



Stability of calcium and magnesium carbonates at Earth's lower mantle thermodynamic conditions



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ABSTRACT

We present a theoretical investigation, based on ab initio calculations and the quasi-harmonic approximation, on the stability properties of magnesium (MgCO_3) and calcium (CaCO_3) carbonates at high temperatures and pressures. The results indicate that those carbonates should be stable in the Earth's lower mantle, instead of dissociating into other minerals, in chemical environments with excess of SiO_2 , MgO , or MgSiO_3 . Therefore, considering the lower mantle chemical composition, consisting mostly of the MgSiO_3 and MgO minerals, calcium and magnesium carbonates are the primary candidates as carbon hosts in that region. For the thermodynamic conditions of the mantle, the results also indicate that carbon should be primarily hosted on MgCO_3 , contrasting with what was found by other theoretical studies, which neglected temperature effects. Finally, the results indicate that carbon, in the form of free CO_2 , is unlikely in the lower mantle.

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1. Introduction

Carbon is a unique chemical element, mainly due to its rich bonding nature, which provides a wide range of stable and metastable structures in several hybridizations and configurations. Particularly, the role of carbon on Earth's natural phenomena has been extensively studied over the last few decades. The carbon cycle affects the atmosphere, oceans, and other shallow crustal phenomena, directly influencing climate, ecosystems, and, consequently, life on Earth. Although there is considerable accumulated knowledge on the carbon cycle near the Earth's surface, there is still scarce information on the processes associated with its deep layers (Hazen and Schiffries, 2013).

In order to build consistent models on the Earth's carbon cycle, it is important to establish a proper understanding of its chemical composition. The knowledge on the solar system composition, based on information from carbonaceous chondritic meteorites that have hit the Earth, allows estimating the expected amount of carbon that should be present on Earth (Marty et al., 2013). However, the quantity of carbon currently known on its shallow layers is about two orders of magnitude smaller than the expected value, suggesting that this missing carbon should be stored on its deep

layers, the so-called deep carbon reservoirs (Hazen and Schiffries, 2013). Estimates indicate that the Earth's deep interior may contain as much as 90% of all available carbon. Such conclusions have been supported by indirect evidence, such as the presence of CO_2 in magmas (Marty et al., 2013) and the mineral inclusions within natural deep diamonds (Walter et al., 2011; Pearson et al., 2014; Maeda et al., 2017).

There are several questions on the properties of deep carbon that remain open, such as determining the amount and distribution of those carbon reservoirs within major mantle minerals and understanding the complete carbon cycle, associated with an exchange of carbon between the Earth's surface and its deep interior. For example, current estimates suggest that the carbon flux into the Earth's mantle through subduction substantially exceeds the carbon flux emitted by volcanoes, opening the question on the minerals that host carbon in the mantle.

Those issues could only be addressed with a deep understanding of the behavior of carbon-related minerals under high pressures and temperatures, at the thermodynamic conditions of the mantle (Oganov et al., 2013). Although some carbon may be stored in the core, the mantle is thought to be its largest reservoir. It is reasonable to assume that a certain amount of carbon could be dissolved in silicates, such as MgSiO_3 , which is by far the most abundant mineral in the lower mantle. Therefore, even if carbon had a low to moderate solubility in this mineral, it could still be the largest carbon reservoir in that region. However, it has been experimentally shown that the carbon solubility in silicates is below

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30–200 ppb by weight (Shcheka et al., 2006), indicating that most of the Earth's carbon must be stored in other minerals. Furthermore, silicates are large diffuse reservoirs, which contrasts with the concentrated phases of the deep carbon identified as magma carbonates (Jones et al., 2013) and diamonds (Shirey et al., 2013), as well as carbon species emitted by volcanoes (Burton et al., 2013).

In the lower mantle, most of the carbon is in a reduced state, such as in form of diamond. However, the oxidized state, such as in carbonates, is possible in subducted slabs. To further explore the potential carriers of carbon, it is important to explore the physical properties of those minerals at lower mantle thermodynamic conditions, specially in terms of carbon-related stable phases. Several theoretical (Marcondes et al., 2016; Oganov et al., 2008; Pickard and Needs, 2015) and experimental (Fiquet et al., 2002; Isshiki et al., 2004) investigations have explored the high-pressure stability of major carbonates, such as MgCO_3 , CaCO_3 , and $\text{MgCa}(\text{CO}_3)_2$. However, there is still scarce information on those properties at high temperatures (Gavryushkin et al., 2017; Smith et al., 2018). Particularly for the lower mantle, such conditions would mean pressures up to 136 GPa and temperatures up to 3000 K.

