Structures and stability of calcium and magnesium carbonates at mantle pressures

Chris J. Pickard

Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, UK
London Institute for Mathematical Sciences, 35a South Street, Mayfair, London, W1K 2XF, UK

Richard J. Needs

Theory of Condensed Matter Group, Cavendish Laboratory,
J J Thomson Avenue, Cambridge CB3 0HE, UK

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Ab initio random structure searching (AIRSS) and density functional theory methods are used to predict structures of calcium and magnesium carbonate (CaCO$_3$ and MgCO$_3$) at high pressures. We find a previously unknown CaCO$_3$ structure which is more stable than the aragonite and "post aragonite" phases in the range 32–48 GPa. At pressures from 67 GPa to well over 100 GPa the most stable phase is a previously unknown CaCO$_3$ structure of the pyroxene type with fourfold coordinated carbon atoms. We also predict a stable structure of MgCO$_3$ in the range 85–101 GPa. Our results lead to a revision of the phase diagram of CaCO$_3$ over more than half the pressure range encountered within the Earth’s mantle, and smaller changes to the phase diagram of MgCO$_3$. We predict CaCO$_3$ to be more stable than MgCO$_3$ in the Earth’s mantle above 100 GPa, and that CO$_2$ is not a thermodynamically stable compound under deep mantle conditions. Our results have significant implications for understanding the Earth’s deep carbon cycle.

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I. INTRODUCTION

The occurrence of CO$_2$ within magmas and volcanic gases indicates a significant carbon presence within the Earth’s lower mantle\cite{1,2}. Carbon has a low solubility in mantle silicates and the majority of the oxidized carbon in the Earth's mantle is believed to exist in the form of carbonates. Calcium and magnesium carbonate (CaCO$_3$ and MgCO$_3$) are the main sources and sinks of atmospheric CO$_2$ within the Earth’s mantle. Carbonates are conveyed into the deep Earth by subduction, and carbon is recycled to the surface via volcanic processes in the form of CO$_2$-containing fluids and solids, and diamonds\cite{3,4}. However, the details of carbon storage within the Earth’s interior are unclear. The Deep Carbon Observatory\cite{5} has been set up to investigate carbon storage within the Earth’s deep interior. CaCO$_3$ and MgCO$_3$ play fundamental roles in the global carbon cycle and influence the climate of our planet\cite{6,7}. Knowledge of the structures, energetics and other properties of CaCO$_3$ and MgCO$_3$ at high pressures is therefore important in understanding the Earth’s mantle, and especially the carbon cycle.

The low-pressure calcite form of CaCO$_3$ is one of the most abundant minerals on the Earth’s surface and is the main constituent of metamorphic marbles. Several metastable calcite-like phases have been observed\cite{8,9,10,11,12,13}, and a calcite-related phase has been reported at around 25 GPa\cite{14,15}. At pressures of about 2 GPa calcite transforms to the aragonite structure\cite{16,17,18} of $P_nma$ symmetry. At about 40 GPa aragonite transforms into the “post aragonite” ($Pnmn$) structure of CaCO$_3$, which is stable up to at least 86 GPa\cite{19,20}. The low pressure magnesium phase of MgCO$_3$ has the same structure as calcite.

Experiments indicate that magnesite is stable up to 80 GPa\cite{21}, and a phase transition occurs above 100 GPa to an unknown magnesite II structure\cite{22,23}.

II. STRUCTURE SEARCHES

Density functional theory (DFT) calculations for high pressure phases of CaCO$_3$ and MgCO$_3$ were performed by Oganov et al. using an evolutionary structure searching algorithm\cite{24,25,26}. These calculations predicted a transition from the calcite to aragonite to "post aragonite" structures of CaCO$_3$, followed by a transition to a structure of $C222_1$ symmetry at pressures over 100 GPa. Similar calculations for MgCO$_3$ predicted transitions from magnesite to a structure of $C2/m$ symmetry at 82 GPa, followed by a transition to a structure of $P2_1$ symmetry at 138 GPa, and a phase of $Pna2_1$ symmetry at 160 GPa\cite{27}.

Calculations using the ab initio random structure searching (AIRSS) technique\cite{28} have led to the discovery of structures that have subsequently been verified by experiment, for example, in silico\cite{29}, aluminium hydride\cite{30}, ammonia monohydrate\cite{31} and ammonia dihydrate\cite{32}. In the basic AIRSS approach a cell volume and shape is selected at random from within reasonable ranges, the atoms are added at random positions, and the system is relaxed until the forces on the atoms are negligible and the pressure takes the required value. This procedure is repeated many times, leading to a reasonably unbiased scheme which allows a significant portion of the “structure space” to be investigated, although the sampling may be rather sparse. This approach is often successful for small systems, but it involves sampling a large portion...
of the high-energy structure space which is not normally of interest. We therefore reduce the size of the structure space investigated by constraining the searches.

