

Novel high-pressure calcium carbonates

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Calcium and magnesium carbonates are believed to be the host compounds for most of the oxidized carbon in the Earth's mantle. Here, using the evolutionary crystal structure prediction method USPEX, we systematically explore the MgO-CO₂ and CaO-CO₂ systems at pressures ranging from 0 to 160 GPa to search for thermodynamically stable magnesium and calcium carbonates. While MgCO₃ is the only stable magnesium carbonate, three calcium carbonates are stable under pressure: well-known CaCO₃, and previously unknown Ca₃CO₅ and CaC₂O₅. Ca₃CO₅ polymorphs are found to contain isolated orthocarbonate CO₄⁴⁻ tetrahedra, and are stable at relatively low pressures (> 11 GPa), whereas CaC₂O₅ is stable above 33 GPa and its polymorphs feature polymeric motifs made of CO₄ tetrahedra. Detailed analysis of the chemical stability of CaCO₃, Ca₃CO₅, and CaC₂O₅ in the environment typical of the Earth's lower mantle reveals that none of these compounds can exist in the Earth's lower mantle. Instead, MgCO₃ is the main host of oxidized carbon throughout the lower mantle.

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I. INTRODUCTION

Behavior of carbon in the Earth's mantle is important for the global carbon cycle. The generally accepted view is that mantle carbon exists in a number of reduced, neutral, and oxidized forms (i.e., Fe₃C cementite, diamond, carbonates) [1]. Over the past few decades, magnesium and calcium carbonates (MgCO₃ and CaCO₃) have received considerable attention because they are believed to be the host compounds for most of the oxidized carbon in the mantle [2–6]. The zero-temperature calculations of Pickard and Needs predicted that CaCO₃ will become more favorable than MgCO₃ at pressures above 100 GPa at mantle chemistry and therefore should be present in the lowermost mantle [6], but thermal effects could overturn this conclusion (and, as we show, this is indeed the case). Moreover, all previous works assumed compositions known at atmospheric pressure (CaCO₃, MgCO₃) as the only possibilities. Recent works [7–9] proved that chemistry is greatly altered by pressure: New unexpected compounds appear so often that they are more of a rule than an exception. It is, therefore, necessary to check for additional possible carbonates.

At mantle pressures, a series of phase transitions occur in MgCO₃ and CaCO₃. Tables S1 and S2 in the Supplemental Material [10] list high-pressure forms of MgCO₃ and CaCO₃ predicted in previous works [3,5,6]. From zero pressure up

to the pressure of the core-mantle boundary (136 GPa), both MgCO₃ and CaCO₃ will experience several interesting phase transitions. For example, it was predicted that while polymorphs of CaCO₃ stable below 76 GPa [6] (or 75 GPa according to our calculations) feature CO₃ triangles, chains of CO₄ tetrahedra are present in the higher-pressure form of CaCO₃.

At ambient pressure and temperature, the carbon atom in CO₂ has *sp* hybridization with linear geometry and twofold coordination, while in CO₃²⁻ it has *sp*² hybridization resulting in planar triangular geometry and threefold coordination. *sp*³ hybridization (resulting in CO₄ tetrahedra) is unfavorable due to the very small size of the C⁴⁺ cation compared to the O²⁻ atom: At realistic (very short) C-O distances, steric O-O repulsion would be too high. However, at high pressure, carbon prefers to be in the *sp*³ state and behaves in many ways akin to silicon at normal pressure. High coordination gives a volume advantage, which offsets the steric effects.

In this work, we assess the traditional assumption of CaCO₃ and MgCO₃ stoichiometries of calcium and magnesium carbonates. As will be detailed below, previously unknown carbonates are indeed predicted, and we examine their stability at different pressures and temperatures, and in the chemical environment of the lower mantle of the Earth.

II. COMPUTATIONAL METHODOLOGY

To search for stable magnesium and calcium carbonates at mantle pressures, we have explored the MgO-CO₂, CaO-CO₂, Mg-C-O, Ca-C-O, and MgO-CaO-CO₂ systems using the

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variable-composition evolutionary algorithm (EA) technique, as implemented in the USPEX code [11–14]. Here we performed EA crystal structure predictions in the pressure range from 0 to 160 GPa with up to 40 atoms in the primitive unit cell. The first generation of structures was created randomly. In all subsequent generations, structures were produced by heredity (40%), symmetric random generator (20%), softmutation (20%) and transmutation (20%) operators, and the best 60% of the previous generation was used as parents to generate the next generation of structures. For all structures generated by USPEX, structure relaxations and total energy calculations were performed using the VASP code [15] in the framework of density functional theory [16]. In these calculations, we used the Perdew-Burke-Ernzerhof generalized gradient approximation functional (PBE-GGA) [17] to treat exchange-correlation, and the all-electron projector augmented wave (PAW) [18] method to describe core-valence interactions— $3s^2 3p^6 4s^2$, $3s^2$, $2s^2 2p^2$, and $2s^2 2p^4$ shells were treated as valence for Ca, Mg, C, and O, respectively. The plane-wave kinetic energy cutoff of 600 eV and uniform k -point meshes for sampling the Brillouin zone with reciprocal-space resolution of $2\pi \times 0.05 \text{ \AA}^{-1}$ were employed. Once stable compounds and structures were found, their properties were computed with denser k -point meshes, which had reciprocal-space resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$.