This investigation explores the stability of carbonates, specially MgCO_3 and CaCO_3 , at lower mantle conditions. Here, we do not explore the $\text{MgCa}(\text{CO}_3)_2$ mineral, since it is well established that it dissociates into MgCO_3 and CaCO_3 for pressures greater than a few GPa (Shirasaka et al., 2002). The results are obtained by first-principles total energy calculations, combined with the quasi-harmonic approximation, in order to obtain the respective Gibbs free energies of the minerals in different crystalline phases, at high temperatures and pressures. We explore the stability of those carbonates, taking into account a number of crystalline phases that have been identified by recent theoretical and experimental investigations. Our results indicate that at high temperatures and high pressures MgCO_3 and CaCO_3 should be stable against dissociation into other minerals at several mantle conditions. Considering the chemical composition of the lower mantle, with major concentrations of MgSiO_3 and MgO , calcium and magnesium carbonates should be the primary candidates as carbon hosts in the lower mantle. However, at the thermodynamic conditions of the mantle, along its geotherm, magnesium carbonate is by far much more likely than calcium carbonate to host carbon. Additionally, the results suggest that carbon in the form of isolated CO_2 is unlikely in the lower mantle.

2. Methods

2.1. Ab initio calculations

The first principles calculations are performed using the Quantum ESPRESSO computational package (Giannozzi et al., 2009). The electronic interactions are described within the density functional theory, considering the exchange-correlation (XC) functional based on the local density approximation (LDA) (Kohn and Sham, 1965). This functional has been widely used to obtain both static and dynamic properties of the Earth's mantle minerals, although many authors have investigated those properties with the generalized gradient approximation (GGA-PBE) (Perdew et al., 1996). It is well established in the literature that static calculations with the LDA underestimate the mineral lattice parameters (generally by about 1 to 2%) and the phase transition pressures, and overestimate the respective elastic constants when compared to experimental values at finite temperatures, while calculations with the GGA-PBE provide the opposite effects (Marcondes et al., 2018). This investigation uses only the LDA functional as justified in detail in the next section.

The electronic wave functions are expanded using the projected augmented wave (PAW) method (Blochl, 1994), with a plane-wave

cutoff of 1200 eV. The valence electronic configurations are described with $3s^2 3p^6 4s^2 3d^0 4p^0$ for calcium, $2s^2 2p^2$ for carbon, $2s^2 2p^6 3s^2 3p^0$ for magnesium, $3s^2 3p^2$ for silicon, and $2s^2 2p^4$ for oxygen (Holzwarth et al., 2001).

The Brillouin zones for computing the electronic properties are sampled by a $4 \times 4 \times 4$ k-mesh for the carbonates and silicates, a $8 \times 8 \times 8$ k-mesh for the alkaline earth oxides (MgO and CaO), and a $6 \times 6 \times 6$ k-mesh for SiO_2 and CO_2 , in order to provide an approximately equivalent density of k-points for all materials.

Strict convergence criteria are taken into account for the simulations, with the atomic positions being considered converged when all forces acting on atoms are smaller than $0.01 \text{ eV \AA}^{-1}$. For each pressure, from 0 to 150 GPa, the structures are optimized by using the damped variable cell shape molecular dynamics method (Wentzcovitch et al., 1993). Then, a third-order Birch–Murnaghan equation of state is used to fit the compression data.

2.2. Thermodynamic properties

The thermodynamic properties are investigated by computing the vibrational modes (phonons) of the crystals using the Density Functional Perturbation Theory (Baroni et al., 2001), with a $12 \times 12 \times 12$ q-mesh to calculate the vibrational density of states (VDOS) (Wang et al., 2010), and the quasi-harmonic approximation (QHA) (Wentzcovitch et al., 2010) to compute the respective Gibbs free energies.

The results for finite temperatures are reported within the validity range of the QHA (Wentzcovitch et al., 2010). It is well established in the literature that the QHA results for the thermal expansion, $\alpha(P, T)$, start diverging beyond a certain temperature, in contrast to available experimental results. Such divergence, in this methodology, is caused by disregarding anharmonic effects (Wentzcovitch et al., 2010, 2004). Moreover, this quantity is also clearly quite sensitive to the choice of the XC functional (Marcondes et al., 2018), and could still be used at high temperatures, providing results consistent with experimental data in the region in which the thermal expansion coefficient does not diverge. Therefore, at high temperatures, the validity region of the QHA has been established (Wentzcovitch et al., 2010; Carrier et al., 2007) as $[\partial^2 \alpha(P, T) / \partial T^2]_P \leq 0$.

