Stability of calcium and magnesium carbonates at lower mantle thermodynamic conditions

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(Dated: April 20, 2018)

Abstract

We present a theoretical investigation, based on ab initio calculations and the quasi-harmonic approximation, on the stability properties of magnesium (MgCO₃) and calcium (CaCO₃) carbonates at high temperatures and pressures. The results indicate that those carbonates should be stable in Earth’s lower mantle, instead of dissociating into other minerals, in chemical environments with excesses of SiO₂, MgO, or MgSiO₃. Therefore, considering the lower mantle chemical composition, filled with major minerals such as MgSiO₃ and MgO, 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 MgCO₃. Finally, the results indicate that carbon, in the form of free CO₂, is unlikely in the lower mantle.

keywords: carbonates, high-pressure minerals, lower mantle
I. 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 atmosphere, oceans and other shallow crustal phenomena, directly influencing climates and ecosystems, and consequently life on Earth. While there is considerable accumulated knowledge on the carbon cycle near Earth’s surface, there is still scarce information on the processes associated with its deep layers \(^1\).

In order to build consistent models on the Earth’s carbon cycle, it is important to establish a proper understanding on its chemical composition. The knowledge on the solar system composition, based on information from carbonaceous chondritic meteorites that have hit the Earth, allows to estimate the expected amount of carbon that should be present on Earth \(^2\). However, the current known carbon reservoirs 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, which has been labelled as deep carbon reservoirs \(^1\). Estimates indicate that the Earth’s deep interior may contain as much as 90% of all available carbon. Such conclusions have been supported by a number of indirect evidences, such as the presence of CO\(_2\) in magmas \(^2\) and mantle mineral inclusions in natural diamonds \(^3 \text{--} 5\).

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 exchange of carbon between Earth’s surface and its deep interior. For example, current estimates suggest that the carbon flux into Earth’s mantle through subduction substantially exceeds the carbon flux emitted by volcanoes, opening the question on the minerals that host such carbon in the mantle.

Those issues could only be addressed with a deep understanding on the behavior of carbon-related minerals under high pressures and temperatures, particularly on the thermodynamic conditions of the mantle \(^6\). 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 this mineral had a low to moderate solubility for carbon, it could still be the largest carbon reservoir in that region. However, it has been experimentally shown that the carbon solubility in silicates is very small, 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 and diamonds, as well as carbon species emitted by volcanoes.

In the lower mantle, it is still not known if carbon exists in a reduced state, such as in the form of diamond, or in an oxidized one, such as in the form of carbonates. To further explore the potential carriers of carbon, it is important to explore the physical properties of those minerals at lower mantle thermodynamic conditions, particularly in terms of carbon-related stable phases. Several theoretical and experimental investigations have explored the high-pressure stability of major carbonates, such as MgCO$_3$, CaCO$_3$, and MgCa(CO$_3$)$_2$. However, there is still scarce information on those properties at high temperatures.

Particularly for the lower mantle, such conditions would mean pressures up to 140 GPa and temperatures up to 3000 K.

This investigation explores the stability of carbonates, particularly MgCO$_3$ and CaCO$_3$, at lower mantle conditions. Here, we did not explore the MgCa(CO$_3$)$_2$ mineral, since it is well established that it dissociates into MgCO$_3$ and CaCO$_3$ for pressures higher than a few GPa. The results were obtained by first principles total energy calculations, combined with the quasi-harmonic approximation, in order to obtain the respective Gibbs free energies of those minerals in different crystalline phases, at high temperatures and pressures. We explored 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 for carbon hosts in the lower mantle. However, in the thermodynamic conditions of the mantle, along its geotherm, magnesium carbonate is more favorable than calcium carbonate. Additionally, the results suggested that carbon in the form of isolated CO$_2$ is unlikely in the lower mantle.
II. METHODS

