Novel high-pressure calcium carbonates

Xi Yao,[1,2] Congwei Xie,[1,3,*] Xiao Dong,[4,5,†] Artem R. Oganov,[1,3,6,‡] and Qingfeng Zeng[2]

[1]*International Center for Materials Discovery, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China*

[2]*Science and Technology on Thermostructural Composite Materials Laboratory, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China*

[3]*Skolkovo Institute of Science and Technology, 3 Nobel Street, Moscow 143026, Russia*

[4]*School of Physics, Nankai University, Tianjin 300071, People's Republic of China*

[5]*Center for High Pressure Science and Technology Advanced Research, Beijing 100193, People's Republic of China*

[6]*Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russia*

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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-CO_2 and CaO-CO_2 systems at pressures ranging from 0 to 160 GPa to search for thermodynamically stable magnesium and calcium carbonates. While $MgCO_3$ is the only stable magnesium carbonate, three calcium carbonates are stable under pressure: well-known $CaCO_3$, and previously unknown Ca_3CO_5 and CaC_2O_5. Ca_3CO_5 polymorphs are found to contain isolated orthocarbonate $CO_4{}^{4-}$ tetrahedra, and are stable at relatively low pressures (>11 GPa), whereas CaC_2O_5 is stable above 33 GPa and its polymorphs feature polymeric motifs made of CO_4 tetrahedra. Detailed analysis of the chemical stability of $CaCO_3$, Ca_3CO_5, and CaC_2O_5 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, $MgCO_3$ 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., Fe_3C cementite, diamond, carbonates) [1]. Over the past few decades, magnesium and calcium carbonates ($MgCO_3$ and $CaCO_3$) 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 $CaCO_3$ will become more favorable than $MgCO_3$ 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 ($CaCO_3$, $MgCO_3$) 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 $MgCO_3$ and $CaCO_3$. Tables S1 and S2 in the Supplemental Material [10] list high-pressure forms of $MgCO_3$ and $CaCO_3$ predicted in previous works [3,5,6]. From zero pressure up to the pressure of the core-mantle boundary (136 GPa), both $MgCO_3$ and $CaCO_3$ will experience several interesting phase transitions. For example, it was predicted that while polymorphs of $CaCO_3$ stable below 76 GPa [6] (or 75 GPa according to our calculations) feature CO_3 triangles, chains of CO_4 tetrahedra are present in the higher-pressure form of $CaCO_3$.

At ambient pressure and temperature, the carbon atom in CO_2 has *sp* hybridization with linear geometry and twofold coordination, while in $CO_3{}^{2-}$ it has sp^2 hybridization resulting in planar triangular geometry and threefold coordination. sp^3 hybridization (resulting in CO_4 tetrahedra) is unfavorable due to the very small size of the C^{4+} cation compared to the O^{2-} 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 $CaCO_3$ and $MgCO_3$ 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-CO_2, CaO-CO_2, Mg-C-O, Ca-C-O, and MgO-CaO-CO_2 systems using the

*Corresponding author: cwxie2011@126.com
†charlary@163.com
‡A.Oganov@skoltech.ru

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—$3s^23p^64s^2$, $3s^2$, $2s^22p^2$, and $2s^22p^4$ 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 $2\pi \times 0.05\ \text{Å}^{-1}$ were employed. Once stable compounds and structures were found, their properties were computed with denser k-point meshes, which had reciprocal-space resolution of $2\pi \times 0.03\ \text{Å}^{-1}$.

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-CO_2 system; at 0, 60, 100, and 160 GPa for the MgO-CO_2 system; and at 25, 50, 100, and 130 GPa for the ternary systems Mg-C-O, Ca-C-O, and MgO-CaO-CO_2. 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 $MgCO_3$ was found to be on the convex hull. This indicates that, besides $MgCO_3$, no other magnesium carbonates can be thermodynamically stable at mantle pressures. At the same time, in the CaO-CO_2 system, besides the well-known $CaCO_3$ we discover two thermodynamically stable calcium carbonates, Ca_3CO_5 and CaC_2O_5 (and one near-ground-state compound Ca_2CO_4), 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 CaC_2O_5 (Pc, $Fdd2$, and $C2$) and $Cmcm$-Ca_3CO_5 can maintain dynamical stability at 0 GPa; see Fig. S1 in the Supplemental Material [10]. This means that Ca_3CO_5 and CaC_2O_5 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 $CaCO_3$, 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-CO_2 and MgO-CO_2 systems (see Fig. S2 in the Supplemental Material [10]), we have obtained their pressure-composition phase diagrams at pressures up to 160 GPa (see Fig. 3). As shown in Fig. 3, stable phases and phase transition pressures in MgO, CaO, CO_2, $MgCO_3$,

