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Novel high-pressure calcium carbonates

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Abstract

Calcium and magnesium carbonates are believed to be the host compounds for most of the oxidized carbon in the Earth's mantle. Here, using 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 newly predicted 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 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. We conclude that MgCO₃ is the main host of oxidized carbon throughout the lower mantle.

Introduction

Behaviour 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]. 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 change this conclusion (and this is indeed the case). Moreover, all previous previous works assumed that 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 compound appear so often that they are more of a rule than 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 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 polymorphs of CaCO_3 stable below 76 GPa ^[6] (or 75 GPa according to our calculations) feature CO_3 -triangles, while chains of CO_4 tetrahedra are present in the higher-pressure form of CaCO_3 .

At ambient pressure and temperature, carbon atom in CO_2 has sp -hybridization with linear geometry and 2-fold coordination, while in CO_3^{2-} it has sp^2 -hybridization resulting in planar triangular geometry and 3-fold coordination. sp^3 -hybridization (resulting in CO_4 tetrahedra) is unfavorable due to very small size of C^{4+} cation compared to 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

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, new 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.

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 variable-composition evolutionary algorithm (EA) technique, as implemented in the USPEX code ^[10-13]. 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 previous generation were 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 ^[14] in the framework of density functional theory ^[15]. In these calculations, we used the Perdew-Burke-Ernzerhof generalized gradient approximation functional (PBE-GGA ^[16]) to treat exchange-correlation, and the all-electron projector augmented wave (PAW ^[17]) 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 $2\pi \times 0.05 \text{ \AA}^{-1}$ were employed. Once stable compounds and structures were found, their properties were computed with denser k -points meshes, which had reciprocal-space resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$.

Results and discussions

1. Phase stability at mantle pressures

We have performed crystal structure predictions at 0 GPa, 15 GPa, 20 GPa, 40 GPa, 60 GPa, 80 GPa 100 GPa and 160 GPa for the CaO-CO₂ system, at 0 GPa, 60 GPa, 100 GPa and 160 GPa for the MgO-CO₂ system, and 25 GPa, 50 GPa, 100 GPa, 130 GPa for 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, except 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 have discovered two hitherto unreported thermodynamically stable calcium carbonates Ca₃CO₅ and CaC₂O₅ (and one near-ground state compound Ca₂CO₄), as shown in Fig. 1(b). Phonon calculations show that the two new stable calcium carbonate phases are dynamically stable, i.e. 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 Supplementary Materials. This means that Ca₃CO₅ and CaC₂O₅ can be quenchable to ambient conditions at low temperature. Lattice parameters and enthalpies of formation of stable and metastable calcium carbonates were listed in Table S3 in Supplementary Materials. For the well-known CaCO₃, we have also listed available experimental and theoretical values for comparison^[18-20].

By calculating enthalpy-pressure curves for all stable compounds in the CaO-CO₂ and MgO-CO₂ systems (see Fig. S2 in Supplementary Materials), 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, CO₂, MgCO₃ and CaCO₃ are in good agreement with previous studies^[3,5,6, 21-23]. We note that, for CaCO₃, Smith *et al.* recently proposed a new *P2₁/c-II* phase which is stable between 27.2 GPa and 37.5 GPa^[24]. Unfortunately, we missed this structure in the present structural predictions; moreover, we are unable to include this structure in the present study because of the lack of its detailed structural parameters. Considering the slight energy difference between *P2₁/c-II* phase and *P2₁/c-I* of CaCO₃, we should

say that $P2_1/c$ -II phase of CaCO_3 will not affect our main conclusion too much. 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 11 GPa, and to transform to tetragonal $I4/mcm$ phase at 55 GPa; (2) For CaC_2O_5 , above 33 GPa, four stable phases (low-pressure Pc , $Fdd2$, high-pressure Pc and $C2$) are predicted. Structural transformation from low-pressure monoclinic Pc -phase to orthorhombic $Fdd2$ -phase occurs at 38 GPa, and from $Fdd2$ -phase to high-pressure monoclinic Pc -phase at 72 GPa, and from high-pressure Pc -phase to monoclinic $C2$ -phase at 82 GPa. Fig.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 newly 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 $C2/m$ ^[5] and $P2_1$ ^[5] phases in MgCO_3 , and $P2_1/c$ ^[6,24], $Pmmn$ ^[3,20] and thermodynamically metastable $P-1$ ^[3,25] in 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 newly predicted calcium carbonates will stimulate experiments.