A. Ab initio calculations

The first principles calculations were performed using the Quantum ESPRESSO computational package\textsuperscript{19}. The electronic interactions were described within the density functional theory, considering the exchange-correlation (XC) potential based on the local density approximation (LDA) functional\textsuperscript{20}. This functional has been widely used to obtain both static and dynamic properties of minerals of the Earth’s mantle, although many authors have investigated those properties with the generalized gradient approximation (GGA)\textsuperscript{21}. 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 overestimate the respective phase transition pressures and elastic constants when compared to experimental values at finite temperatures, while calculations with the GGA provide the opposite effects\textsuperscript{22}. This investigation used only the LDA functional, since by incorporating thermal effects later on, the lattice parameters increase (and elastic constants decrease), going with the appropriate trend toward the respective experimental values.

The electronic wave functions were expanded using the projected augmented wave (PAW) method\textsuperscript{23}, with a plane-wave cutoff of 1200 eV. The valence electronic configurations were 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\textsuperscript{24}. The Brillouin zones for electronic states of crystalline phases were sampled by a \(4 \times 4 \times 4\) k-mesh for the carbonates and silicates, a \(8 \times 8 \times 8\) k-mesh for 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 were taken into account for the simulations, with the atomic positions being considered converged when all forces acting on atoms were smaller than 0.01 eV Å\(^{-1}\). For each pressure, from 0 to 150 GPa, the structures were optimized using the damped variable cell shape molecular dynamics method\textsuperscript{25}. Then, a second order Birch-Murnaghan equation of state was used to fit the compression data.
B. Thermodynamic properties

The thermodynamic properties were investigated by computing the vibrational modes (phonons) of the crystals using the Density Functional Perturbation Theory\textsuperscript{26}, with a 12 × 12 × 12 q-mesh to calculate the vibrational density of states (VDOS)\textsuperscript{27}, and the quasi-harmonic approximation (QHA)\textsuperscript{28} to compute the respective Gibbs free energies.

The results for finite temperatures were reported within the validity range of the QHA\textsuperscript{28}. 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 opposition to available experimental results. Such divergence results from the fact that this methodology disregards anharmonic effects\textsuperscript{28,29}. However, this quantity is also clearly quite sensitive to the choice of XC functional used\textsuperscript{22}, 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\textsuperscript{28,30} as $[\frac{\partial^2 \alpha(P,T)}{\partial T^2}]_P \leq 0$.

Figure 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. The figure shows 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. The figure also shows that within the validity limit of the QHA, the thermal expansion coefficient is in good agreement with available experimental data\textsuperscript{31}.

We explored 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 provided appropriate thermal expansion coefficients under 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\textsuperscript{28,31,34}.
C. Crystalline phases

In order to explore the stability of carbon-related minerals, within the thermodynamic conditions of the lower mantle, we initially studied 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 higher than the one of a different phase. Our results on stability and phase transition pressures of several carbonate and silicate minerals were in good agreement with results from other theoretical and experimental investigations\textsuperscript{11–13,15}.

We considered a number of crystalline phases for CaCO$_3$, MgCO$_3$, MgSiO$_3$, CaSiO$_3$, MgO, CaO, SiO$_2$, and CO$_2$. First of all, MgO was considered only in the Fm$\overline{3}$m phase, since another investigation has shown that it remains in that phase up to 227 GPa\textsuperscript{35}. CO$_2$ was considered only in the I$\overline{4}2d$ phase\textsuperscript{36}. We performed static calculations for several other CO$_2$ phases and we obtained 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\textsuperscript{12}. 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 considered only the tetragonal (I/4mm) phase for all the pressures and temperatures studied here\textsuperscript{37}, since it is the most important phase in the thermodynamic conditions of interest. Moreover, within such conditions, our methodology provides results which comply with the validity criteria described in section II B, i.e. the thermal expansion coefficient of this phase does not diverge up to 3000 K.

