Crystal Structure of BaCa(CO$_3$)$_2$ Alstonite Carbonate and Its Phase Stability upon Compression

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ABSTRACT: New single-crystal X-ray diffraction experiments and density functional theory (DFT) calculations reveal that the crystal chemistry of the CaO–BaO–CO$_2$ system is more complex than previously thought. We characterized the BaCa(CO$_3$)$_2$ alstonite structure at ambient conditions, which differs from the recently reported crystal structure of this mineral in the stacking of the carbonate groups. This structural change entails the existence of different cation coordination environments. The structural behavior of alstonite at high pressures was studied using synchrotron powder X-ray diffraction data and ab initio calculations up to 19 and 50 GPa, respectively. According to the experiments, above 9 GPa, the alstonite structure distorts into a monoclinic C$_2$ phase derived from the initial trigonal structure. This is consistent with the appearance of imaginary frequencies and geometry relaxation in DFT calculations. Moreover, calculations predict a second phase transition at 24 GPa, which would cause the increase in the coordination number of Ba atoms from 10 to 11 and 12. We determined the equation of state of alstonite ($V_0 = 1608(2)$ Å$^3$, $B_0 = 60(3)$ GPa, $B'_0 = 4.4(8)$ from experimental data) and analyzed the evolution of the polyhedral units under compression. The crystal chemistry of alstonite was compared to that of other carbonates and the relative stability of all known BaCa(CO$_3$)$_2$ polymorphs was investigated.

KEYWORDS: alstonite, BaCa(CO$_3$)$_2$, crystal structure, carbonate, phase transition, high pressure, synchrotron X-ray diffraction, DFT calculations

INTRODUCTION

Abundance of carbon on the earth’s surface significantly differs from the solar pattern. The deficiency of carbon on the earth’s surface can be explained by an efficient deep carbon ingassing during the last billion years of earth’s history. That is, missing carbon would be stored in our planet’s interior in stable reduced or oxidized carbon forms. The most probable candidates for the oxidized carbon species in the mantle are carbonates, which enter via subduction processes at convergent boundaries.

Magnesium and calcium carbonates are the most abundant on the earth’s surface. Ca-containing CaCO$_3$ calcite and CaMg(CO$_3$)$_2$ dolomite are the principal carbonate minerals in sedimentary rocks. MgCO$_3$ magnesite, on the other hand, has been suggested as the main host of oxidized carbon throughout the mantle. In fact, the stability of both Ca and Mg simple carbonate minerals differs greatly. While magnesite is stable throughout a large pressure and temperature range (only a dense polymorph has been discovered above 115 GPa and 2100 K),$^{5,6}$ calcite undergoes several phase transitions under compression.$^{5,7}$ In the case of dolomite, two high-pressure (HP) polymorphs have been reported.$^8$ Despite the fact that these carbonates have been extensively studied, the crystal chemistry of calcium carbonates and, in particular, the local environment around the Ca atoms needs to be well understood. For instance, pure CaCO$_3$ has been naturally found at ambient conditions in three structural forms: (i) calcite, the rhombohedral stable phase, where the Ca atoms are octahedrally coordinated by O atoms, (ii) aragonite, an orthorhombic phase, where the Ca atoms have nine O neighbor atoms, and (iii) vaterite, a rare phase with partial atomic occupation factors, where the Ca atoms are 8-fold coordinated in average. The explanation of such behavior has often been oversimplified in the literature to a mere question of the Ca$^{2+}$ cation size, which would delimit the border of the calcite- to aragonite-type structures.

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The presence of other cations like alkaline (Na\(^+\), K\(^+\)), alkaline-earth (Mg\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\)), or transition metals (Mn\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\)) in the carbonate structure, as well as the existence of additional anions that could provide negative charge, conditions the Ca local environments. Thus, whereas CaM(CO\(_3\))\(_2\)\(_{2-}\) (M = Mg, Mn, Zn, Fe) present Ca-centered octahedra,\(^{11}\) the different Ca–Mg stoichiometry of huntite CaMg\(_3(CO_3)\)\(_4\) entails the formation of Ca-centered trigonal prisms.\(^{15}\) In calcium carbonates that include Na\(^+\), K\(^+\), Sr\(^{2+}\), Ba\(^{2+}\) cations, Ca coordination varies from 6 to 9 depending on the structure or even within the same structure.\(^{11-22}\) Naturally occurring calcium silicate-carbonates, for instance, present a range of volumes and bulk moduli, which suggests that other divalent cation species could be accommodated in these sites. Therefore, the study of the atomic arrangements in different Ca carbonate systems and their behavior at high pressures could provide insight into the nature of the Ca–(CO\(_3\)) interactions and potential chemical substitution at inner earth conditions.

