni content drastically decreases with increasing iron index in \( f\)Per, especially for samples from Brazil (Fig. 3B). The samples with \( fe \) of more than 0.6 from Brazil have Ni contents less than 2000 ppm. So, the analyses of natural \( f\)Per grains show that the higher the iron index in the grain, the lower the Ni content.

There is a general (although not very strong) positive correlation between Ni and the partition coefficient of iron (Fig. 4A). The lowest \( K_{D}^{\text{Bridg-fPer}} \) values (0.169 in sample # BZ120 and 0.204 in sample # 3-5) are characterized by the lowest Ni concentrations in \( f\)Per, whereas the samples with the highest \( K_{D}^{\text{Bridg-fPer}} \) values (## BZ210, BZ241 and BZ242) are characterized with the highest Ni contents in \( f\)Per.

Discussion

Role of Ni and Al in the iron partition coefficient distribution

The Ni concentration in \( f\)Per indicates the presence of metallic iron phase(s) in the magmatic system of the deep mantle, as established by Frost et al. (2004). It was shown that the increasing weight fraction of metallic phase (suggesting the conditions present within the lowermost lower mantle) leads to a decrease of Ni concentration in the lower-mantle material and also to a decrease of the concentration of this element in coexisting \( f\)Per and \( Bridg \) (Ryabchikov and Kaminsky 2013). In this process, iron acts as a dilutant of Ni dissolved in
metal. According to experimental data (Frost et al. 2004; Frost and McCammon 2008), metal content in the lower mantle is estimated at 1 wt. % (10,000 ppm) before the release of metallic alloy. This implies that the $f_{\text{Per}}$ grains with high Ni concentrations were formed in media which did not contain metallic alloy (or its quantity was extremely small), suggesting these originated within the uppermost lower mantle, while the low Ni $f_{\text{Per}}$ grains were formed in the presence of metallic alloy within lower parts of the lower mantle. More than 40 % of the studied lower-mantle $f_{\text{Per}}$ grains are low-Ni and high-Fe inclusions. These variations in Fe and Ni concentrations in $f_{\text{Per}}$ point to a radial compositional gradient in the lower mantle at the time of the formation of these minerals, and the anti-correlation of Ni and Fe in $f_{\text{Per}}$ may be applied as a qualitative criterion of the depth of its origin.

The correlation between the $K_{D}^{\text{Bridg-$f_{\text{Per}}$}}$ values and Ni concentrations in $f_{\text{Per}}$ (Fig. 4A) is not strong because of the presence of other elements in minerals, such as Al, Co, Mn, Na, et al. The major factor here is the Al impurity in Bridg, which is the real cause for the existence of the two groups of associations (Fig. 3D). Al$_2$O$_3$ in Bridg comprises 0.69-3.10 wt% in Group A and 10.04-12.58 wt% in Group B. In general, $K_{D}^{\text{Bridg-$f_{\text{Per}}$}}$ correlates with the Al$_2$O$_3$ content in Bridg, which is particularly noticeable for the Brazilian samples (Fig. 5A). However, this correlation is quite weak (Fig. 5A,B) and requires further understanding.

The enrichment of Bridg with Al is strongly pressure dependent (Andrault et al. 2007). In the uppermost part of the lower mantle Al-rich phases, such as majorite and jeffbenite, still occur. In experiments at pressure conditions of 24-28 GPa these minerals dissociate, and the released Al is incorporated into Bridg (Irifune and Tsuchiya 2007). In the natural environment, the reverse scenario occurs: juvenile high-Al Bridg at 24-28 GPa releases Al with the formation
of Al-bearing phases, such as majorite and jeffbenite (formerly known as TAPP; Nestola et al. 2015).

As a result, the following scenario can be outlined for the lower mantle. Bridg has a high, up to 10-12 wt% concentration of Al$_2$O$_3$, which is consistent with its bulk concentration in the primitive mantle of 4-5 mol.% (e.g., McDonough and Sun 1995). Al occupies its position in both cation sites, A and B. In each case Al substitutes for Si and divalent cations with oxygen-vacancy formation as follows:

$$2^{\text{VIII/XII}} \text{Al}^{3+} + O^{2-} \rightarrow 2^{\text{VIII/XII}} (\text{Mg,Fe})^{2+} + V^0; \text{ and}$$