Fig. 1 shows the thermal expansion coefficient at several pressures for CaCO_3 in aragonite and post-aragonite phases, which represents a stringent test for this methodology, showing the respective validity regions of the QHA for those phases, indicating that, at very high pressures, the QHA is still valid at temperatures up to 3000 K. It can be observed that, within the validity limit of the QHA, the thermal expansion coefficient is in good agreement with available experimental data (Litasov et al., 2017). Additionally, Fig. 1(a) displays the thermal expansivity for aragonite obtained with the GGA-PBE functional, showing that the LDA results describe it well up to 800 K for null pressure, while the GGA-PBE results diverge much faster, decreasing the validity range of the QHA. These results provide an additional justification for using the LDA functional in this investigation.

We explore the validity of the QHA at the lowest pressure phases for all minerals considered in this investigation. The region of low pressures and high temperatures represents a stringent test for the QHA methodology since it is when the thermal expansion coefficients present major divergences when compared to experimental data. The QHA provides appropriate thermal expansion coefficients at the thermodynamic conditions of interest in this investigation.

Our results on thermal properties of all minerals investigated here are within the validity region of the QHA and in good agreement with available theoretical and experimental data

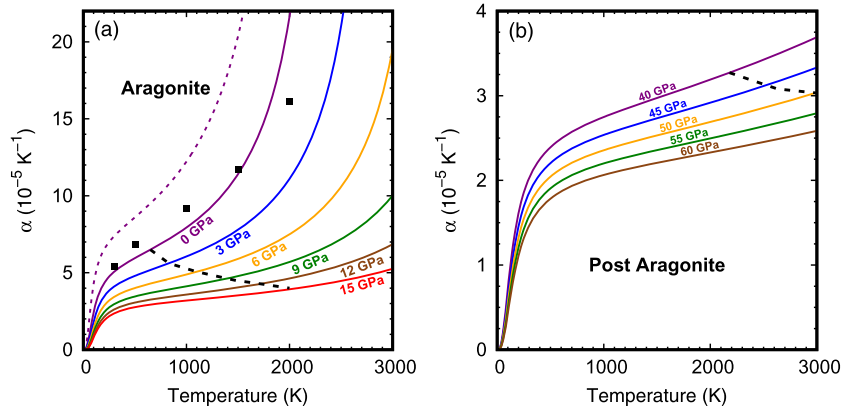


Fig. 1. Thermal expansion coefficient at several pressures as a function of temperature for CaCO_3 in (a) aragonite and (b) post-aragonite phases. The dashed lilac line on frame (a) represents the results obtained with the GGA-PBE functional at 0 GPa. The QHA boundary is defined by the position of the inflection points of $\alpha(P,T)$ (dashed black line), discussed in section 2.2. Experimental results at 0 GPa are presented with black symbols (Litasov et al., 2017). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

(Litasov et al., 2017; Wentzcovitch et al., 2010; Dorogokupets, 2007; Li et al., 2006; Karki et al., 2000).

2.3. Crystalline phases

In order to explore the stability of carbon-related minerals, at the thermodynamic conditions of the lower mantle, we initially study several crystalline phases of CaCO_3 and MgCO_3 carbonates and CaSiO_3 and MgSiO_3 silicates in a wide pressure range, by computing their respective enthalpies and Gibbs free energies.

For any mineral at a certain temperature and pressure, the respective stable phase is determined as the one with the lowest Gibbs free energy value, using the theoretical model described in the previous section. Additionally, a mineral follows a phase transition at a certain pressure when the free energy of the stable phase becomes greater than the one of a different phase. Our results on stability and phase transition pressures of several carbonate and silicate minerals are in good agreement with results from other theoretical and experimental investigations (Shim et al., 2002; Oganov et al., 2008; Pickard and Needs, 2015; Lobanov et al., 2017; Tsuchiya et al., 2004; Murakami et al., 2004; Fiquet et al., 2002; Isshiki et al., 2004).

We consider several crystalline phases for CaCO_3 , MgCO_3 , MgSiO_3 , CaSiO_3 , MgO , CaO , SiO_2 , and CO_2 . First of all, MgO is considered only in the rock salt ($\text{Fm}\bar{3}\text{m}$) phase, since it has been shown that it remains in that phase up to 227 GPa (Duffy et al., 1995). CO_2 is considered only in the β -cristobalite ($\text{I}\bar{4}2\text{d}$) phase (Datchi et al., 2012). We perform static calculations for several other CO_2 phases and we obtain that the above-mentioned phase is the most stable for pressures above 10 GPa, which is fully consistent with results of another investigation that found this phase for pressures from 19 to 150 GPa (Oganov et al., 2008). Additionally, ignoring those other low-pressure stable phases does not compromise our conclusions on the properties of Earth's lower mantle.

For CaSiO_3 , we consider only the perovskite tetragonal ($\text{I}/4\text{mmn}$) phase for all the pressures and temperatures studied here (Shim et al., 2002), since it is the most important phase in the thermodynamic conditions of interest. Moreover, within such conditions, our methodology provides results that comply with the validity criteria described in section 2.2, i.e. the thermal expansion coefficient of this phase does not diverge up to 3000 K.