Figure 2 shows the stable crystalline phases for all other minerals considered in this investigation, as function of pressure at temperatures of 300 and 2000 K, in which there are available experimental data for comparison. For CaCO$_3$ at 300 K between 0 and 150 GPa, the material goes from Pmcn to P$2_1$/c-l at 15 GPa, from P$2_1$/c-l to Pmmm at 42 GPa, and from Pmmm to P$2_1$/c-h at 51 GPa, results which are consistent with another theoretical investigation\textsuperscript{13}. Figure 2 also shows that, as the temperature increases, there is a major
change on the transition pressures. At a high temperature, 2000 K, the Pmmn to P21/c-h phase transition occurs at about 80 GPa, in agreement with the theoretical and experimental values of 76 GPa\textsuperscript{13} and 105 ± 5 GPa\textsuperscript{38}, respectively.

For MgCO\textsubscript{3} at 300 K, the material goes from R\overline{3}c to P\overline{T} at 68 GPa, and from P\overline{T} to C2/m at 110 GPa, all results in good agreement with other theoretical investigations using static calculations\textsuperscript{13}. Our results indicate that at temperatures over 1850 K, this mineral follows a direct transition from R\overline{3}c to C2/m, i.e. above that temperature the P\overline{T} is not stable at any pressure. Therefore, our results indicate that P\overline{T} should be of low geophysical interest for studies of the lower mantle properties.

For MgSiO\textsubscript{3} at 300 K, the mineral goes from Pbnm to Cmcm at 94 GPa, which is consistent with another theoretical investigation\textsuperscript{39}. At 2000 K, this transition occurs at 111 GPa, in good agreement with the experimental value of 120 ± 3 GPa\textsuperscript{40}.

For CaO at 300 K, the material goes from Fm\overline{3}m to Pm\overline{3}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\textsuperscript{41}.

For SiO\textsubscript{2} at 300 K (2000 K), the material goes from P4\textsubscript{2}2/mnm to Pnnm at 48 GPa (62 GPa), and from Pnnm to Pbnc at 88 GPa (99 GPa). Those transition values are in good agreement with experimental data at 300 K\textsuperscript{42,43} and 2000 K\textsuperscript{44,45}.

III. RESULTS

A. 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:

\[ \text{CaCO}_3 \Rightarrow \text{CaO} + \text{CO}_2 \quad \text{(R1)} \]
\[ \text{MgCO}_3 \Rightarrow \text{MgO} + \text{CO}_2 \quad \text{(R2)} \]

Figure 3 shows the relative Gibbs free energy per unit formula (u.f.) as a functions of pressure and temperature. It shows that the direct decompositions of CaCO\textsubscript{3} and MgCO\textsubscript{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 are positive for all the pressures of interest of the lower mantle. However, the energy cost for the CaCO$_3$ reaction is much higher than the one for MgCO$_3$.

It should be stressed that our static results, black lines in figure 3, are in very good agreement with the static results presented in other recent investigations$^{12,13}$, as well as with experimental data$^{14}$. Those investigations, without taking into account temperature effects, have suggested that free CO$_2$ does not occur as an independent phase within the Earth’s mantle. According to the results presented in figures 3(a) and (b), temperature effects do not alter the relative stability of carbonates, when compared to their most elementary constituents. In reality, the phenomenology is quite the contrary, as the figure shows, a temperature increase further reduces the possibility of free CO$_2$ to exist in that region.

**B. 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 the upper and lower mantle have material mixing, resulting from the basaltic part of subducting slabs, which is rich in SiO$_2^{12}$.

\[
\text{MgCO}_3 + \text{SiO}_2 \Rightarrow \text{MgSiO}_3 + \text{CO}_2 \quad \text{(R3)}
\]
\[
\text{CaCO}_3 + \text{SiO}_2 \Rightarrow \text{CaSiO}_3 + \text{CO}_2 \quad \text{(R4)}
\]

Figure 4 shows the relative Gibbs free energies for Mg and Ca carbonates to transform into their respective silicates. The results indicated 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 result of those reactions. Static results, in figure 4(a) indicate that reaction (R3) is unfavorable up to 127 GPa, i.e. MgCO$_3$ is more stable than MgSiO$_3$. 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.