The double carbonate CaBa(CO\(_3\))\(_2\) exists naturally as three different polymorphs: monoclinic barytocalcite,\(^{19}\) and trigonal intimately related alstonite\(^{21}\) and paralstonite\(^{21}\) phases. A new monoclinic polymorph has also been synthesized.\(^{22}\) As it occurs in CaCO\(_3\), Ca atoms in CaBa(CO\(_3\))\(_2\) adopt 6-fold or 8-fold coordination depending on the polymorph. This work determines an ambient condition alstonite structure that differs from a previously reported solution\(^{20}\) and reports its experimental high-pressure behavior. Density functional theory (DFT) calculations of the different CaBa(CO\(_3\))\(_2\) phases shed light on their respective thermodynamical stabilities upon compression. The evolution of the lattice parameters and atomic coordinates at high pressure shows the change of cation environments and allows determining both polyhedra and bulk compressibilities.

\section*{EXPERIMENTAL DETAILS}

Naturally occurring alstonite samples from the Fallowfield mine, in Northumberland (U.K.), were kindly provided by the Yale Peabody Museum (Specimen YPM MIN 034129). A few crystals were optically selected under the microscope. Some of them were crushed to obtain a fine white powder. Qualitative chemical analyses were done on a Philips XL30 scanning electron microscope using energy-dispersive X-ray spectroscopy. According to them, the chemical composition of our alstonite sample was Ba\(_{0.96(3)}\)Sr\(_{0.05(1)}\)Ca\(_{0.99(6)}\)(CO\(_3\))\(_2\). We solved the alstonite structure from angle-dispersive single-crystal X-ray diffraction (XRD) data collected on a Bruker D8 Venture diffractometer at ambient conditions using Mo K\(\alpha\) radiation. Indexing, data reduction, and empirical absorption correction were performed using APEX3 software. Structure solutions and structural refinements were performed with SHELXT\(^25\) and SHELXL\(^26\), respectively, operated using the WinGX interface.\(^{25}\) We found that the sample has a structure slightly different than the one recently reported by Bindi et al.\(^{20}\) The structural solution will be briefly described later.

High-pressure angle-dispersive powder XRD experiments were conducted at the MSPD beamline of the ALBA-CELLS Synchrotron Light Source\(^28\) using a monochromatic incident beam of 0.4246 Å. HP measurements were performed using a diamond-anvil cell (DAC), a technique that allows to strongly modify and subsequently analyze the atomic interaction in solids.\(^29,30\) The alstonite sample was placed in a stainless-steel gasket cavity inside the membrane DAC along with the Cu powder for pressure determination\(^22\) and a 4:1 mixture of methanol—ethanol was used as a pressure-transmitting medium.\(^{32}\) Diffraction patterns were collected at different pressures for 20 s up to 19 GPa. The LaB\(_6\) powder was used for distortion correction, and integration to conventional 2\(\theta\)-intensity data was carried out with Diopas software.\(^{33}\) The indexing and refinement of the powder patterns were performed using the Unitcell\(^24\) and Powdercell\(^35\) program packages.