III. RESULTS AND DISCUSSIONS

A. Phase stability at mantle pressures

We have performed crystal structure predictions at 0, 15, 20, 40, 60, 80, 100, and 160 GPa for the CaO-CO₂ system; at 0, 60, 100, and 160 GPa for the MgO-CO₂ system; and at 25, 50, 100, and 130 GPa for the ternary systems Mg-C-O, Ca-C-O, and MgO-CaO-CO₂. At a given pressure, stable compounds were determined by the thermodynamic convex hull construction. As shown in Fig. 1(a), among all possible magnesium carbonates, only MgCO₃ was found to be on the convex hull. This indicates that, besides MgCO₃, no other magnesium carbonates can be thermodynamically stable at mantle pressures. At the same time, in the CaO-CO₂ system, besides the well-known CaCO₃ we discover two thermodynamically stable calcium carbonates, Ca₃CO₅ and CaC₂O₅ (and one near-ground-state compound Ca₂CO₄), as shown in Fig. 1(b). Phonon calculations show that these two stable calcium carbonate phases are dynamically stable; i.e., they have no imaginary phonon frequencies, as shown in Fig. 2. Unexpectedly, we also found that three high-pressure forms of CaC₂O₅ (*Pc*, *Fdd2*, and *C2*) and *Cmcm*-Ca₃CO₅ can maintain dynamical stability at 0 GPa; see Fig. S1 in the Supplemental Material [10]. This means that Ca₃CO₅ and CaC₂O₅ may be quenchable to ambient pressure at low temperature. Lattice parameters and enthalpies of formation of stable and metastable calcium carbonates are listed in Table S3 in the Supplemental Material [10]. For the well-known CaCO₃, we have also listed available experimental and theoretical values for comparison [19–21].

By calculating enthalpy-pressure curves for all stable compounds in the CaO-CO₂ and MgO-CO₂ systems (see Fig. S2 in the Supplemental Material [10]), we have obtained their pressure-composition phase diagrams at pressures up

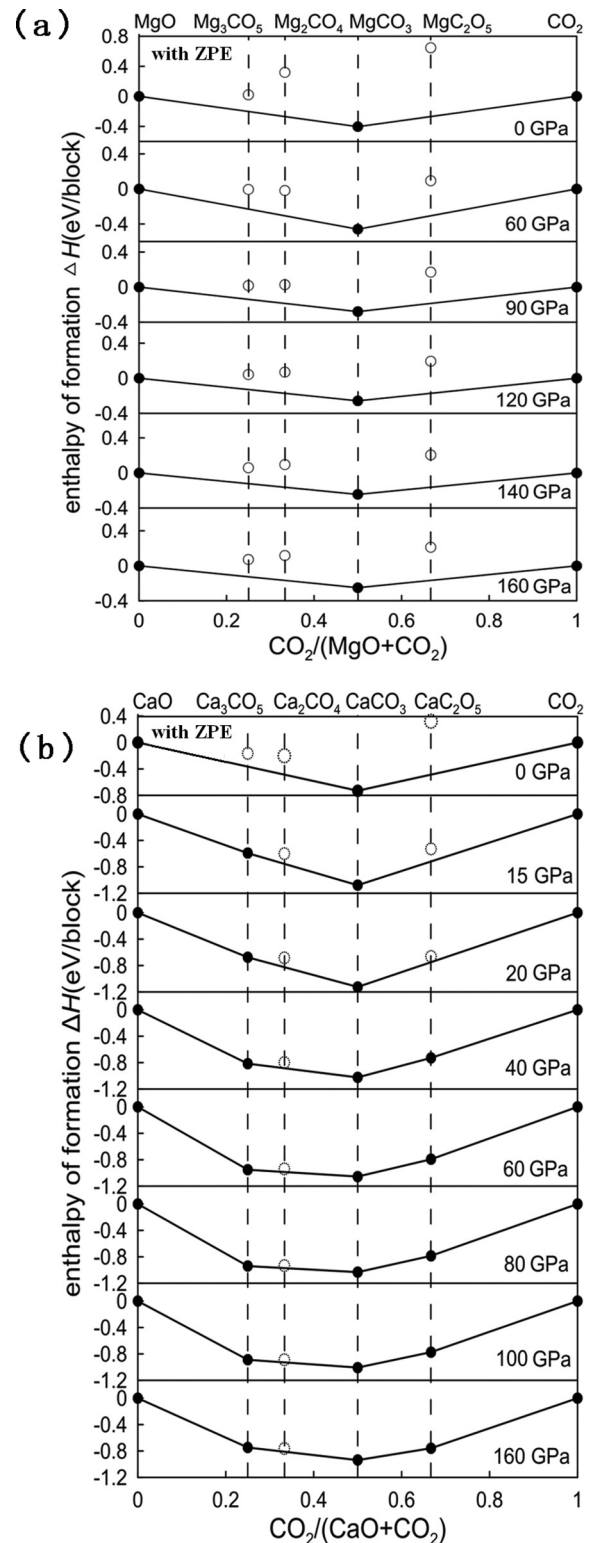


FIG. 1. Thermodynamic convex hulls for MgO-CO₂ and CaO-CO₂ systems at zero temperature and high pressure (with zero-point energy correction). Filled circles denote stable structures and open circles denote metastable structures. Enthalpies of formation from oxides are normalized to one oxide unit.