2. Crystal structures of stable calcium carbonates

Crystal structures of the predicted stable and metastable calcium carbonates, visualized by VESTA package ^[26], 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 $P2_1/c$, post-aragonite $Pmmn$, and high-pressure $P2_1/c$). As shown in Fig. 5(a)-(e), we can find that the former four phases contain triangular CO_3^{2-} ions with sp^2 -hybridization, while the fifth phase adopts 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 $\text{C}_3\text{O}_9^{6-}$ 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 newly predicted phases include stable *Cmcm*- Ca_3CO_5 , *I4/mcm*- Ca_3CO_5 and metastable *P2₁/m*- Ca_2CO_4 , all of which contain isolated CO_4^{4-} tetrahedra, as shown in Fig. 5(f)-(h). Our calculations prove that calcium orthocarbonate Ca_3CO_5 can be stable at very low pressure (11 GPa), which is much lower than the formation pressure of orthocarbonic acid (314 GPa) [27]. Chemically, Ca_3CO_5 can be represented as $\text{CaO} \cdot \text{Ca}_2\text{CO}_4$ 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.

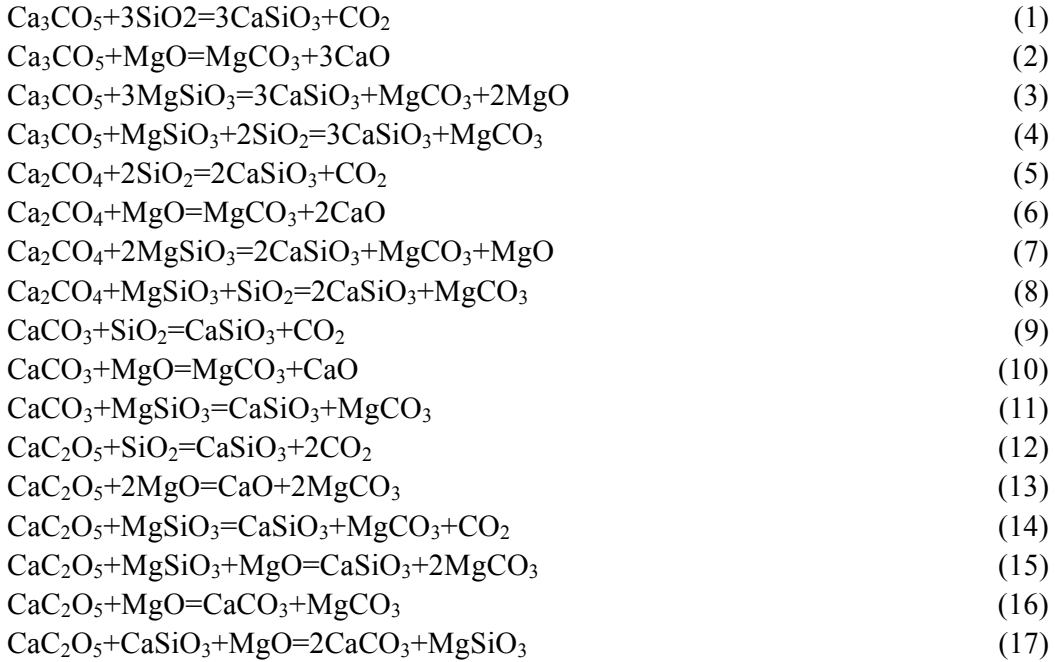
Unlike Ca_3CO_5 and Ca_2CO_4 , with higher CO_2 content in CaC_2O_5 , CO_4^{4-} tetrahedra are connected into 2D-sheets in *Pc*- CaC_2O_5 and *C2*- CaC_2O_5 , and into a 3D-framework in *Fdd2*- CaC_2O_5 , as shown in Fig. 5(i)-(k). Polymerization of CO_3^{2-} can be described as a transformation from carbonyl ($\text{C}=\text{O}$) functional groups to ether bonds ($\text{C}-\text{O}-\text{C}$), 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 $\text{C}_2\text{O}_5^{2-}$ anion, as shown in Fig. 6(b).

As discussed in previous work [28], the oxygen sharing by CO_3^{2-} and CO_2 can be described as 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.