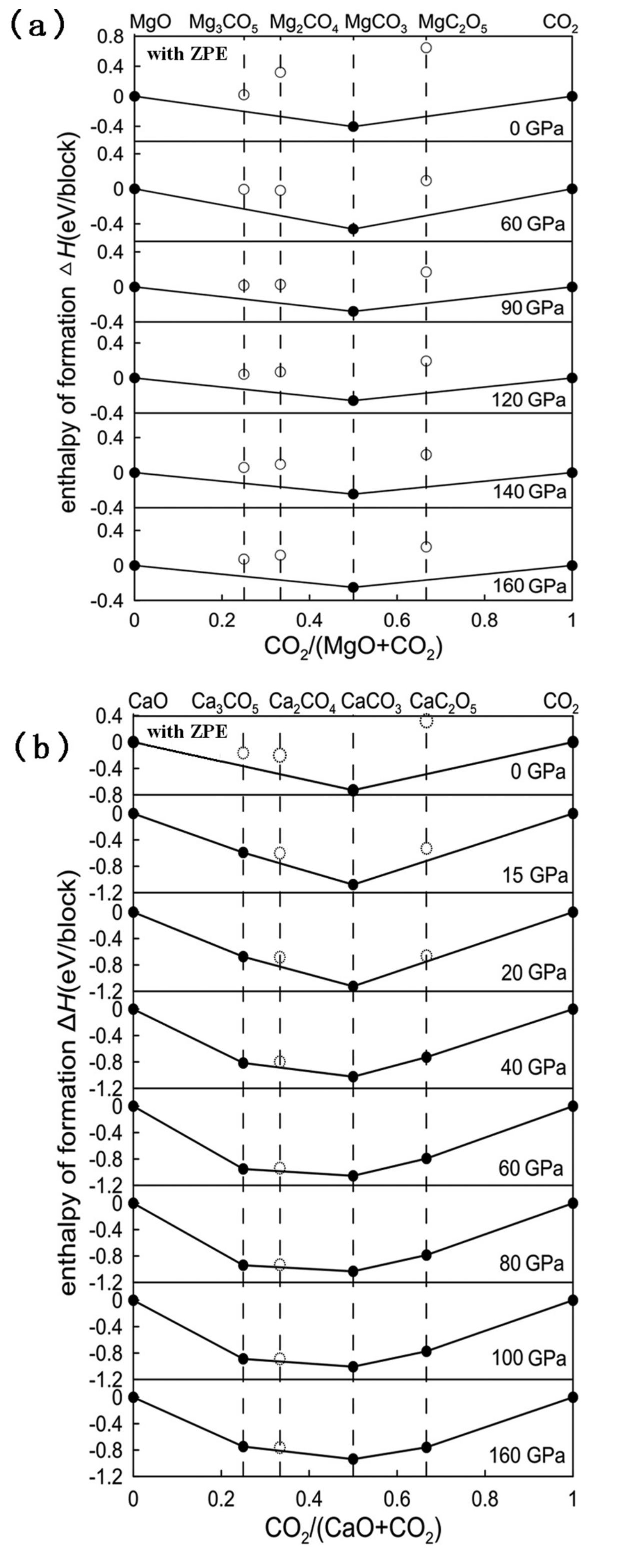

FIG. 1. Thermodynamic convex hulls for MgO-CO_2 and CaO-CO_2 systems at zero temperature and high pressure (with zero-point energy correction). Filled circles denote stable structures and open circles denote metastable structures. Enthalpies of formation from oxides are normalized to one oxide unit.