to 160 GPa (see Fig. 3). As shown in Fig. 3, stable phases and phase transition pressures in MgO, CaO, CO₂, MgCO₃,

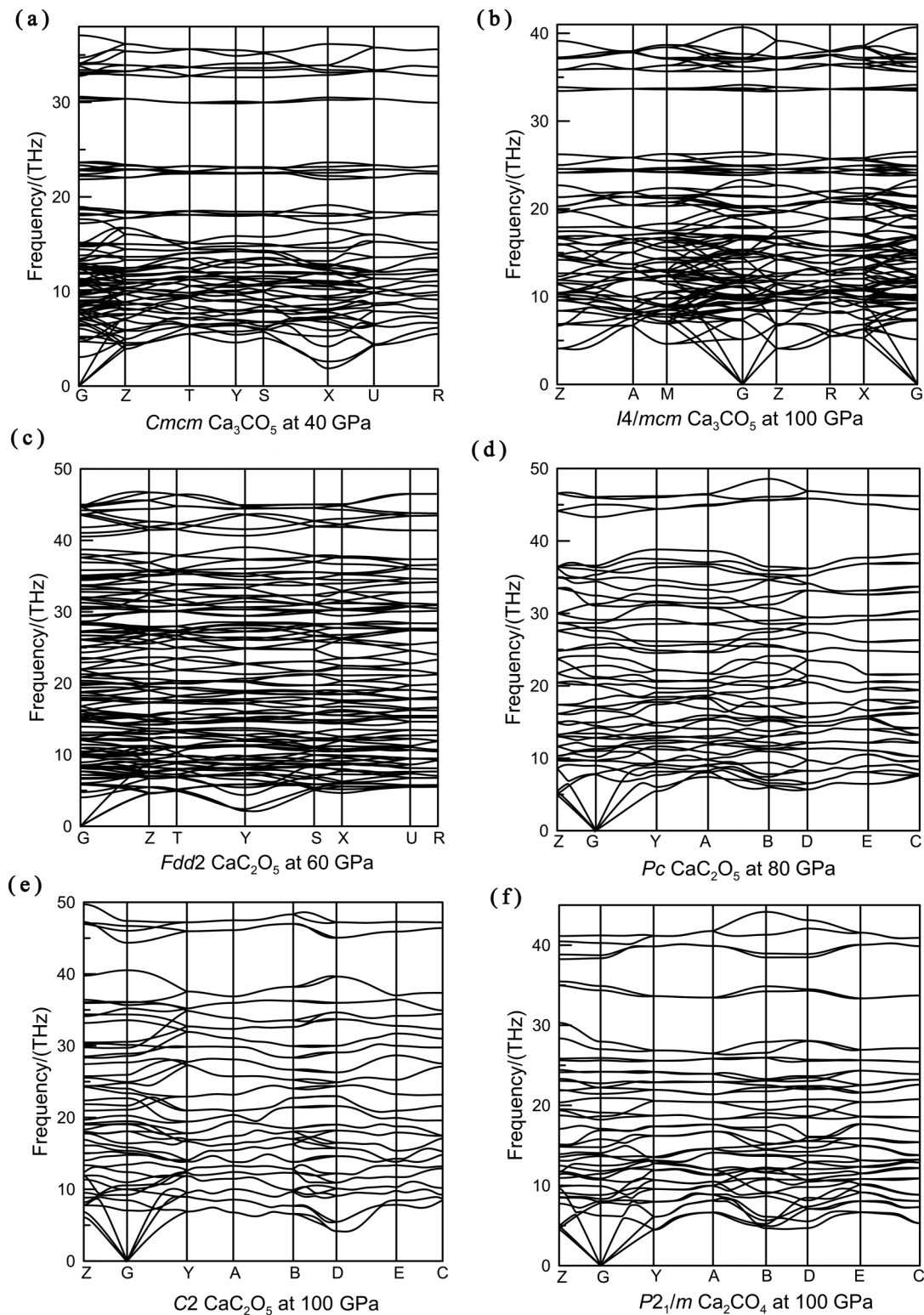


FIG. 2. Phonon dispersion curves of the predicted calcium carbonates at high pressures and zero temperature.

and CaCO_3 are in good agreement with previous studies [3,5,6,22–24]. We note that, for CaCO_3 , Smith *et al.* recently proposed a new $P2_1/c$ -II phase which is stable between 27.2 and 37.5 GPa [25], but did not report its structural parameters. Considering the extremely small enthalpy difference between

the $P2_1/c$ -II and $P2_1/c$ -I phases of CaCO_3 , we should say that omission or inclusion of the $P2_1/c$ -II phase of CaCO_3 will not affect our results. Phase transformations of Ca_3CO_5 and CaC_2O_5 are as follows: (1) For Ca_3CO_5 , the orthorhombic *Cmc* phase is predicted to become stable at