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

By means of the quasi-harmonic approximation (QHA), we first explored thermodynamic stability of all calcium carbonates in the pressure range from 80 GPa to 160 GPa and temperature at 2000 K. We note that, under such pressure and temperature conditions, CO_2 is expected to be solid ^[29]; its Gibbs free energy can thus be accurately computed based on the crystalline structure. As shown in Fig. 7, temperature has a tiny effect on 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 compounds MgSiO_3 ^[30,31], CaSiO_3 ^[32,33], SiO_2 ^[34,35] and MgO - we remind that $(\text{Mg,Fe})\text{SiO}_3$, CaSiO_3 and $(\text{Mg,Fe})\text{O}$ are the dominant compounds of the Earth's lower mantle. These reactions are listed below:



For each chemical reaction, we used the most stable structures of each compound at relevant pressures and temperatures. It should be noted that there are some other phases suggested for some major mantle compounds ^[36], but we would prefer not to

take them as references in view of their thermodynamic metastabilities.

Fig. 8 shows the computed Gibbs free energy of each reaction in the pressure range from 80 GPa to 160 GPa and temperature of 2000 K. For the newly predicted Ca_3CO_5 and CaC_2O_5 , we found that they both cannot exist in the Earth's lower mantle. As shown in Fig. 8(a)&(b), Ca_3CO_5 will always react with MgSiO_3 and SiO_2 ; CaC_2O_5 does not react with the main mantle compound MgSiO_3 , but will react with MgO , and also with a mixture of MgO and CaSiO_3 . For the well-known CaCO_3 , 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 Supplementary Materials), 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). Fig. 9 shows the phase diagram for reaction (11). It shows that CaCO_3 will never exist in the Earth's lower mantle, with large excess of MgSiO_3 . Therefore, we conclude that throughout the Earth's lower mantle polymorphs of MgCO_3 are the main hosts of oxidized carbon.

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 GPa to 160 GPa. For the MgO-CO_2 system, we found that there is only one stable magnesium carbonate MgCO_3 . For the CaO-CO_2 system, in addition to CaCO_3 , we also discovered two hitherto 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 electrophilic reaction: $\text{CO}_3^{2-} + \text{CO}_2$ and an enhanced version of oxo-Grothuss mechanism, which greatly decreases the polymerization pressure of CO_3^{2-} : 33 GPa, compared to 75 GPa in

CaCO₃.

We have checked chemical stability of Ca₃CO₅ and CaC₂O₅ in the Earth's lower mantle environments by investigating possible chemical reactions involving MgCO₃, CO₂, MgSiO₃, CaSiO₃, SiO₂, CaO, and MgO. Our results indicate that, while chemically very interesting, none of these new carbonates can be present in the Earth's mantle. Ca₃CO₅ is so far the lowest pressure stable compound with CO₄ tetrahedra and suggests that already at pressures of ~11 GPa, carbonate melts can have a large concentration of CO₄ groups.

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Figure legend:

Fig. 1 Thermodynamic convex hulls for MgO-CO₂ and CaO-CO₂ systems at zero temperature and high pressure (with zero-point energy correction).

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

Fig. 3 Pressure-composition phase diagrams of MgO-CO₂ and CaO-CO₂ system at zero temperature.

Fig. 4 Equations of state of all stable calcium carbonates at zero temperature.

Fig. 5 Crystal structures of predicted stable and metastable calcium carbonates.

Fig. 6 Mechanism of (a) the polymerization of CO₃²⁻ and (b) the formation of CaC₂O₅.

Fig. 7 Thermodynamic convex hulls for the CaO-CO₂ system at 2000 K and various pressures.

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

Fig. 9 Relative stability of the MgCO₃ + CaSiO₃ assemblage versus CaCO₃ + MgSiO₃.