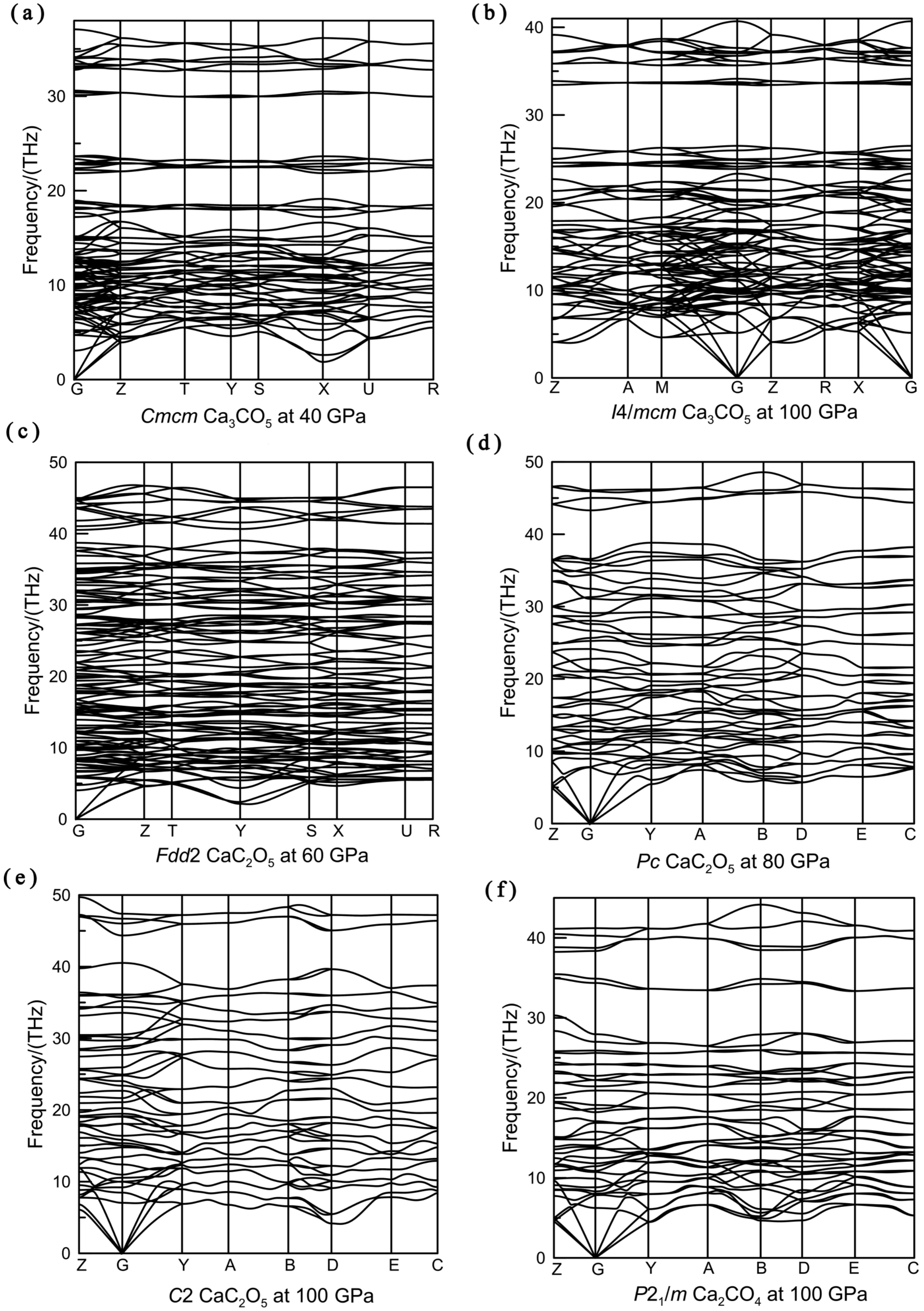

FIG. 2. Phonon dispersion curves of the predicted calcium carbonates at high pressures and zero temperature.