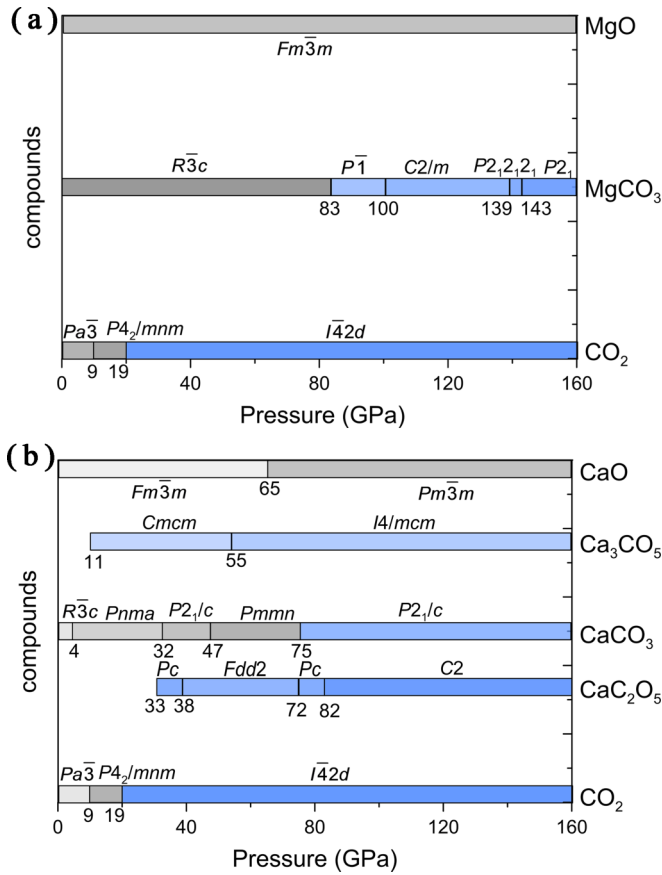


FIG. 3. Pressure-composition phase diagrams of MgO-CO₂ and CaO-CO₂ systems at zero temperature.

11 GPa, and to transform to the tetragonal $I4/mcm$ phase at 55 GPa; (2) for CaC₂O₅, above 33 GPa, four stable phases (low-pressure Pc and $Fdd2$, high-pressure Pc and $C2$) are predicted. Structural transformation from the low-pressure Pc phase to the $Fdd2$ phase occurs at 38 GPa, and from the $Fdd2$ phase to the high-pressure Pc phase at 72 GPa, and then to the $C2$ phase at 82 GPa. Figure 4 shows the computed equations of state (EOS) of all stable calcium carbonates. One

can see that pressure-induced phase transitions in CaCO₃ and Ca₃CO₅, but not in CaC₂O₅, are accompanied by large volume discontinuities.

It should be possible to synthesize the predicted calcium carbonates (Ca₃CO₅ and CaC₂O₅). Several phases of MgCO₃ and CaCO₃, previously predicted by our method and similar techniques, have already been confirmed by experiment, such as the $C2/m$ [5] and $P2_1$ [5] phases of MgCO₃, and $P2_1/c$ [6,25], $Pmmn$ [3,21], and thermodynamically metastable $P-1$ [3,26] phases of CaCO₃. Considering hundreds of papers where it was assumed that CaCO₃ is the only possible calcium carbonate, and the importance of calcium carbonate for fundamental chemistry and physics and the hot ongoing quest for sp^3 (tetrahedral) carbonates, we believe that our predicted calcium carbonates will stimulate experiments.

B. Crystal structures of stable calcium carbonates

Crystal structures of the predicted stable and metastable calcium carbonates, visualized by the VESTA package [27], are shown in Fig. 5. At mantle pressures, crystal structures of CaCO₃ have been carefully studied before [3,6]. With the increase of pressure, CaCO₃ successively adopts five phases (calcite $R\bar{3}c$, aragonite $Pnma$, low-pressure $P2_1/c$, postaragonite $Pmmn$, and high-pressure $P2_1/c$). As shown in Figs. 5(a)–5(e), the former four phases contain triangular CO₃^{2−} ions with sp^2 hybridization, while the fifth phase adopts a pyroxene-type structure with chains of corner-linked CO₄^{4−} tetrahedra above 75 GPa.

High-pressure phases of CaCO₃ (>75 GPa) and MgCO₃ (>83 GPa) contain CO₄^{4−} tetrahedra. In CaCO₃ above 75 GPa, we see chains of corner-sharing tetrahedra. In MgCO₃ above 83 GPa, CO₄^{4−} tetrahedra form C₃O₉^{6−} rings, and above 180 GPa form chains [5,6]. The differences between CaCO₃ and MgCO₃ come from different sites of Ca and Mg. Ca²⁺ is much larger than Mg²⁺, and requires the anion sublattice to have more open space to fit it.