Our static results for reaction (R3), black line in figure 4(a), are in good agreement with static results presented in recent theoretical investigations\textsuperscript{12,13}. However, the transition pressure found here is lower than the one found by those authors. Such differences could be explained by the functionals used to describe electron-electron interactions, since our investigation used the LDA\textsuperscript{20}, while those investigations use the GGA\textsuperscript{21}. The choice of LDA over GGA in this investigation was discussed in detail in section II A.

According to figure 4 (b), the reaction (R4) indicates that CaCO$_3$ is more stable than CaSiO$_3$ up to 150 GPa at any temperature. Since this pressure is much larger than the ones at the bottom of the lower mantle, this reaction would not occur in that region. Our static results on the transition pressure for reaction (R4) disagree with another theoretical investigation\textsuperscript{12}, which predicted a reaction of calcium carbonate with SiO$_2$ within the pressure range of the lower mantle. In fact, that investigation did not take into account the P2$_1$/c-h phase of CaCO$_3$, which may explain the differences in the conclusions. On the other hand, our static results are in good agreement with the ones of a more recent investigation\textsuperscript{13}.

It should be pointed out that our investigation carries some uncertainties on the transition pressures of SiO$_2$, as shown in figure 2, which could play some role on the final conclusions about the reactions (R3) and (R4), particularly on the properties near the core-mantle boundary.

\textbf{C. Stability of carbonates under excess of MgO or MgSiO$_3$}

It is reasonably well established that MgSiO$_3$ and MgO are the two major minerals in the lower mantle. Therefore, it is important to study the stability of MgCO$_3$ or CaCO$_3$ carbonates in a rich environment with those two major minerals. To explore those conditions, we evaluate the energetics associated to reactions (R5) and (R6).

\begin{align*}
\text{MgCO}_3 + \text{CaO} & \Rightarrow \text{CaCO}_3 + \text{MgO} \quad \text{(R5)} \\
\text{CaCO}_3 + \text{MgSiO}_3 & \Rightarrow \text{MgCO}_3 + \text{CaSiO}_3 \quad \text{(R6)}
\end{align*}
Figure 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 \( \text{MgCO}_3 \). Therefore, when there is \( \text{MgO} \) in excess, as expected in a pyrolitic mantle, \( \text{CaCO}_3 \) is the stable carbonate under those thermodynamic conditions. Additionally, our static results are in good agreement with recent results from other investigations\textsuperscript{12,13}.

We now explore the conditions of \( \text{MgSiO}_3 \) excess, which is the main mineral in the lower mantle. Figure 5(b) shows that reaction (R6) presents a much richer phenomenology than reaction (R5) across the pressure range of interest. Our static calculations show that \( \text{MgCO}_3 + \text{CaSiO}_3 \) is more favorable than \( \text{CaCO}_3 + \text{MgSiO}_3 \) at low pressures, but at pressures higher than 75 GPa, then \( \text{CaCO}_3 + \text{MgSiO}_3 \) becomes favorable. However, as the figure shows, there is a dramatic change in the behavior at high temperatures. An increase in temperature increases the pressure in which such reaction could be favorable.

For typical lower mantle temperatures, in the order of at least 2000 K, the reaction (R6) is not favorable anymore. Therefore, the results in figure 5(b) indicated that, at lower mantle conditions under excess of \( \text{MgSiO}_3 \), carbonates appear to be favorable in the form of \( \text{MgCO}_3 \). This conclusion is consistent with an experimental investigation\textsuperscript{15}, which suggested \( \text{MgCO}_3 \) as the main oxidized carbon host in Earth’s mantle.