\section*{COMPUTATIONAL DETAILS}

Calculations were carried out using the projector augmented wave (PAW) method\(^{36}\) implemented in Quantum ESPRESSO.\(^{37}\) The number of valence electrons in the atomic data sets are: 10 (Ba), 10 (Ca), 4 (C), and 6 (O). We used a 100 Ry plane-wave cutoff for the Kohn–Sham states and a 1000 Ry plane-wave cutoff for the exchange potential. The projector augmented wave (PAW) method was used to calculate the electronic states of the crystal structures. The electronic wave functions were expanded in plane waves with a kinetic energy cutoff of 100 Ry. The k-point sampling was performed using a 10x10x10 Monkhorst-Pack grid. The exchange-correlation energy was treated using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional. The electron-ion interactions were described using the projector-augmented wave (PAW) method. The optimized geometries were obtained by minimizing the total energy with respect to the atomic coordinates. The Hellmann–Feynman forces were converged to 0.01 eV/Å. The electronic charge density was analyzed using the AIMAll package. The electron density was calculated using a 0.001 Rybo–Lennard–Jones cutoff. The AIM analysis was performed using a 0.005 Hartree–Bohr radius cutoff. The nuclear magnetic shielding was calculated using the gauge-including atomic orbitals (GIAO) method. The nuclear magnetic shielding was calculated using the GIAO method. The high-pressure phase transitions were analyzed using high-pressure angle-dispersive powder XRD experiments. The high-pressure phase transitions were analyzed using high-pressure angle-dispersive powder XRD experiments. The high-pressure phase transitions were analyzed using high-pressure angle-dispersive powder XRD experiments.
cutoff for the electron density. The functional used was B86PBE, combined with the exchange–hole dipole moment (XDM) model for dispersion. To confirm the results, we also used the PBEsol functional, which gives equivalent results to B86PBE-XDM. We explored the convergence of the total energy and stress tensor with respect to k-point grid size. Satisfactory convergence was achieved using the following (shifted) k-point grids: 3 × 3 × 3 (paralstonite), 1 × 1 × 4 (alstonite), 1 × 1 × 4 (C2 HP-alstonite), and 3 × 3 × 3 (C2 synthetic phase, ref 22).

Geometry optimizations were carried out with tight convergence parameters (10−5 Ry in the energies and 10−4 Ry/bohr in the forces). For each phase, the equilibrium geometry was determined at zero pressure and at 50 GPa, and a uniform volume grid was built between the two structures containing 41 points. Constant-volume geometry optimizations were run at each point in the volume grid, and the resulting energy–volume equation of state was input into the gibbs2 program to fit analytical equations of state and determine the phase stability under pressure. We also calculated the Gamma for alstonite using the phonopy software.

### RESULTS

**Crystal Structure of Alstonite at Ambient Conditions.** Since its first identification in the mid-XIX century, the crystal structure of BaCa(CO3)2 has remained unknown until very recently, when Bindi et al. reported that it could be described by a trigonal P31m space group (SG) with lattice parameters a = 17.4360(6) Å and c = 6.1295(2) Å (V = 1613.80(9) Å3, Z = 12). The crystal structure of reported alstonite is depicted in Figure 1. The latter is characterized by alternating layers of Ca and Ba atoms along the c axis, which shows that the structure could be described by a half-length a axis. The other difference is the arrangement of the [CO3] groups, in which parastonite are staggered at three heights between cation layers (at z/c = 0 and 0.5) stacked in a ABAB... conformation, one is Ba-rich with a ratio Ba/Ca = 3 in cation sites, and in the other layer the ratio Ba/Ca is the inverse. As it can be seen in the ac projection, the carbonate groups are located among the cation layers and are arranged parallel to these, the [CO3]2− units being at two different heights between the Ba/Ca layers (at z/c ~ 1/4, 1/3 or 3/4, 5/6). The chemical composition of the cation layers in alstonite is one of the main differences with respect to the parastonite polymorph, depicted in Figure 1. The latter is characterized by alternating layers of Ca and Ba atoms along the c axis, which shows that the structure could be described by a half-length a axis. The other difference is the arrangement of the [CO3]2− groups, in which parastonite are staggered at three heights between cation layers (at z/c = 1/6, 1/4, 1/3 or 2/3, 3/4, 5/6). Both crystal structures have the Ba atoms in 10-fold coordination and Ca atoms in 8-fold coordination, but the shape of the cation-centered O polyhedra are different. For instance, the difference between shorter and longer Ca(1)–O distances in the [Ca(1)O6] polyhedron of the reported P31m alstonite (2.184(13) – 2.752(7) Å) is significantly larger than that observed in parastonite [CaO6] polyhedra (2.36(2) – 2.59(1) Å).