$$2^{\text{VI}} \text{Al}^{3+} + V^0 \rightarrow 2^{\text{VI}} \text{Si}^{4+} + O^{2-};$$

and in the case of Al positioning in both A and B sites, a charge-coupled mechanism, for which no oxygen vacancies are required for charge balance, takes place (Richmond and Brodholt 1998):

$$^{\text{VI}} \text{Al}^{3+} + ^{\text{VIII/XII}} \text{Al}^{3+} \rightarrow ^{\text{VI}} \text{Si}^{4+} + ^{\text{VIII/XII}} (\text{Mg,Fe})^{2+};$$

which, according to ab initio calculations, dominates at lower mantle pressures and temperatures (Akber-Knutson and Bukowinski 2004). The concentration of Al in Bridg, particularly in the A site may indicate the depth of the mineral’s origin, because previous studies have shown that Al concentration in Bridg increases with increasing pressure along a representative lower-mantle geotherm (Irifune et al., 2010). Recently an experimental study of the system MgSiO$_3$-Al$_2$O$_3$ under pressures up to 52 GPa and 2000 K, with the use of sintered diamond anvils combined with in situ synchrotron X-ray diffraction observations in a multi-anvil apparatus, demonstrated that the Al$_2$O$_3$ content in bridgmanite increases from 12 mol.% at 27 GPa to 29 mol.% at 52 GPa, suggesting that the Al$_2$O$_3$ content in bridgmanite can be used as a pressure indicator at pressures above 30 GPa (Liu et al., 2016).
As was shown above (Section 2, Table 1), iron in Bridg is in the A site, most likely in a ferrous divalent form. fPer with depth (and correspondingly increasing pressure) has a decreasing concentration of Ni and increasing fe values, reflecting the increase in the iron content in the lower mantle. The decrease of Ni content in fPer may, therefore, be used as another qualitative geobarometer in the lower mantle.

In contrast to experimental conditions, most of which were performed with a pyrolitic compositions (fe = 0.05-0.15), our results on natural samples show that iron indices in Bridg and fPer have positive correlation (Fig. 3), demonstrating the total enrichments of the lower-mantle media in iron. This enrichment is correlated with the Ni (negatively, Fig. 3C) and Al₂O₃ (positively, Fig. 3D) concentrations, each of which is an independent criterion of the increasing pressure. One may conclude that the Fe content of the lower mantle increases with depth and may differ from the pyrolitic composition. Iron in fPer is predominantly in a divalent form; the share of Fe³⁺ ions is Fe³⁺/ΣFe = 8-12 at% (Kaminsky et al. 2015a). Ferric iron in fPer grains is located in exsolved non-stoichiometric Fe³⁺-enriched nanometer-sized clusters Mg₁₊ₓFe₃₊₂₋ₓO₄ₓ/₂, while all remaining iron in fPer is in the ferrous, Fe²⁺, state.

The discussion above opens new scenarios regarding the actual composition of the main minerals of the lower mantle, and the situation may be even more complex if we include additional phases which are present in the natural systems. Our interpretation of the new data on Fe, Ni and Al distribution in Bridg and fPer explains the controversies in aforementioned high P-T experimental results of experiments, carried out in simplified closed systems.

Regional differences in the distribution of iron in ferropericlase and bridgmanite
There are observed differences in the iron index of fPer values and related characteristics from different regions. For example, fPer from Canada, South Australia and South Africa have \( f_e = 0.10-0.20 \) that are close to the pyrolite values. fPer from Guinea, along with similar \( f_e \) values, also has higher \( f_e \) values of 0.25. Moreover, iron-rich fPer from Brazil (reaching the composition of magnesiowüstite) comprises almost a half of all grains in this region (c. 46.5 %). It has been suggested that such differences represent different depths, at which the host diamonds sampled the lower mantle. In a pyrolytic lower mantle, the average amount of iron in the lower-mantle minerals is commonly believed to be close to 10 %, chiefly distributed between Bridg and fPer phases (Irifune et al. 2010). Here our analyses of the iron indices in these phases have shown that the total iron content in some of these minerals can be much higher than what is expected for a ‘normal’ lower mantle. As shown in Fig. 2, the occurrence of these ‘anomalous’, high-Fe fPer and high-Fe Bridg pairs with \( f_e = 0.17-0.36 \) and 0.07-0.14, respectively, indicates that the lower mantle is chemically inhomogeneous with respect to iron content at least in certain regions where these assemblages originated.