Figure 6 shows the phase diagram for reaction (R6), along with some Earth’s geotherms\textsuperscript{15,46–48}. According to the figure, all geotherms lie in the region of stability of \( \text{MgCO}_3 \), indicating this mineral as the most likely carbon host in the lower mantle, as expected in a pyrolitic mantle. However, it should be pointed that there is still controversy on the temperatures at the lower mantle bottom, therefore, the stability of \( \text{CaCO}_3 \) over \( \text{MgCO}_3 \) would require a much colder mantle.

IV. SUMMARY

In summary, this investigation explored the stability of \( \text{MgCO}_3 \) and \( \text{CaCO}_3 \) carbonates in the thermodynamic conditions of Earth’s lower mantle. The results indicated that a direct decomposition of those carbonates is unfavorable at high temperatures and pressures. Assuming an iron free pyrolitic lower-mantle composition, the investigation also explored
the stability of those carbonates in conditions of excess of SiO$_2$, MgO, and MgSiO$_3$.

In a MgO-rich environment, the results showed that calcium carbonate is more stable than magnesium carbonate, and the relative energy reduction with increasing temperature was not large enough to change the stability of CaCO$_3$. On the other hand, in a MgSiO$_3$-rich environment, the static results showed that at the upper half of the lower mantle, the MgCO$_3$ + CaSiO$_3$ reaction is more favorable than the CaCO$_3$ + MgSiO$_3$ one, while at pressures higher than 75 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 pressure at which this reaction becomes favorable, and finally the magnesium carbonate turns out to be more stable than the calcium carbonate.

Since magnesium silicate is the main component of a pyrolitic 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 in the bottom of the mantle or in a region with MgO in excess that calcium carbonate could become preferable. However, in the bottom of the mantle, this carbonate would be favorable only considering geotherms with very low increase in temperature close to the core-mantle boundary.

The results also showed that both carbonates do not decompose into their respective alkaline oxides plus CO$_2$ through the entire lower mantle, which indicates low concentration of free carbon dioxide in those regions. However, the decomposition reaction of MgCO$_3$ into MgO+CO$_2$ would only be possible very close to the core-mantle boundary. Furthermore, free CO$_2$ could be produced in an environment with excess of SiO$_2$, as in small silica-rich basaltic parts of the subducted slabs.

All those results add new evidences for the presence of carbon on deep mantle in the form of carbonates$^{11}$. However, it is still uncertain how the presence of iron, and its rich phenomenology associated to spin transition at high pressure$^{49,50}$, 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.

Acknowledgments

This investigation was supported by the Brazilian agencies CNPq and CAPES. We ac-
knowledge resources from the Blue Gene/Q supercomputer supported by the Center for Research Computing (Rice University) and the Superintendência de Tecnologia da Informação (Universidade de São Paulo).