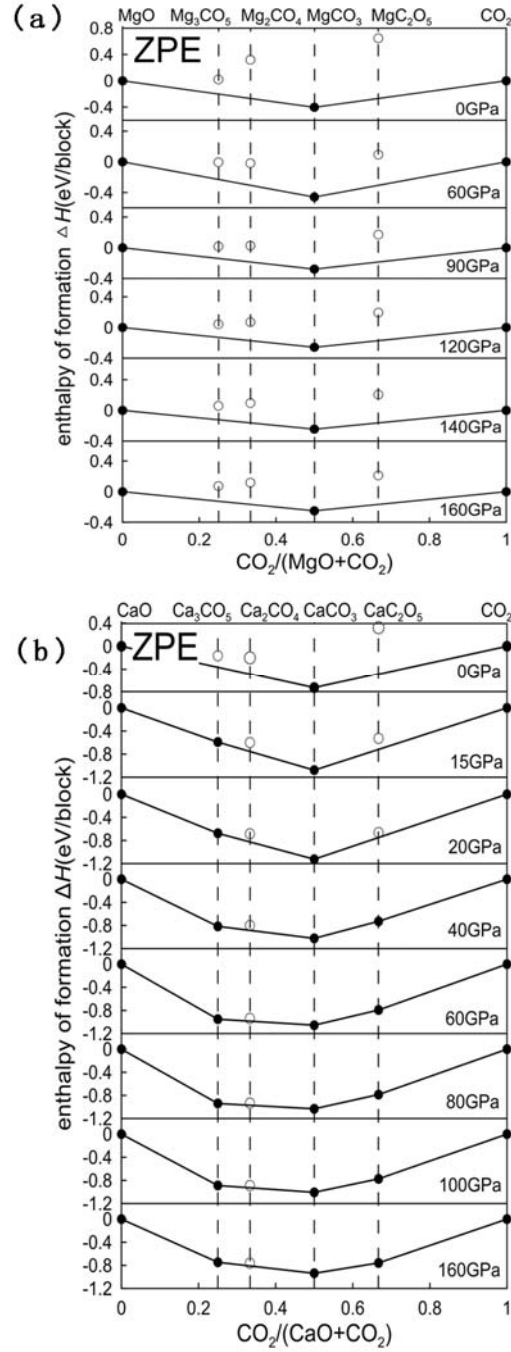


Fig. 1 Thermodynamic convex hulls for MgO-CO₂ and CaO-CO₂ systems at zero temperature and high pressure (with zero-point energy correction). Filled circles denote stable structures and open circles denote metastable structures. Enthalpies of formation from oxides are normalized to one oxide unit.