Fig. 2 shows the stable crystalline phases for all other minerals considered in this investigation, as function of pressure at temperatures of 300 K and 2000 K, in which there are available experimental data for comparison. For CaCO_3 at 300 K between

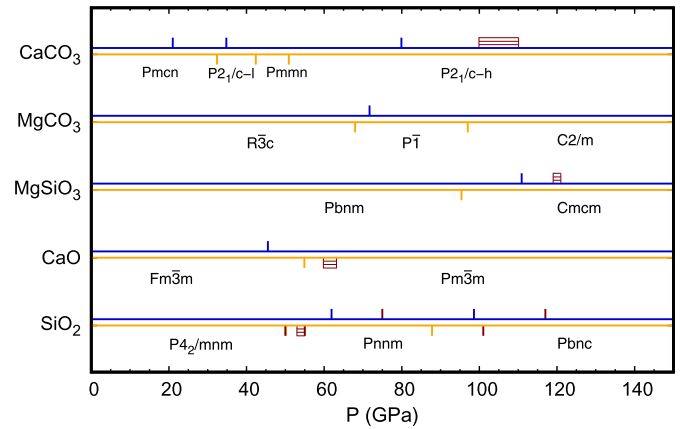


Fig. 2. Stable crystalline phases, as function of pressure, of CaCO_3 , MgCO_3 , MgSiO_3 , CaO , and SiO_2 materials considered in this investigation, computed with theoretical approximations presented in section 2.1. The figure presents results for two temperatures: 300 K (orange line) and 2000 K (blue line), with the respective transitions represented by vertical lines. Experimental values for phase transitions, with respective experimental error bars, are presented with brown symbols for: CaCO_3 (Lobanov et al., 2017), MgSiO_3 (Murakami et al., 2004), CaO (Yamanaka et al., 2002), and SiO_2 (Hemley et al., 2000; Andrault et al., 1998; Ono et al., 2002; Murakami et al., 2003).

0 and 150 GPa, the material goes from aragonite (Pmcn) to a monoclinic-low pressure phase ($\text{P}_{21}/\text{c-l}$) at 32 GPa, from $\text{P}_{21}/\text{c-l}$ to post-aragonite (Pmmn) at 42 GPa, and from post-aragonite to a monoclinic-high pressure phase ($\text{P}_{21}/\text{c-h}$) at 51 GPa, results that are consistent with another theoretical investigation (Pickard and Needs, 2015). Fig. 2 also shows that, as the temperature increases, there is a major change in the transition pressures. At a high temperature, 2000 K, the post-aragonite to monoclinic-high phase transition occurs at about 80 GPa, in agreement with the theoretical and experimental values of 76 GPa (Pickard and Needs, 2015) and 105 ± 5 GPa (Lobanov et al., 2017), respectively. We observe that when the temperature is increased from 300 K to 2000 K, the value of the phase transition pressure increases by about 30 GPa, showing the relevance of thermal effects when comparing theoretical and experimental results.

For MgCO_3 at 300 K, the material goes from magnesite ($\text{R}\bar{3}\text{c}$) to $\text{P}\bar{1}$ phase at 68 GPa, and from $\text{P}\bar{1}$ phase to magnesite-II ($\text{C2}/\text{m}$) at 97 GPa. All these results are in good agreement with other theoretical investigations using static calculations (Pickard and Needs, 2015). We also find that at temperatures over 1850 K, this mineral follows a direct phase transition from magnesite to magnesite-II, i.e. above that temperature the $\text{P}\bar{1}$ phase is not stable at any pres-

sure. Therefore, our results indicate that this phase should be of low geophysical interest for studies of the lower mantle properties.

For MgSiO_3 at 300 K, the mineral goes from perovskite (Pbnm) to post-perovskite (Cmcm) at 95 GPa, which is consistent with another theoretical investigation (Tsuchiya et al., 2004). At 2000 K, this transition occurs at 111 GPa, in good agreement with the experimental value of 120 ± 3 GPa (Murakami et al., 2004).

For CaO at 300 K, the material goes from rock salt ($\text{Fm}\bar{3}\text{m}$) to CsCl-type phase ($\text{Pm}\bar{3}\text{m}$). The transition between these two phases is found at 55 GPa, in good agreement with experimental data that identified this transition between 59.8 and 63.2 GPa (Yamanaka et al., 2002).

For SiO_2 at 300 K (2000 K), the material goes from stishovite ($\text{P4}_2/\text{mmn}$) to CaCl_2 -type phase (Pnnm) at 51 GPa (62 GPa), and from CaCl_2 -type phase to columbite-type phase (Pbnc) at 88 GPa (99 GPa). These transition values are in good agreement with experimental data at 300 K (Hemley et al., 2000; Andrault et al., 1998) and 2000 K (Ono et al., 2002; Murakami et al., 2003), as shown in Fig. 2.