1 R. M. Hazen, C. M. Schiffries, Why deep carbon?, Rev. Mineral. Geochem. 75 (2013) 1.
2 B. Marty, C. M. O. Alexander, S. N. Raymond, Primordial origins of Earth’s carbon, Rev. Mineral. Geochem. 75 (2013) 149.
3 M. J. Walter, S. C. Kohn, D. Araujo, G. P. Bulanova, C. B. Smith, E. Gaillou, J. Wang, A. Steele, S. B. Shirey, Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions., Science 334 (2011) 54–7.
4 D. G. Pearson, F. E. Brenker, F. Nestola, J. McNeill, L. Nasdala, M. T. Hutchison, S. Matveev, K. Mather, G. Silversmit, S. Schmitz, B. Vekemans, L. Vincze, Hydrous mantle transition zone indicated by ringwoodite included within diamond., Nature (London) 507 (2014) 221.
5 F. Maeda, E. Ohtani, S. Kamada, T. Sakamaki, N. Hirao, Y. Ohishi, Diamond formation in the deep lower mantle: a high-pressure reaction of MgCO$_3$ and SiO$_2$. Sci. Rep-UK 7 (2017) 40602.
6 A. R. Oganov, R. J. Hemley, R. M. Hazen, A. P. Jones, Structure, bonding, and mineralogy of carbon at extreme conditions, Rev. Mineralog. Geochem. 75 (2013) 47–77.
7 F. E. Brenker, C. Vollmer, L. Vincze, B. Vekemans, A. Szymanski, K. Janssens, I. Szaloki, L. Nasdala, W. Joswig, F. Kaminsky, Carbonates from the lower part of transition zone or even the lower mantle, Earth Planet. Sc. Lett. 260 (2007) 1–9.
8 A. P. Jones, M. Genge, L. Carmody, Carbonate melts and carbonatites, Rev. Mineralog. Geochem. 75 (2013) 289.
9 S. B. Shirey, P. Cartigny, D. J. Frost, S. Keshav, F. Nestola, P. Nimis, D. G. Pearson, N. V. Sobolev, M. J. Walter, Diamonds and the geology of mantle carbon, Rev. Mineralog. Geochem. 75 (2013) 355.
10 M. R. Burton, G. M. Sawyer, D. Granieri, Deep carbon emissions from volcanoes, Rev. Mineralog. Geochem. 75 (2013) 323–354.
11 M. L. Marcondes, J. F. Justo, L. V. C. Assali, Carbonates at high pressures: possible carriers for deep carbon reservoirs in the Earth’s lower mantle, Phys. Rev. B 94 (2016) 104112.
A. R. Oganov, S. Ono, Y. Ma, C. W. Glass, A. Garcia, Novel high-pressure structures of MgCO$_3$, CaCO$_3$ and CO$_2$ and their role in Earth’s lower mantle, Earth Planet. Sci. Lett. 273 (2008) 38–47.

C. J. Pickard, R. J. Needs, Structures and stability of calcium and magnesium carbonates at mantle pressures, Phys. Rev. B 91 (2015) 104101.

G. Fiquet, F. Guyot, M. Kunz, J. Matas, D. Andrault, M. Hanfland, Structural refinements of magnesite at very high pressure, Am. Mineralog. 87 (2002) 1261–1265.

M. Isshiki, T. Irifune, K. Hirose, S. Ono, Y. Ohishi, T. Watanuki, E. Nishibori, M. Takata, M. Sakata, Stability of magnesite and its high-pressure form in the lowermost mantle., Nature 427 (2004) 60–63.

P. N. Gavryushkin, N. S. Martirosyan, T. M. Inerbaev, Z. I. Popov, S. V. Rashchenko, A. Y. Likhacheva, S. S. Lobanov, A. F. Goncharov, V. B. Prakapenka, K. D. Litasov, Aragonite-II and CaCO$_3$-VII: new high-pressure, high-temperature polymorphs of CaCO$_3$. Cryst. Growth Des. 17 (2017) 6291–6296.

D. Smith, K. V. Lawler, M. Martinez-Canales, A. W. Daykin, Z. Fussell, G. A. Smith, C. Childs, J. S. Smith, C. J. Pickard, A. Salamat, Postaragonite phases of CaCO$_3$ at lower mantle pressures, Phys. Rev. Materials 2 (2018) 013605.

M. Shirasaka, E. Takahashi, Y. Nishihara, K. Matsukage, T. Kikegawa, In situ X-ray observation of the reaction dolomite = aragonite + magnesite at 900-1300 K, Am. Mineralog. 87 (2002) 922.

P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials., J. Phys.: Condens. Mat. 21 (2009) 395502.

W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133–A1138.

J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple., Phys. Rev. Lett. 77 (1996) 3865–3868.

M. L. Marcondes, R. M. Wentzcovitch, L. V. C. Assali, Importance of van der Waals interaction
on structural, vibrational, and thermodynamic properties of NaCl, Solid State Commun. 273 (2018) 11–16.