We first perform searches in small cells, constraining the initial structures so that all of the atoms are at least 1 Å apart. The low-enthalpy structures obtained from these calculations give us information about the favorable bonding configurations and likely nearest neighbor distances between the different atomic types. At low pressures we find that the low-enthalpy structures contain well-defined triangular CO$_3$ or ring C$_3$O$_9$ units, and therefore we place these units and Ca or Mg atoms randomly within the cells of random shapes. We ensure that the atoms are not too close together by constraining the minimum distances between atoms for each of the six possible pairs of atomic species. The six minimum distances are obtained from low-enthalpy small-cell structures. To construct new larger structures that approximately satisfy the distances from low-enthalpy small-cell structures to previous structures found in the small-cell searches. To construct the initial structures at higher pressures we use minimum distance constraints. This approach helps to space out the different species appropriately, while retaining a high degree of randomness. We perform searches at both low and high pressures, using structures which are constrained to have a certain symmetry which is enforced during the relaxation, but are otherwise random. This approach is useful because low energy structures often possess symmetry, although symmetry constraints break up the allowed structure space into disconnected regions and can prevent some structures from relaxing to lower energy ones. We consider structures containing up to eight formula units (f.u.) for CaCO$_3$ and twelve f.u. for MgCO$_3$.

Our first-principles DFT calculations are performed using the CASTEP plane-wave basis set pseudopotential code. We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) density functional, default CASTEP ultrasoft pseudopotentials, and a plane-wave basis set energy cutoff of 440 eV. We use a Brillouin zone sampling grid of spacing $2\pi \times 0.1$ Å$^{-1}$ for the searches, and a finer spacing of $2\pi \times 0.05$ Å$^{-1}$ for the final results reported in this paper.

III. CaCO$_3$, PRESSURE $\leq$ 50 GPA

Calculated enthalpy-pressure curves for CaCO$_3$ phases are shown in Fig. 1 relative to the enthalpy of the “post aragonite” phase. The transition from aragonite to “post aragonite” becomes energetically favorable at about 42 GPa, in agreement with previous DFT results and experiment. We performed calculations for the CaCO$_3$-VI structure reported in Ref., which was suggested as a possible high pressure phase of CaCO$_3$. However, we found it to be very high in enthalpy, with a strongly anisotropic stress and large forces on the atoms.

![Fig. 1](image-url) (Color online) Enthalpies per f.u. of CaCO$_3$ phases relative to “post aragonite”, with the number of f.u. per primitive unit cell given within square brackets. The enthalpies of phases known prior to the current study are shown as dashed lines, while those found in the current study are shown as solid lines. The dotted red line shows the collapse of the CaCO$_3$-$P2_1/c$-h structure into the more stable CaCO$_3$-$P2_1/c$-l structure at 80–90 GPa.

Relaxation of the CaCO$_3$-VI structure at 40 GPa led to a reasonably stable structure with an enthalpy close to that of aragonite, but the relaxed structure does not have a region of stability on our phase diagram (Fig. 1). We also found a structure of $P$na symmetry ("CaCO$_3$-$P$na-h", where h denotes “high pressure”) that is predicted to be more stable than aragonite above 40 GPa, and more stable than “post aragonite” below 47 GPa. However, CaCO$_3$-$P$na-h does not have a region of thermodynamic stability on our phase diagram because we find a previously unknown structure of $P2_1/c$ symmetry ("CaCO$_3$-$P2_1/c$-l", where l denotes “low pressure”) which is calculated to be the most stable phase in the pressure range 32–48 GPa, see Fig. 1.

At 42 GPa CaCO$_3$-$P2_1/c$-l is calculated to be about 0.05 eV per f.u. more stable than aragonite and “post aragonite” and, because these $sp^2$ bonded structures are similar, we expect that DFT calculations should give rather accurate enthalpy differences between them. However, our CaCO$_3$-$P2_1/c$-l and CaCO$_3$-$P$na-h structures do not provide as good a fit to the experimental X-ray diffraction data as the “post aragonite” phase. It is possible that large energy barriers hinder formation of the CaCO$_3$-$P2_1/c$-l structure. Another possibility is that the laser-heated sample melts and the least stable polymorph crystallizes from the melt first, in analogy to “Ostwald’s rule”. In any case, the conditions within the Earth’s mantle are not the same as in diamond anvil cell experiments, and the timescales associated with geological processes are enormously longer than those for laboratory experiments.
IV. CaCO$_3$, PRESSURE $>$ 50 GPA