3. Results

3.1. Decomposition of carbonates at high pressures and temperatures

Most of the Earth's oxidized carbon is expected to be harbored by Mg and/or Ca carbonate forms under mantle pressures and temperatures. In order to identify the potential carbon hosts in this region, we initially explore the energetics associated with the following decomposition reactions:



Fig. 3 shows the relative Gibbs free energy per unit formula (u.f.) as a function of pressure and temperature. It shows that the direct decompositions of CaCO_3 and MgCO_3 into their respective alkaline earth oxides plus CO_2 are unfavorable all over the lower mantle. CaCO_3 and MgCO_3 show similar trends with pressure, i.e., increasing the pressure reduces the Gibbs free energy difference for decomposition, which is positive for all the pressures of interest of the lower mantle. However, the energy cost for the decomposition of CaCO_3 is much greater than the one for MgCO_3 .

It should be stressed that our static results, dashed black line in Fig. 3, are in very good agreement with recent static results (Oganov et al., 2008; Pickard and Needs, 2015), as well as with experimental data (Fiquet et al., 2002). Those researchers have suggested that free CO_2 does not occur as an independent phase within the Earth's mantle. According to the results presented in Figs. 3(a) and (b), temperature effects do not alter the relative stability of carbonates, when compared to their most elementary constituents. Therefore, a temperature increase further reduces the possibility of free CO_2 to exist in that region.

3.2. Stability of carbonates under excess of SiO_2

We now evaluate the stability of carbonates in a condition of excess of SiO_2 , as represented by reactions (R3) and (R4). This condition is particularly important when one takes into account that there is material mixing in the upper and lower mantle, resulting from the basaltic part of subducting slabs, which is rich in SiO_2 (Oganov et al., 2008).

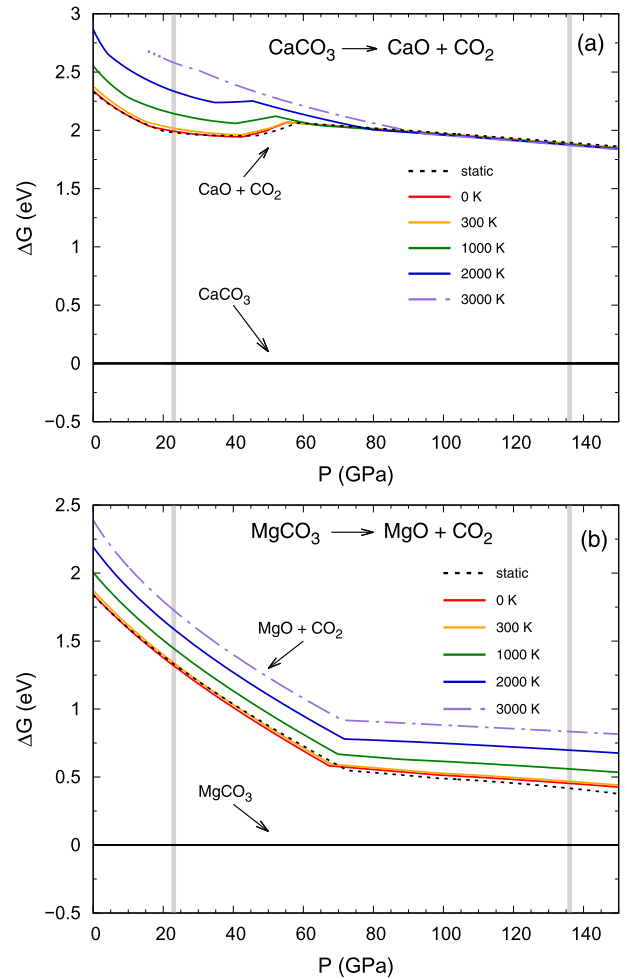
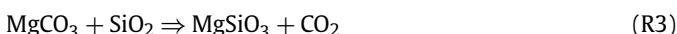


Fig. 3. The relative Gibbs free energies per u.f. as function of pressure, at several temperatures, for (a) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ and (b) $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ reactions. The dashed black line represent the respective relative enthalpies. The vertical gray lines indicate the pressures at the top (23 GPa) and bottom (136 GPa) of the lower mantle. The kinks in the curves arise from phase transitions that occur in the minerals described in section 2.3 and shown in Fig. 2, which are used to explore the dissociation reactions.