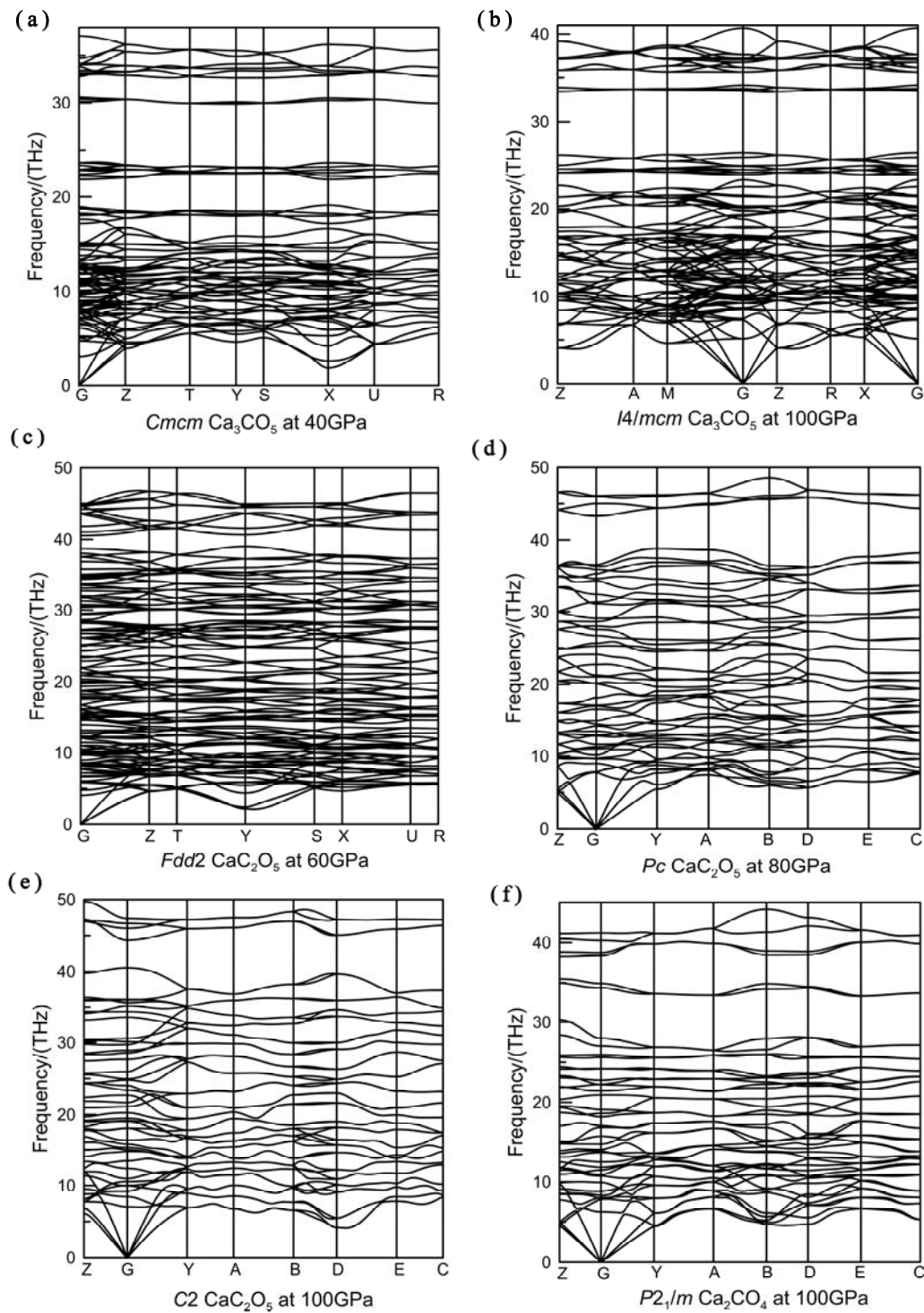


Fig. 2 Phonon dispersion curves of the newly predicted calcium carbonates at high pressures and zero temperature.

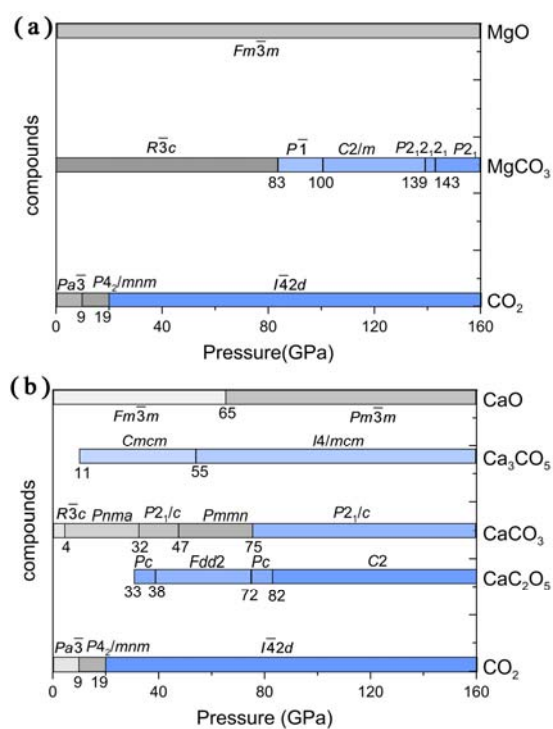


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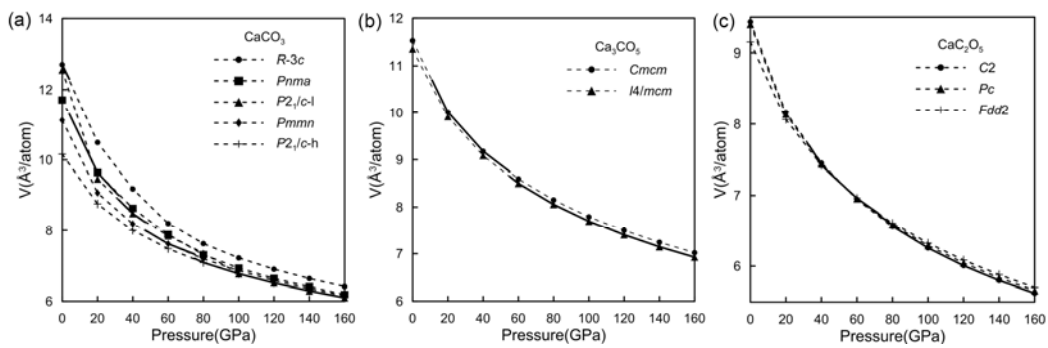


Fig. 4 Equations of state of all stable calcium carbonates at zero temperature. Solid lines denote equations of state of each phase in its region of stability.