As a previous step to the study of our alstonite sample, we selected a clean, transparent, and crack-free crystal with dimensions 100 × 100 × 20 μm³ under the optical microscope to perform an ambient condition single-crystal XRD experiment and solve its structure. After the data collection, the indexation confirmed a hexagonal symmetry with lattice parameters a = 17.460(3) Å and c = 6.125(2) Å. The data integration suggested noncentrosymmetric space groups P62m (Rint = 0.1445), P31m (Rint = 0.1385), and P321 (Rint = 0.1026). Considering that the structure had been recently solved by Bindi et al., in space group P31m, we solved the structure of our alstonite sample in P31m and P321 with the lowest internal R value. For the structural solution, we employed SHELXT, which located all of the metallic ions and a large number of oxygens and carbons, yielding in both space groups R1 values of 0.158 and 0.143 for P31m and P321, respectively. Further refinement cycles with the SHELXL program helped to locate the remaining atoms in both space groups obtaining, with the isotropic refinement of all atoms, R1 values of 0.0732 (P321) and 0.0908 (P31m). Though these ordered solutions with full-site occupations seemed reasonable, both refinements showed residual charge densities for most positions and, in particular, in one of the Ca positions. We refined then allowing site occupancy for this Ca position with some Sr (also present in our sample) considerably lowering the R1 value but providing unrealistic atomic distances in both space groups. Hence, we stepped back and continued with fully ordered refinement but this time refining the metallic atoms anisotropically. This yielded residual values of R1 = 0.0643 for 1740 diffraction peaks whose Fo > 4σ(Fo) and 106 refined parameters in P321, and R1 = 0.0837 for 1816 diffraction peaks whose Fo > 4σ(Fo) and 117 refined parameters in P31m. Crystal refinement details of both space groups are shown in Table 1. Hence, we conclude that the

| Table 1. Parameters and Results of Single-Crystal XRD Data Collection, Data Reduction, and Crystal Refinement |
|-------------------------------------------------|-------------------------------------------------|
| **Crystal Data**                                | **Data Collection**                              |
| chemical formula                                | temperature (K)                                  |
| BaCa(CO3)2                                      | 299(2)                                           |
| BaCa(CO3)2                                      | 0.71073                                          |
| cell parameters                                 | reflection range                                 |
| a(Å)                                            | −22 ≤ h ≤ 22                                    |
| 17.459(3)                                       | −22 ≤ h ≤ 22                                    |
| c(Å)                                            | −20 ≤ k ≤ 21                                    |
| 6.125(2)                                        | −7 ≤ l ≤ 7                                      |
| V(Å³)                                           | 12    | 12                                           |
| 1616.98(8)                                      | 12000                                         |
| Z                                               | 2411                                           |
| 12                                              | 0.1026                                         |
| space group                                     | rint, obs                                       |
| P321                                            | 3.668                                          |
| P31m                                            | 3.668                                          |
| μ(g/cm³)                                        | 3.668                                          |
| 3.668                                           | 3.668                                          |
| **Refinement**                                  | no. of parameters                               |
|                                               | 106                                             |
|                                               | 117                                             |
| R1                                              | 0.0643                                          |
| wR2                                            | 0.0837                                          |
| GooF                                           | 0.2184                                          |
|                                               | 0.2713                                          |
|                                               | 1.036                                          |
|                                               | 1.006                                          |

structure of our alstonite sample is better described in space group P321 with the residual charge density being most probably due to uncounted occupational disorder.

The new P321 structure of alstonite is shown in Figure 1e,f. It is intimately related to parastonite. In parastonite, the metal atoms are arranged alternating pure Ca and pure Ba hexagonal layers and the unit-cell parameters are a = 8.692(3) Å and c =
Table 2. Atomic Coordinates and Thermal Displacements (\( U_{eq} / U_{iso} \)) of P321 \( \text{BaCa(CO}_3\text{)}_{2} \) Alstonite from Single-Crystal XRD Data at Ambient Conditions