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 $P2_1/c$-l 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 *Cmcm* phase is predicted to become stable at

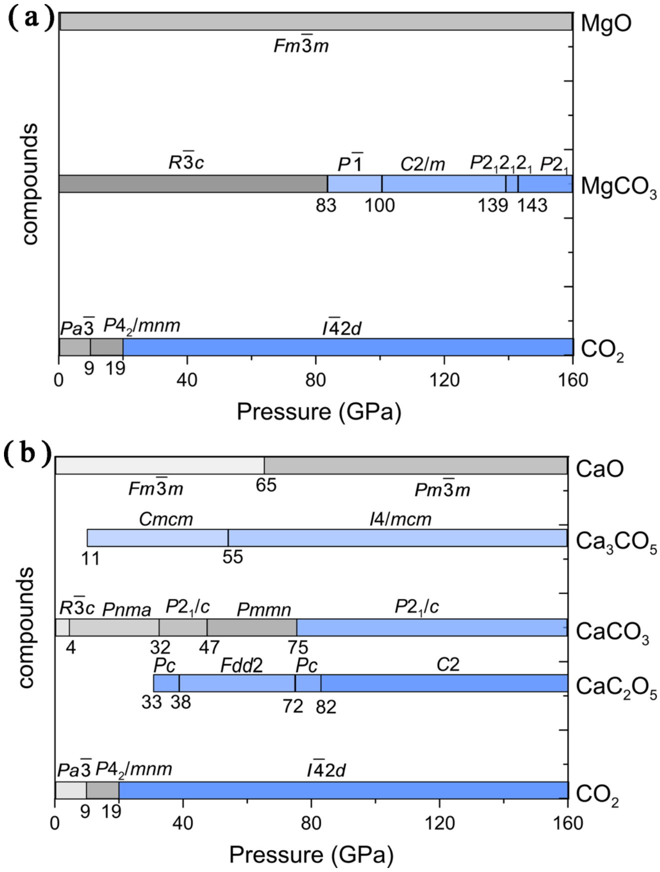

FIG. 3. Pressure-composition phase diagrams of MgO-CO_2 and CaO-CO_2 systems at zero temperature.

11 GPa, and to transform to the tetragonal $I4/mcm$ phase at 55 GPa; (2) for CaC_2O_5, 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 $CaCO_3$ and Ca_3CO_5, but not in CaC_2O_5, are accompanied by large volume discontinuities.

It should be possible to synthesize the predicted calcium carbonates (Ca_3CO_5 and CaC_2O_5). Several phases of $MgCO_3$ and $CaCO_3$, 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 $MgCO_3$, and $P2_1/c$ [6,25], $Pmmn$ [3,21], and thermodynamically metastable P-1 [3,26] phases of $CaCO_3$. Considering hundreds of papers where it was assumed that $CaCO_3$ 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 $CaCO_3$ have been carefully studied before [3,6]. With the increase of pressure, $CaCO_3$ successively adopts five phases (calcite R-3c, 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 CO_3^{2-} ions with sp^2 hybridization, while the fifth phase adopts a pyroxene-type structure with chains of corner-linked CO_4^{4-} tetrahedra above 75 GPa.

High-pressure phases of $CaCO_3$(>75 GPa) and $MgCO_3$(>83 GPa) contain CO_4^{4-} tetrahedra. In $CaCO_3$ above 75 GPa, we see chains of corner-sharing tetrahedra. In $MgCO_3$ above 83 GPa, CO_4^{4-} tetrahedra form $C_3O_9^{6-}$ rings, and above 180 GPa form chains [5,6]. The differences between $CaCO_3$ and $MgCO_3$ come from different sites of Ca and Mg. Ca^{2+} is much larger than Mg^{2+}, and requires the anion sublattice to have more open space to fit it.

On the Ca-rich side, our predicted phases include stable $Cmcm$-Ca_3CO_5, $I4/mcm$-Ca_3CO_5, and metastable $P2_1/m$-Ca_2CO_4, all of which contain isolated CO_4^{4-} tetrahe-