On the Ca-rich side, our predicted phases include stable $Cmcm$ -Ca₃CO₅, $I4/mcm$ -Ca₃CO₅, and metastable $P2_1/m$ -Ca₂CO₄, all of which contain isolated CO₄^{4−} tetrahe-

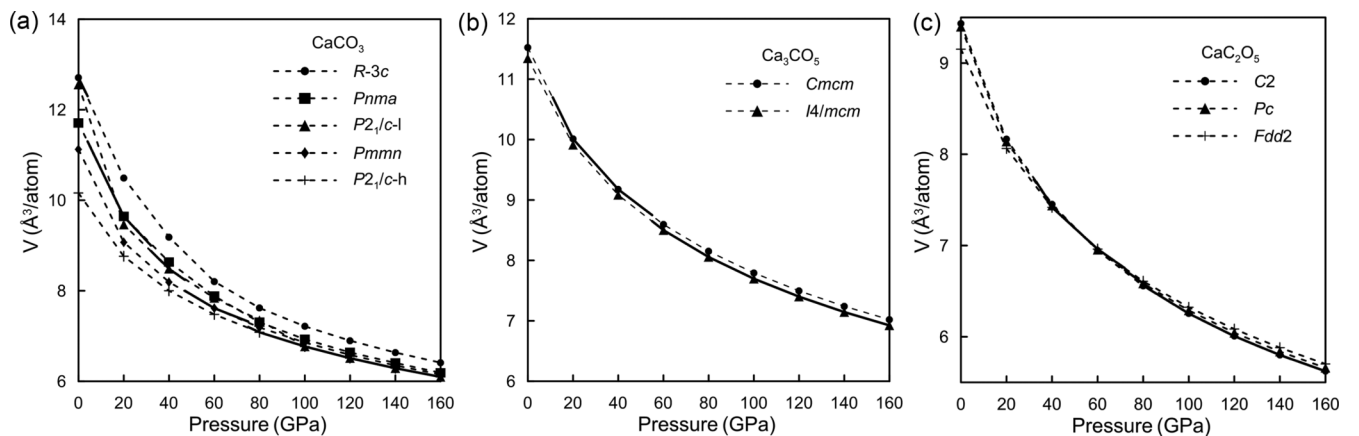


FIG. 4. Equations of state of all stable calcium carbonates at zero temperature. Solid lines denote equations of state of each phase in its region of stability.

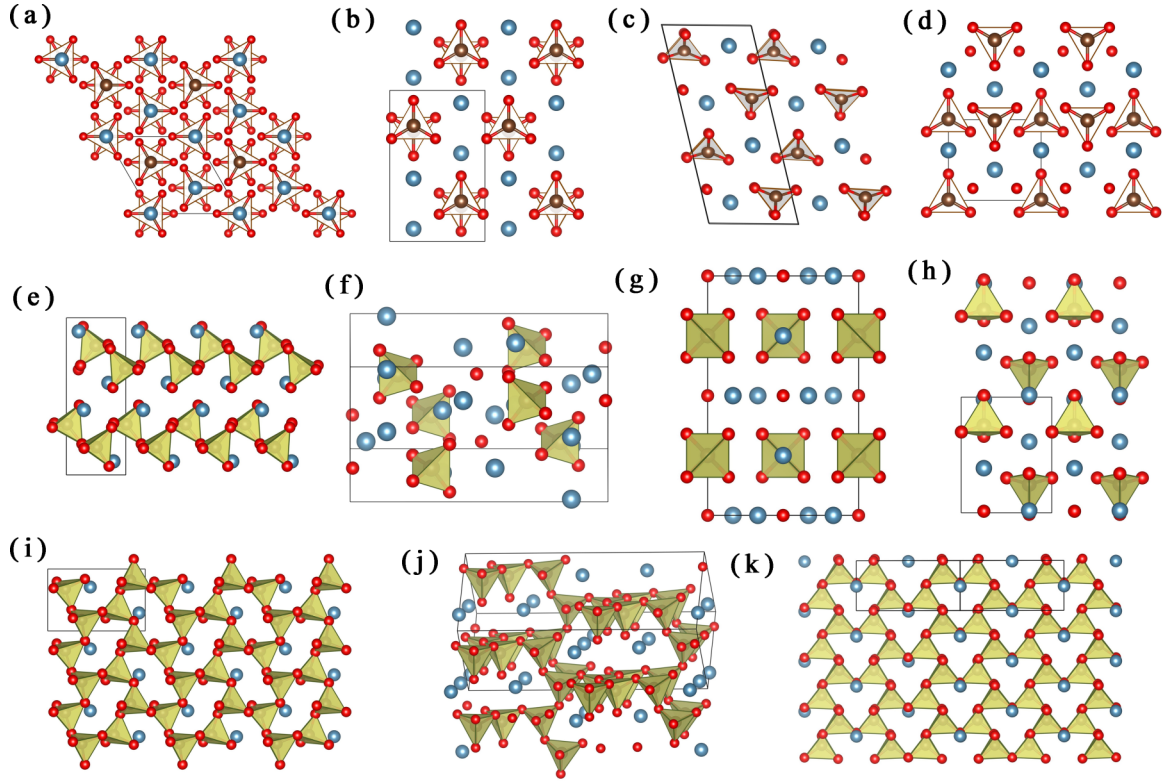


FIG. 5. Crystal structures of predicted stable and metastable calcium carbonates. (a) $R\bar{3}c$ (calcite); (b) $Pnma$ (aragonite); (c) $P2_1/c-1$; (d) $Pmmn$ (post-aragonite); (e) $P2_1/c-h$; (f) Cmc Ca_3CO_5 ; (g) $I4/mcm$ Ca_3CO_5 ; (h) $P2_1/m$ Ca_2CO_4 ; (i) Pc CaC_2O_5 ; (j) $Fdd2$ CaC_2O_5 ; (k) $C2$ CaC_2O_5 .