23 P. E. Blochl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.

24 N. A. W. Holzwarth, A. R. Tackett, G. E. Matthews, A projector augmented wave (PAW) code for electronic structure calculations, part I: atompaw for generating atom-centered functions, Comput. Phys. Commun. 135 (2001) 329–347.

25 R. M. Wentzcovitch, J. L. Martins, G. D. Price, Ab initio molecular dynamics with variable cell shape: application to MgSiO$_3$, Phys. Rev. Lett. 70 (1993) 3947–3951.

26 S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Rev. Mod. Phys. 73 (2001) 515–562.

27 Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, Z. K. Liu, A mixed-space approach to first-principles calculations of phonon frequencies for polar materials, J. Phys.: Condens. Mat. 22 (2010) 202201.

28 R. M. Wentzcovitch, Y. G. Yu, Z. Wu, Thermodynamic properties and phase relations in mantle minerals investigated by first principles quasiharmonic theory, Rev. Mineralog. Geochem. 71 (2010) 59.

29 R. M. Wentzcovitch, B. B. Karki, M. Cococcioni, S. de Gironcoli, Thermoelastic properties of MgSiO$_3$-perovskite: insights on the nature of the Earth’s lower mantle, Phys. Rev. Lett. 92 (2004) 18501.

30 P. Carrier, R. Wentzcovitch, J. Tsuchiya, First-principles prediction of crystal structures at high temperatures using the quasiharmonic approximation, Phys. Rev. B 76 (2007) 064116.

31 K. D. Litasov, A. Shatskiy, P. N. Gavryushkin, A. E. Bekhtenova, P. I. Dorogokupets, B. S. Danilov, Y. Higo, A. T. Akilbekov, T. M. Inerbaev, P-V-T equation of state of CaCO$_3$ aragonite to 29 GPa and 1673 K: In situ X-ray diffraction study, Phys. Earth Planet. Int. 265 (2017) 82.

32 P. I. Dorogokupets, Equation of state of magnesite for the conditions of the earth’s lower mantle, Geochem. Int+ 45 (2007) 561–568.

33 L. Li, D. J. Weidner, J. Brodholt, D. Alfé, G. D. Price, R. Caracas, R. Wentzcovitch, Elasticity of CaSiO$_3$ perovskite at high pressure and high temperature, Phys. Earth Planet. Int. 155 (2006) 249–259.