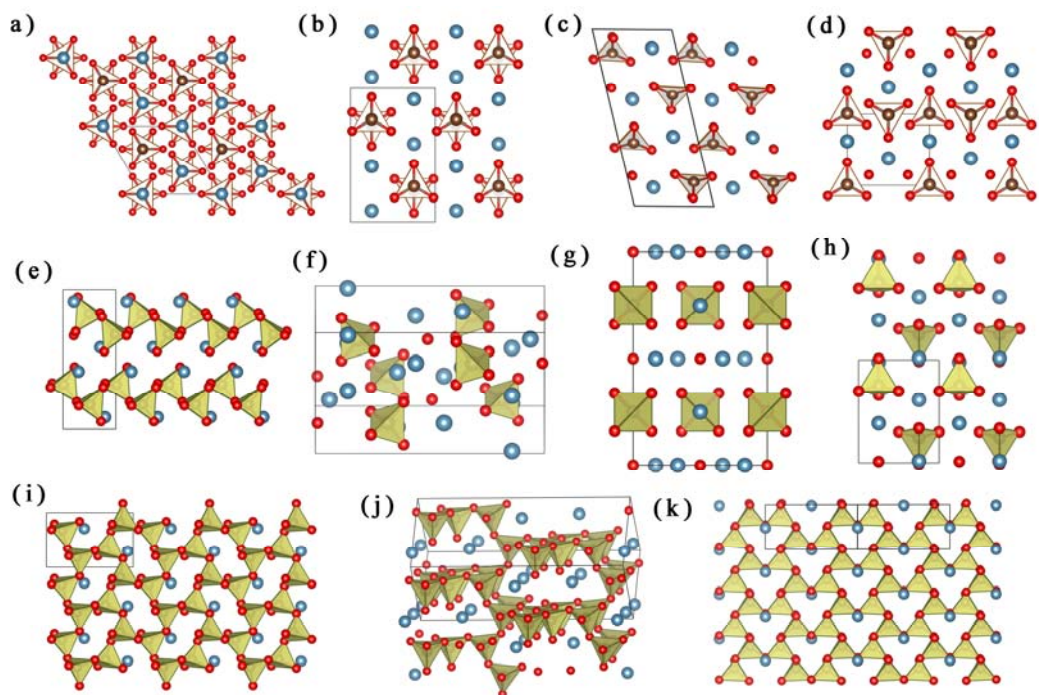


Fig. 5 Crystal structures of predicted stable and metastable calcium carbonates. (a) $R\bar{3}c$ (calcite); (b) $Pnma$ (aragonite); (c) $P2_1/c-l$; (d) $Pmmn$ (post-aragonite); (e) $P2_1/c-h$; (f) $Cmcmm$ Ca_3CO_5 ; (g) $I4/mcm$ Ca_3CO_5 ; (h) $P2_1/m$ Ca_2CO_4 ; (i) Pc CaC_2O_5 ; (j) $Fdd2$ CaC_2O_5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

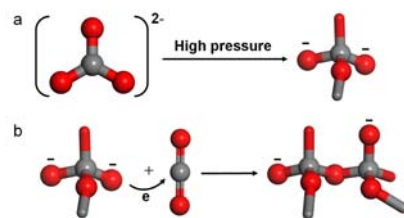


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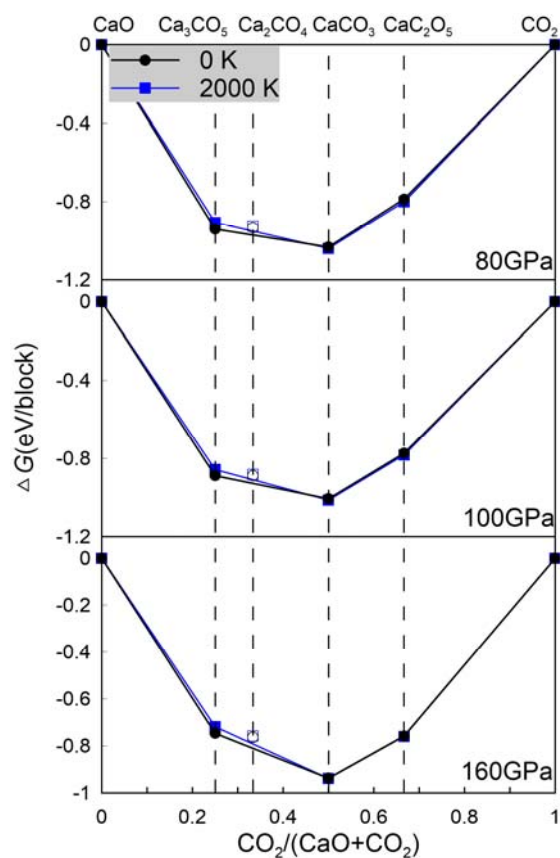