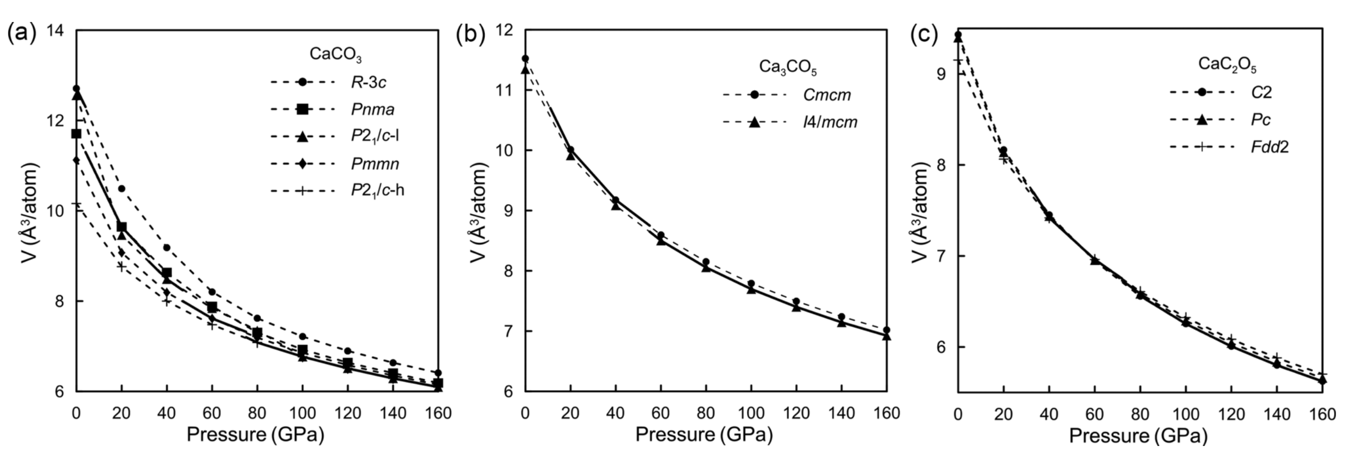

FIG. 4. Equations of state of all stable calcium carbonates at zero temperature. Solid lines denote equations of state of each phase in its region of stability.