Fig. 4 shows the relative Gibbs free energies for Mg and Ca carbonates to transform into their respective silicates. The results indicate that reactions (R3) and (R4) are mostly unfavorable, carbonates do not react to form silicates within those thermodynamic conditions. Therefore, there should be no CO_2 formation in the lower mantle as a result of those reactions. Static results in Fig. 4(a) indicate that reaction (R3) is unfavorable up to 127 GPa, i.e. $\text{MgCO}_3 + \text{SiO}_2$ is more stable than $\text{MgSiO}_3 + \text{CO}_2$. This pressure is lower than the one in the lower mantle-core boundary of 136 GPa, such that static results suggested that reaction (R3) would be favorable at the bottom of the lower mantle, which could lead to the generation of free CO_2 . The figure shows that reaction (R3) becomes less favorable with increasing temperature, such that this reaction seems unfavorable at typical temperatures of the lower mantle bottom, indicating that free CO_2 is unlikely in this region.

Our static results for reaction (R3), dashed black line in Fig. 4(a), are in good agreement with static results presented in recent theoretical investigations. However, the transition pressure found here (127 GPa) is smaller than the one found by those authors at 135 GPa (Oganov et al., 2008) and 137 GPa (Pickard and Needs, 2015). Such differences could be explained by the functionals used to describe electron–electron interactions, since our investigation uses the LDA, while those investigations use the GGA-PBE. The

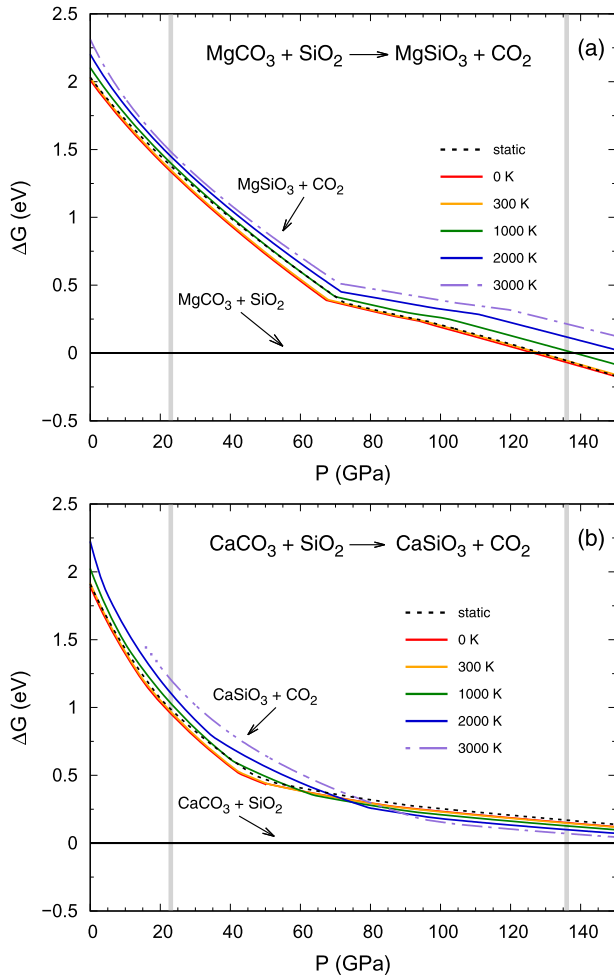


Fig. 4. The relative Gibbs free energy per u.f. as function of pressure, at several temperatures, for (a) $\text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_2$ and (b) $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$ reactions. The dashed black line represent the relative enthalpies for the reactions. The vertical gray lines indicate the pressures at the top and bottom of the lower mantle.

choice of LDA over GGA-PBE in this investigation is discussed in detail in section 2.1.

According to Fig. 4(b), the reaction (R4) is energetically unfavorable, i.e., $\text{CaCO}_3 + \text{SiO}_2$ is more stable than $\text{CaSiO}_3 + \text{CO}_2$ up to 150 GPa at any temperature. Therefore, in a situation where all these compounds are available, CaCO_3 formation is more likely than CaSiO_3 . Since this pressure is greater than the ones at the bottom of the lower mantle, this reaction would not occur in that region. Our static results are in good agreement with those of another investigation (Pickard and Needs, 2015).

It should be pointed out that our investigation carries some uncertainties on the transition pressures of SiO_2 , as shown in Fig. 2, which could play some role on the final conclusions about the reactions (R3) and (R4), specially on the properties near the core-mantle boundary.

3.3. Stability of carbonates under excess of MgO or MgSiO_3

It is reasonably well established that MgO and MgSiO_3 are the two major minerals in the lower mantle. Therefore, it is important to study the stability of MgCO_3 or CaCO_3 in a rich environment with those two minerals. To explore these conditions, we evaluate the energetics associated with reactions (R5) and (R6).