dra, as shown in Figs. 5(f)–5(h). Our calculations predict that calcium orthocarbonate Ca_3CO_5 becomes stable at very low pressure (11 GPa), which is much lower than the formation pressure of orthocarbonic acid (314 GPa) [28]. Chemically, Ca_3CO_5 can be represented as $CaO \cdot Ca_2CO_4$ with coexistence of both O^{2-} and CO_4^{4-} anions, while metastable Ca_2CO_4 is a typical orthocarbonate. Stability of Ca_3CO_5 at a surprisingly low pressure of 11 GPa means that the CO_4^{4-} units may also be present at such pressures in carbonate melts. Phonon calculations show that Ca_3CO_5 can be quenchable to ambient conditions at low temperatures.

Unlike Ca_3CO_5 and Ca_2CO_4 , with higher CO_2 content in CaC_2O_5 , CO_4^{4-} tetrahedra are connected into two-dimensional (2D) sheets in Pc - CaC_2O_5 and $C2$ - CaC_2O_5 , and into a three-dimensional (3D) framework in $Fdd2$ - CaC_2O_5 , as shown in Figs. 5(i)–5(k). Polymerization of CO_3^{2-} can be described as a transformation from carbonyl (C=O) functional groups to ether bonds (C-O-C), as shown in Fig. 6(a). The charged oxygen atom bonded to carbon is a nucleophilic site, whereas carbon atoms in CO_2 molecules are positively charged. This makes an electrophilic reaction possible, with polymerized CO_3^{2-} sharing one electron pair with CO_2 upon formation of a polymeric framework $C_2O_5^{2-}$ anion, as shown in Fig. 6(b).

As discussed in previous work [29], the oxygen sharing by CO_3^{2-} and CO_2 can be described as the oxo-Grothuss mechanism. Here the formation of CaC_2O_5 is its enhanced version. The combination of CO_3^{2-} and CO_2 offsets the

electrostatic repulsion between CO_3^{2-} anions. This is why the participation of CO_2 greatly decreases the polymerization pressure (compared with $CaCO_3$) from 75 to 33 GPa.

C. Are Ca_3CO_5 and CaC_2O_5 possible in the Earth's lower mantle?

By means of the quasiharmonic approximation (QHA), we first explored thermodynamic stability of all calcium carbonates in the pressure range from 80 to 160 GPa and a temperature of 2000 K. We note that, under such pressure and temperature conditions, CO_2 is expected to be solid [30]; its Gibbs free energy can thus be accurately computed based on

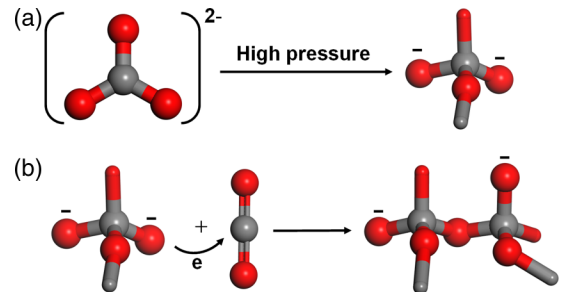


FIG. 6. Mechanism of (a) the polymerization of CO_3^{2-} and (b) the formation of CaC_2O_5 .

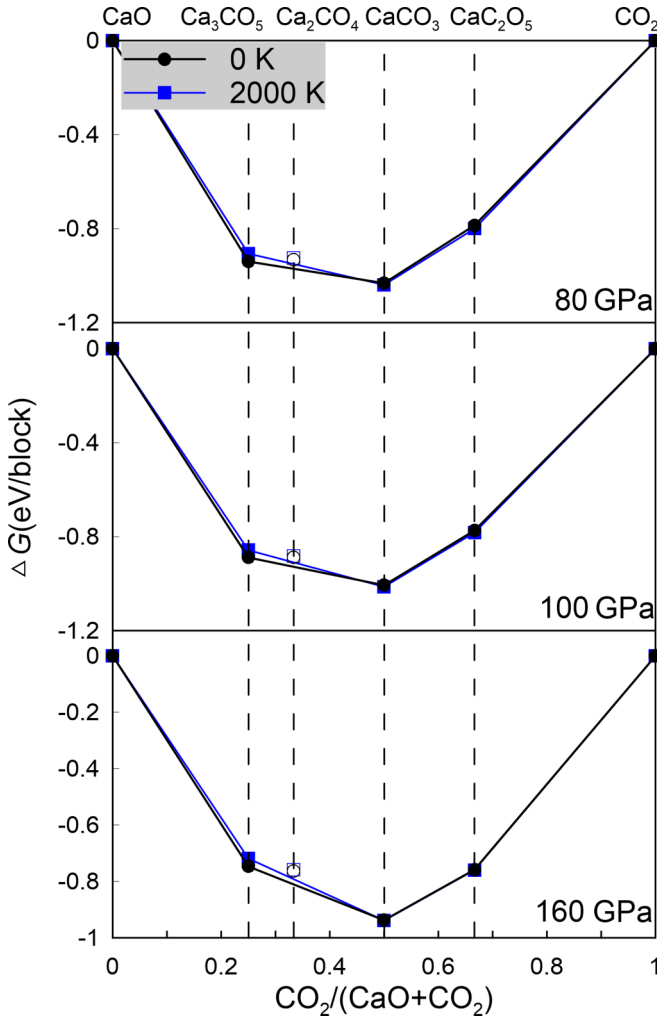


FIG. 7. Thermodynamic convex hulls for the CaO-CO₂ system at 2000 K and various pressures. Filled symbols denote stable structures, open symbols—metastable structures. Gibbs free energies of formation from oxides are normalized to one oxide unit.