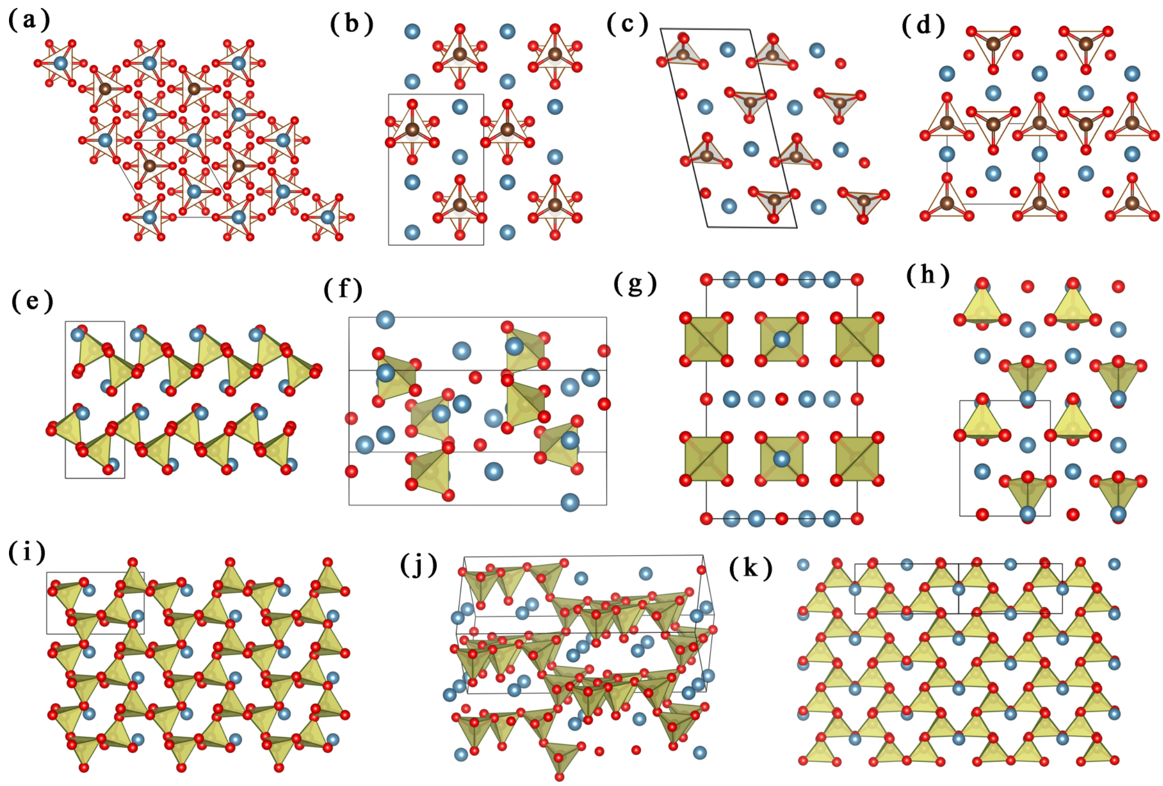

FIG. 5. Crystal structures of predicted stable and metastable calcium carbonates. (a) *R*-3*c* (calcite); (b) *Pnma* (aragonite); (c) $P2_1/c$-l; (d) *Pmmn* (post-aragonite); (e) $P2_1/c$-h; (f) *Cmcm* Ca_3CO_5; (g) $I4/mcm$ Ca_3CO_5; (h) $P2_1/m$ Ca_2CO_4; (i) *Pc* CaC_2O_5; (j) *Fdd*2 CaC_2O_5; (k) *C*2 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 *C*2-CaC_2O_5, and into a three-dimensional (3D) framework in *Fdd*2-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-Grotthuss 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

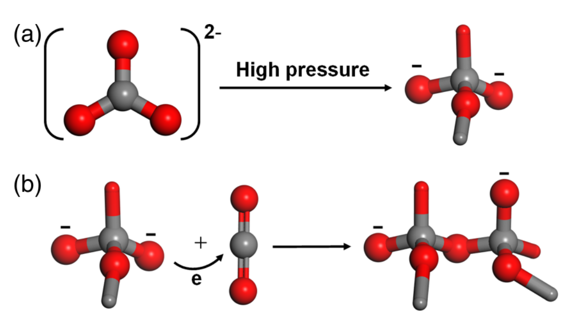

FIG. 6. Mechanism of (a) the polymerization of $CO_3{}^{2-}$ and (b) the formation of CaC_2O_5.

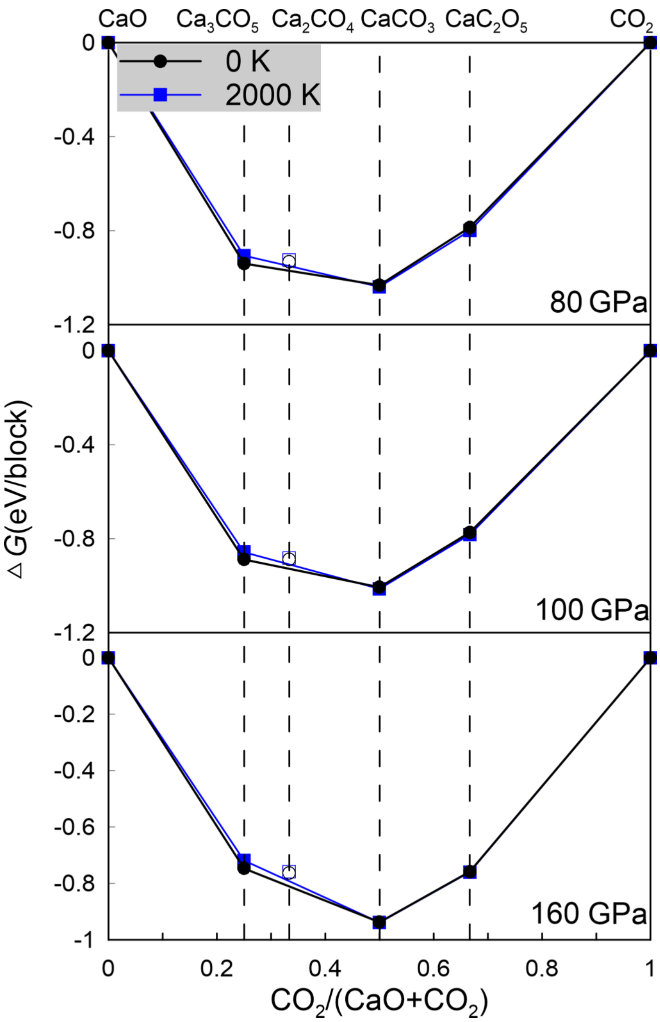

FIG. 7. Thermodynamic convex hulls for the CaO-CO_2 system at 2000 K and various pressures. Filled symbols denote stable structures, open symbols–metastable structures. Gibbs free energies of formation from oxides are normalized to one oxide unit.