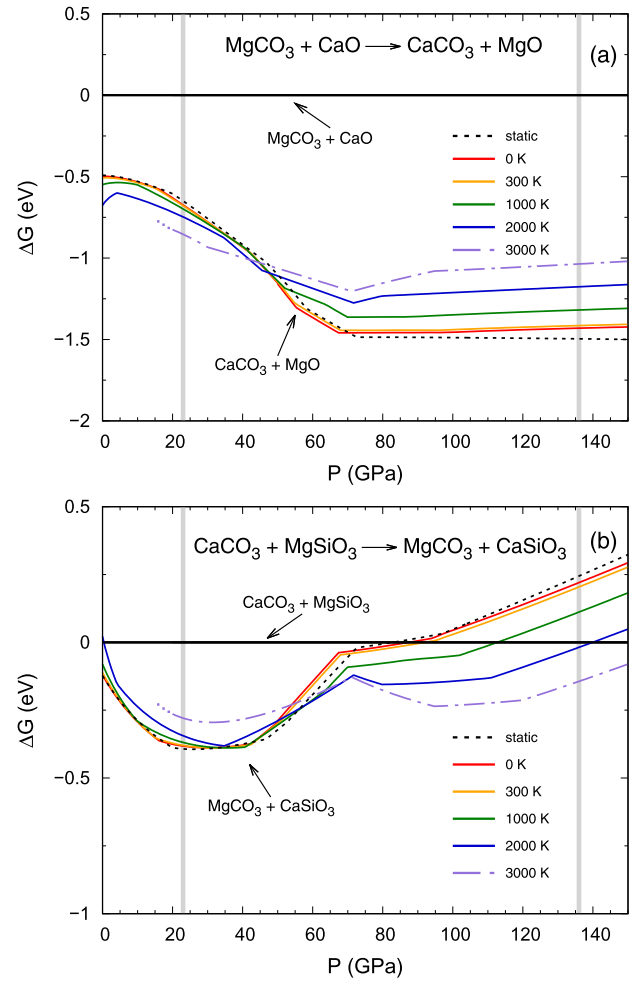


Fig. 5. The relative Gibbs free energy per u.f. as function of pressure, at several temperatures, for (a) $\text{MgCO}_3 + \text{CaO} \rightarrow \text{CaCO}_3 + \text{MgO}$ and (b) $\text{CaCO}_3 + \text{MgSiO}_3 \rightarrow \text{MgCO}_3 + \text{CaSiO}_3$ reactions. The dashed black line represent the relative enthalpies in (a) and (b). The vertical gray lines indicate the pressures at the top and bottom of the lower mantle.

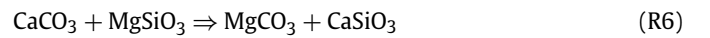


Fig. 5(a) shows that the reaction (R5) is energetically favorable, i.e. $\text{CaCO}_3 + \text{MgO}$ is more stable than $\text{MgCO}_3 + \text{CaO}$, at lower mantle conditions. Although by increasing the temperature, the relative Gibbs free energy is reduced, this effect is not large enough to change the stability of MgCO_3 . Therefore, when there is MgO in excess, as expected in a pyrolytic mantle, CaCO_3 is the stable carbonate under those thermodynamic conditions. Additionally, our static results are in good agreement with recent results (Oganov et al., 2008; Pickard and Needs, 2015).

We now explore the conditions of MgSiO_3 excess, which is the main mineral in the lower mantle. Fig. 5(b) shows that reaction (R6) presents a much richer phenomenology than reaction (R5) across the pressure range of interest. The results of our static calculations show that $\text{MgCO}_3 + \text{CaSiO}_3$ is more favorable than $\text{CaCO}_3 + \text{MgSiO}_3$ at low pressures, while at pressures greater than 84 GPa, $\text{CaCO}_3 + \text{MgSiO}_3$ becomes favorable. Analogously to the reaction (R3), the transition pressure found here is lower than the one found by other authors at 135 GPa (Oganov et al., 2008) and 100 GPa (Pickard and Needs, 2015). However, as the figure shows, there is a dramatic change in the behavior of the reaction (R6) at high temperatures. An increase in temperature increases the pressure in which such reaction could be favorable.