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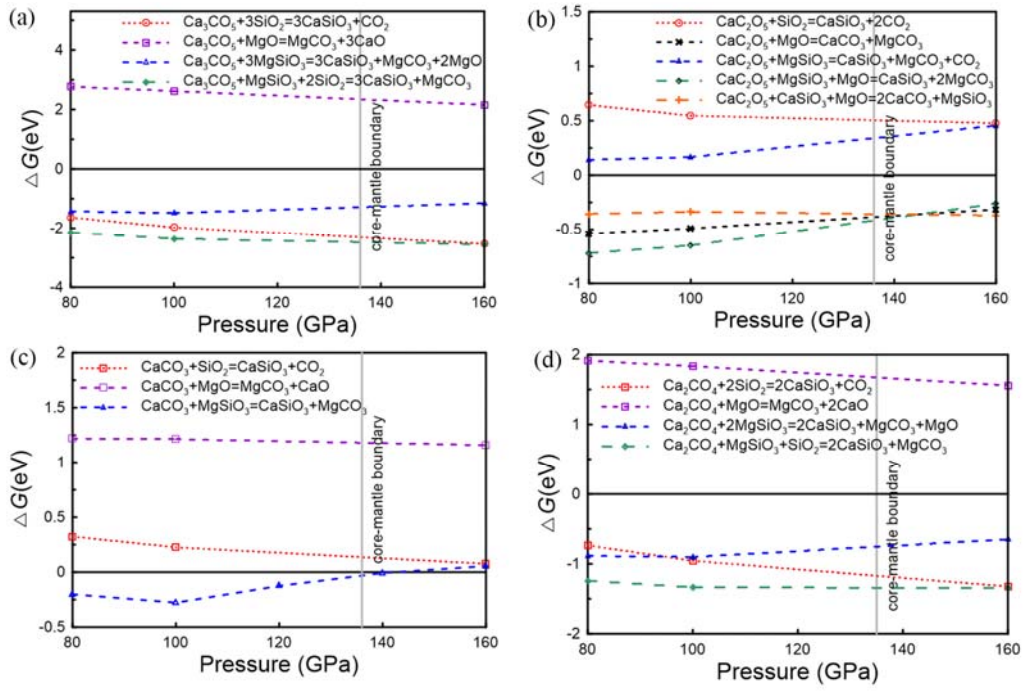


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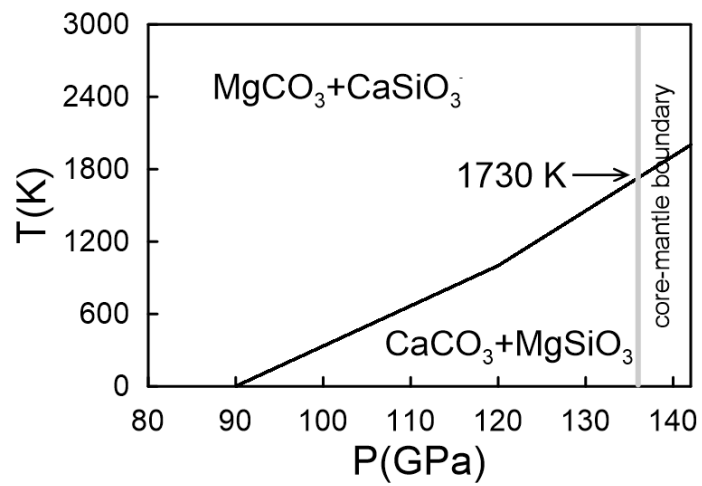


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