Recent high-resolution seismic tomography studies have revealed detailed seismic signatures of the lower mantle where strong seismic heterogeneities exist. Specifically, the Large Low Shear Velocity Provinces (LLSVPs) beneath the central Pacific and South Africa, extending from the core-mantle boundary up to approximately 1000 km above, exhibit reduced shear wave velocities and enhanced densities (e.g., Garnero and McNamara 2008). These regions are believed to contain dense, iron-rich piles that contribute to the ‘low shear velocity’ and high density signatures in seismic observations; the iron enrichment in the regions may be due to core-mantle interaction, residuals of the magma ocean, and/or recycling of primordial materials, relative to the surrounding lower mantle (Garnero and McNamara 2008). On the other hand, thin
patches of the Ultralow Velocity Zones (ULVZs), that are 5 to 40 km thick patches directly above the core-mantle boundary, exhibit reduced $P$- and $S$-wave velocities by up to 10% and 30%, respectively, and enhanced densities of up to 10% (Bower et al. 2011). These characteristics have been explained as a result of some partial melts and/or iron-enrichment in Bridg or silicate post-perovskite due to core-mantle reaction at the lowermost mantle (Garnero and McNamara 2008; Mao et al. 2010). We suggest that our analyzed $Bridg + fPer$ pairs, which contain abnormally high iron indices, as shown in the second group in Fig. 3B,C,D, may originate from these regions that likely contain much higher amounts of iron than “normal” lower mantle regions.

**Major differences in iron partitioning between natural samples and mineral physics results**

In considering a natural system, we should expect the following scenario for depth, which should take into account the iron partitioning induced by the spin and valence transitions of iron ions proposed experimentally and theoretically, as well as significant iron chemistry heterogeneities at relevant P-T conditions of the lower mantle.

In the last decade, the discovery of a high-spin to low-spin crossover of Fe in the lower-mantle $fPer$ and Bridg has been shown to influence their physical, chemical, rheological and transport properties that can produce significant geophysical and geochemical consequences for our understanding of the deep Earth (e.g., Badro et al. 2003; Cammarano et al. 2010; Lin et al. 2013; Wu and Wentzcovitch 2014; Yang et al. 2015). The spin crossover of Fe$^{2+}$ in $fPer$ has been theoretically predicted to occur and experimentally observed at $P-T$ conditions corresponding to the middle and the lower parts of the lower mantle (e.g., Lin et al. 2007; Tsuchiya et al. 2006); though, the spin transition of Fe$^{3+}$ in magnesioferrite and its associated effects remain unknown.
On the other hand, mineral physics studies of Bridg demonstrated that Bridg can contain a very significant amount of Fe$^{3+}$ in its lattice at the top lower mantle conditions, in which both Fe$^{2+}$ and Fe$^{3+}$ in the pseudo-dodecahedral site (A site) of the orthorhombic structure likely remain in the high-spin state at lower-mantle pressures, while a high-spin to low-spin transition of Fe$^{3+}$ in the octahedral site (B site) occurs at pressures of 15-50 GPa (e.g., Hsu et al. 2012; Lin et al. 2013). Recent theoretical calculations considering a wide range of oxygen fugacity conditions and different iron spin and valence states, in the lower-mantle pyrolite assemblage, have further indicated that the Fe$^{3+}$ content in Bridg decreases with increasing depth in the lower mantle; at lowermost lower mantle conditions, Fe$^{3+}$ content in Bridg becomes almost negligible (Xu et al. 2016). Analyses of the natural Bridg and fPer assemblages show that most of the iron residing in the A site of Bridg lattice is in the Fe$^{2+}$ state, which confirms these mineral physics studies.