For typical lower mantle temperatures, of at least 2000 K, the reaction (R6) is not favorable anymore. Therefore, the results in

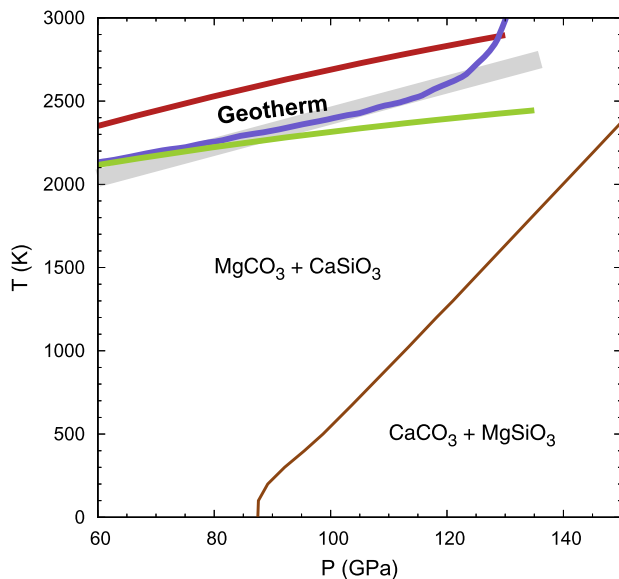


Fig. 6. Phase diagram for the stability (brown line) of $\text{MgCO}_3 + \text{CaSiO}_3$ versus $\text{CaCO}_3 + \text{MgSiO}_3$. The figure also shows several geotherms: thick gray (Isshiki et al., 2004), green (Brown and Shankland, 1981), blue (Boehler, 2000), and red (Anderson, 1982) lines.

Fig. 5(b) indicate that, at lower mantle conditions under an excess of MgSiO_3 , carbonates appear to be favorable in the form of MgCO_3 . This conclusion is consistent with an experimental investigation (Isshiki et al., 2004), which suggested MgCO_3 as the main oxidized carbon host in the Earth's mantle.

Fig. 6 shows the phase diagram for reaction (R6), along with some Earth's geotherms (Isshiki et al., 2004; Brown and Shankland, 1981; Boehler, 2000; Anderson, 1982). According to the figure, all geotherms lie in the region of stability of MgCO_3 , indicating this mineral as the most likely carbon host in the lower mantle, as expected in a pyrolytic mantle. However, it should be pointed out that there is still controversy on the values of the temperatures at the lower mantle bottom and, therefore, the stability of CaCO_3 over MgCO_3 would require a much colder mantle.

4. Summary

This investigation explores the stability of MgCO_3 and CaCO_3 in the thermodynamic conditions of the Earth's lower mantle. The results indicate that a direct decomposition of those carbonates is unfavorable at high temperatures and pressures. Assuming an iron-free pyrolytic lower-mantle composition, the investigation also explores the stability of those carbonates in conditions of excess of SiO_2 , MgO , and MgSiO_3 .

In a MgO -rich environment, the results show that $\text{CaCO}_3 + \text{MgO}$ is more stable than $\text{MgCO}_3 + \text{CaO}$, and the relative energy reduction with increasing temperature is not large enough to change the stability of CaCO_3 . On the other hand, in a MgSiO_3 -rich environment, the static results show that at the upper half of the lower mantle, $\text{MgCO}_3 + \text{CaSiO}_3$ is more favorable than $\text{CaCO}_3 + \text{MgSiO}_3$, while at pressures greater than 84 GPa, the latter becomes favorable. However, when the effects of temperature are taken into account, this behavior changes dramatically and the increase in temperature increases the value of the pressure at which this reaction (R6) becomes favorable and, finally, the magnesium carbonate turns out to be more stable than the calcium carbonate. Consequently, the incorporation of the temperature effects leads to the situation where calcium carbonate should not be considered as a host of the subducted carbon, in contrast to the conclusions of static calculations (Pickard and Needs, 2015), which suggested a

competition between those two carbonates as carbon hosts in the lower mantle.

Since magnesium silicate is the main component of a pyrolytic mantle, it can be inferred that carbonates appear to be favorable in the form of MgCO_3 . Therefore, the magnesium carbonate should be the main host of oxidized carbon in most of the lower mantle. Only at the bottom of the mantle or in a region with an excess of MgO that calcium carbonate could become preferable. However, at the bottom of the mantle, this carbonate would be favorable only considering geotherms with a very low increase in temperature close to the core–mantle boundary.

The results also show that both carbonates do not decompose into their respective alkaline earth oxides plus CO_2 through the entire lower mantle, which indicates a low concentration of free carbon dioxide in those regions. However, the decomposition reaction of MgCO_3 into $\text{MgO} + \text{CO}_2$ would only be possible very close to the core–mantle boundary. Furthermore, free CO_2 could be produced in an environment with an excess of SiO_2 , as in small silica-rich basaltic parts of the subducted slabs.

All those results add a new evidence for the presence of carbon on the deep mantle in the form of carbonates (Hazen and Schiffrics, 2013; Marcondes et al., 2016). However, it is still uncertain how the presence of iron, and its rich phenomenology associated to spin transition at high pressures (Wentzcovitch et al., 2009; Liu et al., 2015), would affect the stability of carbonates in the lower mantle. Moreover, the decomposition of CO_2 into diamond plus oxygen should be explored to enrich the discussion of the presence of carbon in the deep mantle in a reduced state.

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