| atom | \( x \) | \( y \) | \( z \) | \( U_{eq} \) | \( U_{iso} \) |
|------|-------|------|-----|-------|-------|
| Ba01 | 0.15617 (16) | 0.50234 (15) | 0.9997 (3) | 0.0111 (5) |
| Ba02 | 0.3385 (16) | 0.33825 (16) | 0 | 0.0082 (7) |
| Ba03 | 0.15772 (17) | 0.15772 (17) | 0.5 | 0.0117 (7) |
| Ca01 | 0.1798 (4) | 0.6818 (4) | 0.4999 (9) | 0.0022 (12) |
| Ca02 | 0 | 0.1777 (7) | 0 | 0.017 (3) |
| Ca03 | 0 | 0.328 (7) | 0.5 | 0.012 (2) |
| O01 | 0.0715 (12) | 0.9966 (12) | 0.756 (3) | 0.013 (4) |
| O02 | 0.2324 (12) | 0.4055 (12) | 0.177 (3) | 0.008 (4) |
| O03 | 0.1617 (13) | 0.4105 (12) | 0.640 (3) | 0.009 (4) |
| O04 | 0.9950 (12) | 0.4278 (13) | 0.740 (3) | 0.016 (4) |
| O05 | 0.7379 (15) | 0.4102 (14) | 0.175 (3) | 0.017 (5) |
| O06 | 0.0843 (13) | 0.3268 (13) | 0.168 (3) | 0.013 (4) |
| O07 | 0.2359 (14) | 0.3393 (13) | 0.651 (3) | 0.012 (4) |
| O08 | 0.9253 (12) | 0.5081 (12) | 0.743 (3) | 0.019 (4) |
| O09 | 0.0748 (13) | 0.5755 (13) | 0.742 (3) | 0.025 (4) |
| O10 | 0.1593 (13) | 0.2559 (14) | 0.139 (3) | 0.012 (5) |
| O11 | 0.0883 (13) | 0.2642 (13) | 0.667 (3) | 0.012 (5) |
| O12 | 0.6594 (16) | 0.4027 (15) | 0.646 (4) | 0.025 (6) |
| C01 | 0.66667 | 0.33333 | 0.177 (7) | 0.002 (9) |
| C02 | 0.9996 (11) | 0.5054 (11) | 0.740 (3) | 0.001 (5) |
| C03 | 0.161 (2) | 0.3360 (18) | 0.657 (4) | 0.008 (5) |
| C04 | 0.66665 | 0.33332 | 0.652 (8) | 0.009 (11) |
| C05 | 0 | 0.3283 (19) | 0.165 (4) | 0.015 (6) |
| C06 | 0 | 0 | 0.762 (7) | 0.022 (19) |

6.148(4) \( \text{Å} \) \((Z = 3)\).\(^{21}\) In the alstonite structure, the Ba-rich layer contains 3/4 parts of Ba atoms and 1/4 of Ca atoms, while in the Ca-rich layer is the opposite. Thus, the Ca(2) atoms at 3e sites and Ba(3) atoms at 3f sites occupy positions in the Ba- and Ca-rich layers, respectively. The resulting cation layers are identical to those reported by Bindi et al. using the SG \( P31m \) to describe the structure. Between layers, the carbonate groups lie approximately parallel to the \( ab \) plane in three different levels, as opposed to the two levels reported using the \( P31m \) structural model. The cation rearrangement with respect to parastonite entails that certain carbonate groups appear rotated as a consequence of the accommodation of cations of differents sizes in adjacent layers. For instance, half of the \([\text{CO}_3]\) groups at \( y/b = 0 \) and all of the \([\text{CO}_3]\) groups at \( y/b = 1/2 \) are rotated 60° relative to those of parastonite, in such a way that all Ba and Ca atoms could adopt the 10-fold and 8-fold coordination, respectively. This structural arrangement can only be described with a unit-cell where the \( a \) axis is doubled with respect to parastonite \((Z = 12)\). Note that alstonite defined within the \( P321 \) SG provides more uniform Ca–O distances \((3.31(1)-2.65(1) \text{ Å})\) than the \( P31m \) structural model (see above). The atomic coordinates of the refined structure are collected in Table 2.

The correct determination of the crystal structure of our alstonite mineral is supported by the slightly better match of the experimental powder XRD pattern with the \( P321 \) model (see Figure 2). The diffraction peak intensities calculated with both the \( P321 \) and the \( P31m \) structural models are similar in the whole 2θ range, except between 29 and 32° (Cu K\(\alpha\) wavelength). The reflections \((202)\) and \((022)\) modeled by the \( P321 \) structural description explain the experimental diffraction peak at 31.6° better.