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 (Ca_3CO_5, $CaCO_3$, and CaC_2O_5) 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 Ca_3CO_5, CaC_2O_5, and $CaCO_3$ and metastable Ca_2CO_4 by exploring their possible reactions with the compounds $MgSiO_3$, $CaSiO_3$, SiO_2, and MgO—we remind the reader that (Mg,Fe)SiO_3, $CaSiO_3$, 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:

$$Ca_3CO_5 + 3SiO_2 = 3CaSiO_3 + CO_2, \quad (1)$$

$$Ca_3CO_5 + MgO = MgCO_3 + 3CaO, \quad (2)$$

$$Ca_3CO_5 + 3MgSiO_3 = 3CaSiO_3 + MgCO_3 + 2MgO, \quad (3)$$

$$Ca_3CO_5 + MgSiO_3 + 2SiO_2 = 3CaSiO_3 + MgCO_3, \quad (4)$$

$$Ca_2CO_4 + 2SiO_2 = 2CaSiO_3 + CO_2, \quad (5)$$

$$Ca_2CO_4 + MgO = MgCO_3 + 2CaO, \quad (6)$$

$$Ca_2CO_4 + 2MgSiO_3 = 2CaSiO_3 + MgCO_3 + MgO, \quad (7)$$

$$Ca_2CO_4 + MgSiO_3 + SiO_2 = 2CaSiO_3 + MgCO_3, \quad (8)$$

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2, \quad (9)$$

$$CaCO_3 + MgO = MgCO_3 + CaO, \quad (10)$$

$$CaCO_3 + MgSiO_3 = CaSiO_3 + MgCO_3, \quad (11)$$

$$CaC_2O_5 + SiO_2 = CaSiO_3 + 2CO_2, \quad (12)$$

$$CaC_2O_5 + 2MgO = CaO + 2MgCO_3, \quad (13)$$

$$CaC_2O_5 + MgSiO_3 = CaSiO_3 + MgCO_3 + CO_2, \quad (14)$$

$$CaC_2O_5 + MgSiO_3 + MgO = CaSiO_3 + 2MgCO_3, \quad (15)$$

$$CaC_2O_5 + MgO = CaCO_3 + MgCO_3, \quad (16)$$

$$CaC_2O_5 + CaSiO_3 + MgO = 2CaCO_3 + MgSiO_3. \quad (17)$$

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. Ca_3CO_5 and CaC_2O_5 cannot exist in the Earth's lower mantle: as shown in Figs. 8(a) and 8(b), Ca_3CO_5 will always react with $MgSiO_3$ and SiO_2; CaC_2O_5 will react with MgO. We found that $CaCO_3$ will not react with MgO, SiO_2, and $MgSiO_3$ 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)—$CaCO_3$ will always react with $MgSiO_3$ at pressures below 140 GPa, as shown in Fig. 8(c). Figure 9 shows the phase diagram for reaction (11). It shows that $CaCO_3$ 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 $MgSiO_3$). $MgCO_3$ is the only stable carbonate in the lower mantle. Therefore, we conclude that throughout the Earth's lower mantle polymorphs of $MgCO_3$ are the main hosts of oxidized carbon.

IV. CONCLUSIONS

In summary, evolutionary crystal structure predictions have been performed for MgO-CO_2 and CaO-CO_2 systems with the aim of exploring stable magnesium and calcium carbonates at pressures ranging from 0 to 160 GPa. For the MgO-CO_2 system, we found that there is only one stable magnesium