At higher pressures we find another CaCO$_3$ structure of $P_{2_1}/c$ symmetry ("CaCO$_3$-$P_{2_1}/c$-h") to be stable from 67 GPa to well above 100 GPa. Our CaCO$_3$-$P_{2_1}/c$-h structure is about 0.18 eV per f.u. more stable than the $C_{222_1}$ structure found by Oganov et al.$^{15}$, see Fig. 1. $C_{222_1}$ does not have a region of thermodynamic stability. We also find that at about 80–90 GPa CaCO$_3$-$P_{2_1}/c$-l transforms into the more stable CaCO$_3$-$P_{2_1}/c$-h structure without any apparent energy barrier (dotted red line in Fig. 1). Our calculations lead to the prediction of a new and more stable polymorph of CaCO$_3$ at pressures $>$ 67 GPa.

V. MgCO$_3$

Calculated enthalpy-pressure curves for MgCO$_3$ phases in the pressure range 50–200 GPa are shown in Fig. 2, relative to the $C2/m$ phase. We find a previously unreported structure of $P\bar{1}$ symmetry to be the most stable in the range 85–101 GPa. We also find a phase of $P_{2_1}/2_1$ symmetry that is marginally the most stable at pressures around 144 GPa, see Fig. 3.

VI. STRUCTURES AND BONDING

The carbon atoms in the calcite, aragonite, "post aragonite", and our CaCO$_3$-$P_{2_1}/c$-l and CaCO$_3$-$Pnma$-h$ structures contain threefold coordinated carbon atoms, as does the magnesite phase of MgCO$_3$. These structures contain triangular CO$_3^{2-}$ ions with $sp^2$ bonding. In aragonite and "post aragonite" the CO$_3^{2-}$ ions are coplanar, but in our CaCO$_3$-$Pnma$-h$ structure they are somewhat tilted, while in CaCO$_3$-$P_{2_1}/c$-l they are tilted at approximately 90° to one another, see Fig. 3. More details of the structures are given in the Supplemental Material.$^{16}$

The high-pressure CaCO$_3$-$P_{2_1}/c$-h and $C_{222_1}$ structures contain fourfold coordinated carbon atoms and are of the pyroxene type. CaCO$_3$-$P_{2_1}/c$-h and $C_{222_1}$ possess very similar calcium lattices but the packing of the pyroxene chains is different, as can be seen in Fig. 3. In $C_{222_1}$ each of the chains is orientated in the same manner, but CaCO$_3$-$P_{2_1}/c$-h and $C_{222_1}$ alternate chains run in the reverse direction, see Fig. 3, and consequently the unit cell of CaCO$_3$-$P_{2_1}/c$-h contains four f.u., whereas $C_{222_1}$ contains two. When viewed along the axis of the chains, the CaCO$_3$-$P_{2_1}/c$-h and $C_{222_1}$ structures appear almost identical. CaCO$_3$-$P_{2_1}/c$-h and $C_{222_1}$ have very simi-
lar volumes at high pressures, with $C222_1$ being slightly denser, which leads to almost parallel enthalpy-pressure relations, see Fig. 1. The lower enthalpy of CaCO$_3$-$P2_1/c$ must therefore arise from more favorable electrostatic interactions between the pyroxene chains.

### A. High-pressure X-ray data for CaCO$_3$

Ono et al. performed laser-heated diamond anvil cell experiments on CaCO$_3$ at 182 GPa. X-ray diffraction data for the $C222_1$ and CaCO$_3$-$P2_1/c$-h structures are compared in Fig. 5 with the experimental data from Fig. 1(b) of Ref. 34. Data at 182 GPa are reported, with an incident wavelength of 0.415 Å. The stars indicate that the peak immediately to the right arises from platinum.

![FIG. 4. (Color online) The $C222_1$ (top) and CaCO$_3$-$P2_1/c$-h pyroxene-type (bottom) structures of CaCO$_3$ at 60 GPa. The Ca atoms are in green, carbon in grey, and oxygen in red.](image)

![FIG. 5. (Color online) X-ray diffraction patterns of the $C222_1$ and CaCO$_3$-$P2_1/c$-h phases of CaCO$_3$, compared with experimental data from Fig. 1(b) of Ref. 34. Data at 182 GPa are reported, with an incident wavelength of 0.415 Å. The stars indicate that the peak immediately to the right arises from platinum.](image)