High P-T experiments have further shown that the partition coefficient $K_{D}^{\text{Bridg-fPer}}$ is observed to increase from approximately 0.5 at 23 GPa up to 0.85 at about 28 GPa (~800 km in depth) and that can be associated with the Al$^{3+}$-Fe$^{3+}$ coupled substitution in Bridg in a pyrolytic composition, where iron ions partition almost equally between the fPer and Bridg lattices (Irifune et al. 2010). Results from such high P-T experiments showed that the $K_{D}^{\text{Bridg-fPer}}$ value stays almost constant at ~ 0.85 at pressures of between 28 and 40 GPa (~800-1000 km in depth) and then notably decreases to 0.4-0.5 with increasing pressures at 40-50 GPa (1000-1200 km in depth) (Irifune et al. 2010). This dramatic decrease is most likely associated with the spin transition of Fe$^{2+}$ in fPer, which results in a volume collapse of about 2% (e.g., Lin et al. 2013) promoting iron ions in Bridg to favorably partition into the low-spin fPer which is energetically more stable than the high-spin Bridg and fPer. Without the alumina substitution in Bridg at such conditions, the $K_{D}^{\text{Bridg-fPer}}$ values decrease to approximately 0.2 (e.g., Sakai et al. 2009), i.e.,
lower than the value suggested from high $P$-$T$ experiments using a pyrolytic composition (Irifune et al. 2010). That is, in an alumina poor environment in the lower mantle, such as the olivine-rich peridotite environment, the $K_D^{Bridg-fPer}$ value is expected to remain low at approximately 0.2 with or without the spin transition effect. If the lower mantle is chemically pyrolytic, these changes in the iron partitioning indicate that the deeper parts of the lower mantle, especially toward the lowermost parts would likely contain iron-enriched, low-spin $fPer$ and iron-poor, alumina-rich $Bridg$, whereas in the upper parts of the lower mantle, especially at approximately 800 km in depth, iron would almost equally partition between $Bridg$ and $fPer$ (Irifune et al. 2010).

Comparison of these experimental results with our analyses on natural samples, however, clearly shows contradictory $K_D^{Bridg-fPer}$ values; the natural samples show very diverse $K_D^{Bridg-fPer}$ values that cannot be simply explained by the alumina dissolution in $Bridg$ and the spin transition of Fe$^{2+}$ in $fPer$. These major differences in the iron indices and $K_D^{Bridg-fPer}$ values demonstrate the complex, inhomogeneous iron speciation and chemistry in the lower mantle that are well beyond the knowledge of current mineral physics studies.

**Conclusions**

We conclude, based upon determined iron contents in coexisting natural $fPer$ and $Bridg$ and on the distribution of the partition coefficient of iron in natural $Bridg + fPer$ assemblages that some areas in the deep lower mantle are iron-rich and differ markedly from a pyrolytic composition, implying that the bulk composition of the Earth is non-chondritic.

The juvenile iron partitioning in the $Bridg + fPer$ association ($K_D^{Bridg-fPer}$) is as low as 0.1-0.2. During the crystallization of diamonds at relatively shallower depth of the lower mantle, in
which $K_D^{\text{Brd-fPer}}$ increases to 0.4-0.5 and even as high as 0.7, they sample and deliver to the surface such associations. This regularity, established on geological samples, was supported by recently published theoretical calculations by Muir and Brodholt (2016), showing a decrease of $K_D^{\text{Brd-fPer}}$ with depth from 0.32 to 0.06.

The details of the element partitioning between natural Bridg and fPer, in the lower mantle (at least in some areas), are as follows:

- According to crystal-chemical calculations, iron in Bridg is ferrous, Fe$^{2+}$, in the A site, substituting for Mg$^{2+}$;
- Almost all iron in fPer is ferrous Fe$^{2+}$; the share of ferric, Fe$^{3+}$, iron in fPer is Fe$^{3+}/\Sigma$Fe = 8-12 at%; Fe$^{3+}$ is concentrated in exsolved clusters of Mg$_{1+x}$Fe$_{3+}$O$_{4-x/2}$, while all remaining iron in fPer is in the ferrous, Fe$^{2+}$, state;
- Iron contents in both Bridg and fPer increase with depth (pressure), reflecting the increasing Fe content in the lower part of the lower mantle;
- Al content in Bridg from the lower part of the lower mantle is at ~10-12 wt% Al$_2$O$_3$ (Table 2);
- Al in Bridg occurs mainly in the cation B site and partly in the cation A site, in both cases substituting for Si, Mg and Fe with vacancy formation; and in the case of Al positioning in both, B and A sites, a charge-balanced reaction.

These observations in natural samples cannot be simply explained by the dissolution of Al in Bridg and the spin transition of Fe$^{2+}$ in fPer. The differences between observations in natural samples and experimental results should be taken into account in future calculations and experimental works.
Acknowledgements

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10.1103/PhysRevLett.96.198501


Tables

Table 1. Cation fractions of natural lower-mantle bridgmanite (in atomic numbers). $A_{\text{total}}$ and $B_{\text{total}}$ represent the total cation fraction in the A and B site, respectively.