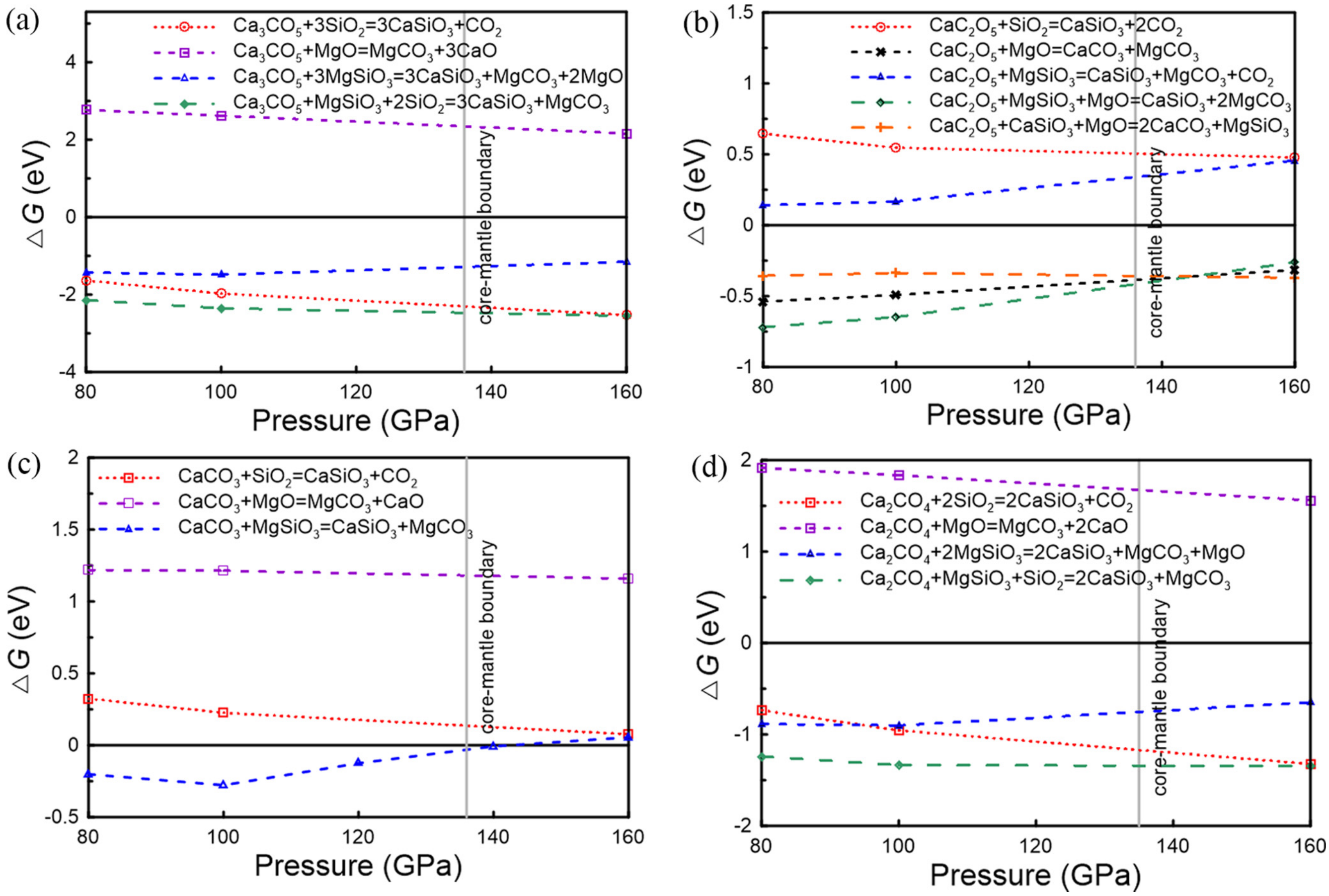

FIG. 8. Gibbs free energies of mantle-relevant reactions as a function of pressure (at 2000 K).

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 $CaO \cdot Ca_2CO_4$, and is a calcium orthocarbonate, and is stable at a remarkably low pressure of 11 GPa. This is the lowest-pressure material with

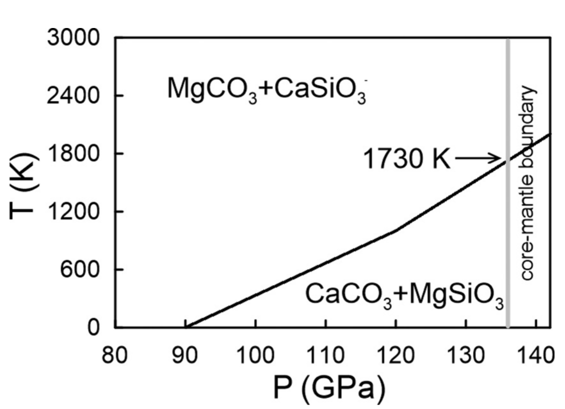

FIG. 9. Relative stability of the $MgCO_3 + CaSiO_3$ assemblage versus $CaCO_3 + MgSiO_3$.

CO_4 tetrahedra. CaC_2O_5 is the product of an electrophilic reaction: $CO_3^{2-} + CO_2$ and an enhanced version of the oxo-Grotthuss 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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