the crystalline structure. As shown in Fig. 7, temperature has a small effect on the Gibbs free energy of formation of each calcium carbonate, and all three calcium carbonates (Ca₃CO₅, CaCO₃, and CaC₂O₅) that are stable at 0 K are still stable at 2000 K, indicating that they will not decompose at the Earth's lower mantle conditions.

Then, we studied the chemical stability of stable Ca₃CO₅, CaC₂O₅, and CaCO₃ and metastable Ca₂CO₄ by exploring their possible reactions with the compounds MgSiO₃, CaSiO₃, SiO₂, and MgO—we remind the reader that (Mg,Fe)SiO₃, CaSiO₃, and (Mg,Fe)O are the dominant compounds of the Earth's lower mantle, in their most stable forms at relevant conditions (e.g., [31]). These reactions are listed below:

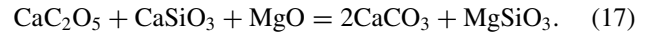
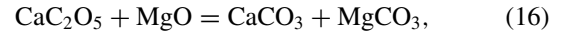
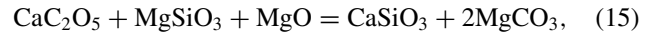
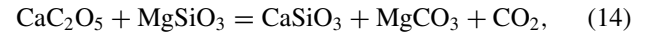
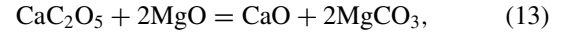
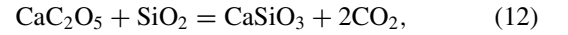
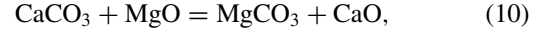
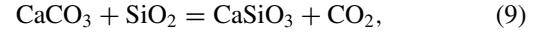
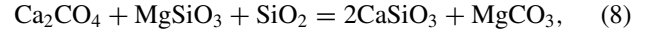
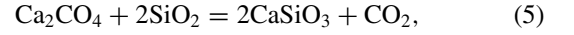
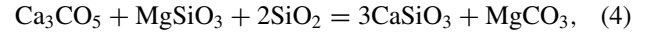
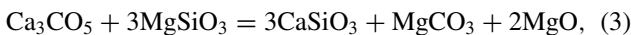
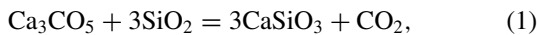


Figure 8 shows the computed Gibbs free energy of each reaction in the pressure range from 80 to 160 GPa and a temperature of 2000 K. Ca₃CO₅ and CaC₂O₅ cannot exist in the Earth's lower mantle: as shown in Figs. 8(a) and 8(b), Ca₃CO₅ will always react with MgSiO₃ and SiO₂; CaC₂O₅ will react with MgO. We found that CaCO₃ will not react with MgO, SiO₂, and MgSiO₃ at zero temperature and pressure above 90 GPa (see Fig. S3 in the Supplemental Material [10]), in agreement with previous results [5,6]. However, at 2000 K, there is a big change in the behavior of reaction (11)—CaCO₃ will always react with MgSiO₃ at pressures below 140 GPa, as shown in Fig. 8(c). Figure 9 shows the phase diagram for reaction (11). It shows that CaCO₃ will never exist in the Earth's lower mantle (i.e. at pressures in the range 24–136 GPa, temperatures >1800 K, and excess of MgSiO₃). MgCO₃ is the only stable carbonate in the lower mantle. Therefore, we conclude that throughout the Earth's lower mantle polymorphs of MgCO₃ are the main hosts of oxidized carbon.

IV. CONCLUSIONS

In summary, evolutionary crystal structure predictions have been performed for MgO-CO₂ and CaO-CO₂ systems with the aim of exploring stable magnesium and calcium carbonates at pressures ranging from 0 to 160 GPa. For the MgO-CO₂ system, we found that there is only one stable magnesium