### VII. CHEMICAL REACTIONS IN EARTH’S MANTLE

We have investigated possible chemical reactions involving the mantle materials CaCO$_3$, MgCO$_3$, CO$_2$, MgSiO$_3$, CaSiO$_3$, SiO$_2$, CaO and MgO, following the approach of Oganov et al. The most stable structures of each compound at the relevant pressures are used, as provided by DFT studies. We use the $P\bar{a}3$, $P\bar{4}2/mnm$, and $I\bar{4}2d$ structures of CO$_2$, the stishovite, CaCl$_2$ and pyrite structures of SiO$_2$, the rocksalt structure of MgO, the orthorhombic structure of perovskite CaSiO$_3$ and the perovskite and post-perovskite structures of MgSiO$_3$.

Decomposition of CaCO$_3$ and MgCO$_3$ into the alkaline earth oxides plus CO$_2$ is found to be unfavorable. Under conditions of excess SiO$_2$, the reaction

$$\text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_2$$

is found to be energetically unfavorable up to 138 GPa, which is just above the pressure at the mantle-core boundary, see Fig. 6. We find that the reaction

$$\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$$

does not occur below 200 GPa, see Fig. 7 which is much higher than the value of 135 GPa reported in Ref. 19. We conclude that both MgCO$_3$ and CaCO$_3$ are stable within the Earth’s mantle under conditions of excess SiO$_2$. These results suggest that free CO$_2$ does not occur as an equilibrium phase within the Earth’s mantle.

MgCO$_3$ has generally been believed to be the dominant carbonate throughout the Earth’s mantle. This
assumption can be tested when excess MgO is present by determining the relative stability of CaCO$_3$+MgO and MgCO$_3$+CaO. We find that CaCO$_3$+MgO is the more stable up to pressures of about 200 GPa, so that CaCO$_3$ is the stable carbonate under these conditions. In the case of excess MgSiO$_3$ we consider the reaction

$$\text{CaCO}_3 + \text{MgSiO}_3 \rightarrow \text{CaSiO}_3 + \text{MgCO}_3,$$

finding that CaCO$_3$ is more stable than MgCO$_3$ from 100 GPa up to pressures well above those of 136 GPa found at the mantle-core boundary, see Fig.

FIG. 6. (Color online). The relative stabilities per f.u. as a function of pressure of MgCO$_3$+SiO$_2$ and MgSiO$_3$+CO$_2$. The vertical gray line indicates the pressure at the base of the mantle (136 GPa). In this and the following figures, the kinks arise from phase transitions.

FIG. 7. (Color online). The relative stabilities per f.u. as a function of pressure of CaSiO$_3$+CO$_2$ and CaCO$_3$+SiO$_2$. The vertical gray line indicates the pressure at the base of the mantle (136 GPa).

FIG. 8. (Color online) Enthalpy per f.u. of CaCO$_3$+MgSiO$_3$ compared with that of CaSiO$_3$+MgCO$_3$. Below 100 GPa we find that CaSiO$_3$+MgCO$_3$ is the most stable, while above 100 GPa CaCO$_3$+MgSiO$_3$ is the most stable.

VIII. CONCLUSIONS

In conclusion, we have searched for structures of CaCO$_3$ and MgCO$_3$ at mantle pressures using AIRSS$^{20,21}$. We have found a CaCO$_3$-$P2_1/c$-l structure with $sp^2$ bonded carbon atoms that is predicted to be stable within the range 32–48 GPa. We have also found a high pressure CaCO$_3$-$P2_1/c$-h structure with $sp^3$ bonded carbon atoms that is about 0.18 eV per f.u. more stable than the $C222_1$ phase proposed by Oganov et al.$^{15}$. Both the CaCO$_3$-$P2_1/c$-h and $C222_1$ structures are compatible with the available X-ray diffraction data.$^{34}$ However, CaCO$_3$-$P2_1/c$-h is the most stable structure from 67 GPa to pressures well above those encountered within the Earth’s lower mantle ($\leq$ 136 GPa). Our AIRSS calculations suggest a previously unknown phase of MgCO$_3$ of $P1$ symmetry that is predicted to be thermodynamically stable in the pressure range 85–101 GPa. Our results suggest that CO$_2$ is not a thermodynamically stable compound under deep mantle conditions. Under conditions of excess MgSiO$_3$ we find that CaCO$_3$ is more stable than MgCO$_3$ above 100 GPa. This result arises directly from our discovery of the highly stable CaCO$_3$-$P2_1/c$-h phase. The results of our study change our understanding of the carbon cycle in the lower part of the mantle and may have important consequences for geodynamics$^{40–42}$ and geochemistry$^{43,44}$.
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