34 B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, S. Baroni, Ab initio lattice dynamics of MgSiO$_3$ perovskite at high pressure, Phys. Rev. B 62 (2000) 14750–14756.
35 T. S. Duffy, R. J. Hemley, H.-k. Mao, Equation of state and shear strength at multimegabar pressures: magnesium oxide to 227 GPa, Phys. Rev. Lett. 74 (1995) 1371–1374.
36 F. Datchi, B. Mallick, A. Salamat, S. Ninet, Structure of Polymeric Carbon Dioxide CO$_{2}$–V, Phys. Rev. Lett. 108 (2012) 125701.
37 S. Shim, R. Jeanloz, T. S. Duffy, Tetragonal structure of CaSiO$_{3}$ perovskite above 20 GPa, Geophys. Res. Lett. 29 (2002) 2166.
38 S. S. Lobanov, X. Dong, N. S. Martirosyan, A. I. Samtsevich, V. Stevanovic, P. N. Gavryushkin, K. D. Litasov, E. Greenberg, V. B. Prakapenka, A. R. Oganov, A. F. Goncharov, Raman spectroscopy and x-ray diffraction of $sp^{3}$ CaCO$_{3}$ at lower mantle pressures, Phys. Rev. B 96 (2017) 104101.
39 T. Tsuchiya, J. Tsuchiya, K. Umemoto, R. M. Wentzcovitch, Phase transition in MgSiO$_{3}$ perovskite in the earth’s lower mantle, Earth Planet. Sci. Lett. 224 (2004) 241 – 248.
40 M. Murakami, K. Hirose, K. Kawamura, N. Sata, Y. Ohishi, Post-perovskite phase transition in MgSiO$_{3}$, Science 304 (2004) 855.
41 T. Yamanaka, K. Kittaka, T. Nagai, B1-B2 transition in CaO and possibility of CaSiO$_{3}$-perovskite decomposition under high pressure, J. Miner. Petrol. Sci. 97 (4) (2002) 144–152.
42 R. J. Hemley, J. Shu, M. A. Carpenter, J. Hu, H. K. Mao, K. J. Kingma, Strain/order parameter coupling in the ferroelastic transition in dense SiO$_{2}$, Solid State Commun. 114 (2000) 527–532.
43 D. Andrault, G. Fiquet, F. Guyot, M. Hanfland, Pressure-induced landau-type transition in stishovite, Science 282 (1998) 720–724.
44 S. Ono, K. Hirose, M. Murakami, M. Isshiki, Post-stishovite phase boundary in SiO$_{2}$ determined by in situ X-ray observations, Earth Planet. Sci. Lett. 197 (2002) 187–192.
45 M. Murakami, K. Hirose, S. Ono, Y. Ohishi, Stability of CaCl$_{2}$-type and α-PbO$_{2}$-type SiO$_{2}$ at high pressure and temperature determined by insitu X-ray measurements, Geophys. Res. Lett. 30 (2003) 1207.
46 J. M. Brown, T. J. Shankland, Thermodynamic parameters in the earth as determined from seismic profiles, Geophys. J. Int. 66 (1981) 579–596.
47 R. Boehler, Highpressure experiments and the phase diagram of lower mantle and core materials, Rev. Geophys. 38 (2000) 221–245.
48 O. L. Anderson, The earth’s core and the phase diagram of iron, Philos. T. R. Soc. A 306 (1982) 21–35.
R. M. Wentzcovitch, J. F. Justo, Z. Wu, C. R. S. da Silva, D. A. Yuen, D. Kohlstedt, Anomalous compressibility of ferropericlase throughout the iron spin cross-over., Proc. Nat. Acad. Sci. USA 106 (2009) 8447–8452.

J. Liu, J.-F. Lin, V. B. Prakapenka, High-pressure orthorhombic ferromagnesite as a potential deep-mantle carbon carrier, Sci. Rep-UK 5 (2015) 7640.
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 QHA boundary is defined by the position of the inflection points of $\alpha(P,T)$, discussed in section II B. Experimental results at 0 GPa are presented with black symbols.
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 II A. 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$$^{38}$, MgSiO$_3$$^{40}$, CaO$^{41}$, and SiO$_2$$^{42-45}$. 

- CaCO$_3$: Pmcn, P$_{2_1}$/c-I, Pmnn, P$_{2_1}$/c-h
- MgCO$_3$: R$_3$c, P$_T$, C2/m
- MgSiO$_3$: Pbnnm, Cmcm
- CaO: Fm3m, Pm3m
- SiO$_2$: P$_{4_2}$/mnm, Pnnm, Pbnc

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FIG. 3: The relative Gibbs free energies per u.f. as function of pressure, at several temperatures, for (a) CaCO$_3$ → CaO + CO$_2$ and (b) MgCO$_3$ → MgO + CO$_2$ reactions. The dotted black lines 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 II C and shown in figure 2, which are used to explore the dissociation reactions.
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 dotted lines represent the relative enthalpies for the reactions. The vertical gray lines indicate the pressures at the top and bottom of the lower mantle.
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 black dotted lines 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. 6: Phase diagram for the stability (brown line) of MgCO$_3$ + CaSiO$_3$ versus CaCO$_3$ + MgSiO$_3$. The figure also shows several geotherms: thick gray, green, blue, and red lines.