Table 2. Compositions of coexisting bridgmanite and ferropericlase included in lower-mantle diamonds.

Note: * Bridg: bridgmanite; fPer: ferropericlase; Di?: suggested diopside; CaSiPrv: CaSi-perovskite; ‘Ol’: phase with an olivine composition; SiMg: unidentified Si-Mg phase; Ni: native Ni; Ga: garnet.

** Reference numbers are the same as in Table 1.

Captions to figures

Figure 1. Summary of literature experimental results of iron partitioning between bridgmanite and ferropericlase at high pressures and temperatures. A – $fe_{\text{Bridg}}$ vs. $fe_{\text{fPer}}$ in all experiments performed to date. I and II – general trends. B – partition coefficient $fe_{\text{fPer}}$ under different pressure values.
Figure 2. Exsolution of Fe\textsuperscript{3+}-rich phases in ferropericlase. A - Mg\textsubscript{1.30}Fe\textsubscript{1.80}O\textsubscript{4} truncated octahedra (bright) in a ferropericlase dark matrix; high-angle annular dark field scanning transmission electron-microscopy image by A. Abakumov (Kaminsky et al. 2015a). B – Magnesioferrite, MgFe\textsubscript{3+}\textsubscript{2}O\textsubscript{4}, octahedral and cubic grains, developed along dislocations in ferropericlase. Dark field TEM image by R. Wirth (Kaminsky et al. 2015b).

Figure 3. Iron indices $fe = \text{Fe}/(\text{Fe}+\text{Mg})_{at}$ in coexisting natural ferropericlase and bridgmanite in lower-mantle diamond inclusions. A – General plot. B – With $K_D^{\text{Bridg-fPer}}$ values, shown as circles, the radii of which are proportional to the $K_D^{\text{Bridg-fPer}}$ values. C – With Ni concentrations in ferropericlase, shown as circles, the radii of which are proportional to the Ni concentrations. D – With Al\textsubscript{2}O\textsubscript{3} concentrations in bridgmanite, shown as circles, the radii of which are proportional to the Al\textsubscript{2}O\textsubscript{3} concentrations. Four groups of samples from Brazil, Canada, Guinea, and Australia with the $fPer$ and $Bridg$ grains that associate with each other are used.

Figure 4. Variations of Ni concentrations in natural ferropericlase. A - $K_D^{\text{Bridg-fPer}}$ vs. Ni content in ferropericlase. B - Ni content vs. iron index in all analyzed to date ferropericlase grains entrapped by lower-mantle diamonds. Data from Kaminsky et al. (2012) and references therein.

Figure 5. Iron partitioning coefficient $K_D^{\text{Bridg-fPer}}$ vs. Al\textsubscript{2}O\textsubscript{3} content in bridgmanite. A – General plot. B – With Ni concentrations in ferropericlase from Brazil, Canada, Guinea and Australia, shown as circles, the radii of which are proportional to the Ni contents.
Supporting information

Table S1. Chemical compositions of coexisting natural bridgmanite and ferropericlase grains included in diamond.
Figure 1B

**P, GPa**

- Sinmyo & Hirose 2013
- Irifune et al. 2010
- Tange et al., 2009
- Sakai et al. 2009
- Auzende et al. 2008
- Murakami et al. 2005
- Kobayashi et al. 2005
- Wood 2000
- Kesson et al. 1998
- Katsura & Ito. 1996
- Irifune 1994
Figure 2A

Ferropericlase

$\text{Mg}_{1.30}\text{Fe}^{3+}_{1.80}\text{O}_4$
Figure 2B

50 nm

Magnesioferrite

Ferropericlas
Figure 3A
Figure 3B

\( K_D^{\text{Bridg-fPer}} \text{ value} \)

Group B

Group A

\( f_{fe}^{\text{Bridg}} \)

\( f_{fe}^{\text{fPer}} \)
Figure 3C
Figure 4A
Figure 4B

Ni, ppm

fe = Fe/(Fe+Mg)$_{at}$
Figure 5A
Figure 5B
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Note: * Bridg: bridgmanite; fPer: ferropericlase; Dio?: suggested diopside; CaSiPrv: CaSi-perovskite; 'Ol': phase with an olivine composition; SiMg: unidentified Si-Mg phase; Ni: native Ni; Ga: garnet.

** Reference numbers are the same as in Table 1.