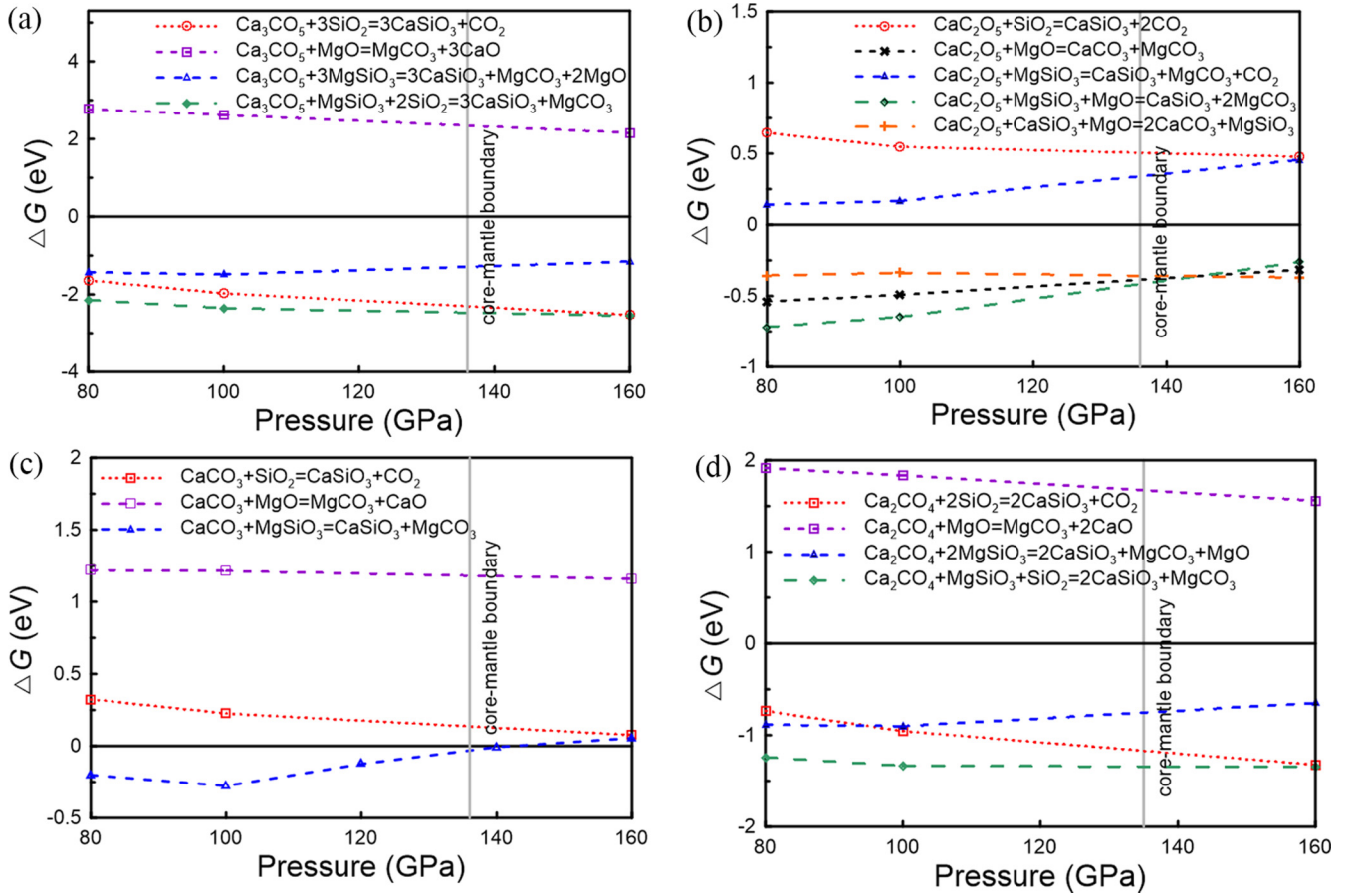


FIG. 8. Gibbs free energies of mantle-relevant reactions as a function of pressure (at 2000 K).

carbonate, MgCO_3 . For the CaO-CO_2 system, in addition to CaCO_3 , we also report two previously unknown stable calcium carbonates, Ca_3CO_5 , CaC_2O_5 , and one near-ground-state compound Ca_2CO_4 .

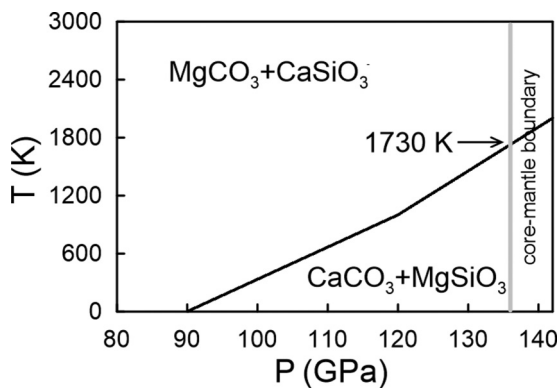
Ca_3CO_5 can be represented as $\text{CaO} \cdot \text{Ca}_2\text{CO}_4$, and is a calcium orthocarbonate, and is stable at a remarkably low pressure of 11 GPa. This is the lowest-pressure material with

CO_4 tetrahedra. CaC_2O_5 is the product of an electrophilic reaction: $\text{CO}_3^{2-} + \text{CO}_2$ and an enhanced version of the oxo-Grothuss mechanism, which greatly decreases the polymerization pressure of CO_3^{2-} : 33 GPa, compared to 75 GPa in CaCO_3 .

We have checked the chemical stability of Ca_3CO_5 and CaC_2O_5 in the Earth's lower mantle environments by investigating possible chemical reactions involving MgCO_3 , CO_2 , MgSiO_3 , CaSiO_3 , SiO_2 , CaO , and MgO . Our results indicate that MgCO_3 is the only carbonate that can exist in the Earth's lower mantle.

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FIG. 9. Relative stability of the $\text{MgCO}_3 + \text{CaSiO}_3$ assemblage versus $\text{CaCO}_3 + \text{MgSiO}_3$.

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