Additionally, we carried out DFT calculations of all of the known \( \text{BaCa(CO}_3\text{)}_{2} \) polymorphs up to 50 GPa, that is, \( P2_1/m \) barytocalcite,\(^{19}\) \( P321 \) paralstonite,\(^{21}\) the synthetic \( C2\),\(^{22}\) and the \( P31m\)\(^{20}\) and \( P321 \) [this study] alstonite phases. Figure 3a,b shows the energy as a function of calculated volume curves and the enthalpies calculated for each phase referred to the enthalpy of alstonite \( P31m \) phase,\(^{20}\) respectively. The enthalpies of alstonite \( P321 \), paralstonite, and barytocalcite are very similar over the studied pressure range, within 3 KJ/mol (0.08 eV) per formula unit of each other. This indicates that either of these phases may be observable under the proper experimental conditions, and it is not possible to predict on the basis of stability calculations alone whether one or the other will appear. At equilibrium and zero pressure, the \( P31m \) alstonite variant\(^{20}\) has higher energy than the three aforementioned phases (approx. 9 KJ/mol, or 0.19 eV per formula unit higher than barytocalcite), which indicates that
this phase is less stable. The synthetic C2 phase is unstable at all pressures relative to any of the other phases. This discussion on the stability of the different BaCa(CO3)2 polymorphs is based on enthalpy differences alone, the entropic effects being disregarded (they may be important at high temperatures).

**Structural Properties of Alstonite under Pressure.**
Quasi-hydrostatic compression increases density and alters the interatomic interactions, which may lead to phase transitions to minimize the overall free energy of the system.47 In this section, we study the structural response of alstonite to increasing pressure.

High-pressure synchrotron powder XRD patterns present texturing effects due to uneven crystal sizes. This effect causes inaccuracies in the relative intensities of the diffraction maxima and precludes full structural refinements. Only Le Bail refinements could be performed. Under compression, the diffraction peaks shift to higher angles as expected for a decrease of interplanar distances, but no additional maxima are observed (see Figure 4). XRD peaks of our patterns were indexed with the trigonal unit-cell of alstonite in all of the pressure range of this study, which suggests that alstonite is stable up to 19 GPa.

The indexed lattice parameters and unit-cell volumes at different pressures are collected and shown in Table 1S of the Supporting Material.

The evolution of the unit-cell parameters (Figure 5) and volume (Figure 6) as a function of pressure presents a good overall agreement with our ab initio total-energy calculations below 9 GPa. In the following, theoretical values are denoted in parentheses. The lattice parameters of the trigonal P321 unit-cell vary smoothly with increasing pressure up to 9 GPa, which supports the absence of phase transitions in this pressure range. The absolute experimental contractions for the a- and c-axes at this pressure are 0.438(7) and 0.403(5) Å, respectively. Experimental (theoretical) axial linear compressibilities for alstonite in the 0−9 GPa range are \( \beta_a = 2.51(5) \times 10^{-3} \) (2.48(7) \times 10^{-3} \) and \( \beta_c = 7.20(12) \times 10^{-3} \) (7.47(13) \times 10^{-3} \) GPa\(^{-1} \), and indicate strong axial anisotropy. The axial compression ratio defined as \( \beta_a/\beta_c \) is 2.87(3) (3.01(8)). This result shows that the c axis is approximately 3 times more compressible than the a axis. The a/c axis ratio increases with pressure according to the expression \( a/c = 2.850(1) - 0.0143(2)\cdot P \) (see the inset of Figure 6). This response to external pressure arises from the fact that the relatively incompressible [CO3] carbonate units are arranged approximately parallel to the ab plane, whereas the compressibility of the c axis can be directly attributable to the [BaO10] and [CaO6] polyhedral compression. A third-order Birch–Murnaghan equation of state (BM-EoS) fit\(^{18} \) to our P−V data set yields a zero-pressure volume \( V_0 = 1608(2) \text{ Å}^3 \), a bulk modulus of \( B_0 = 60(3) \text{ GPa} \), and a bulk modulus first-pressure derivative of \( B'_0 = 4.4(8) \). These experimental results compare well with those obtained from theoretical calculations: \( V_0 = 1608.0(1) \text{ Å}^3, B_0 = 64.25(4) \text{ GPa}, \) and \( B'_0 = 3.99(1) \). The bulk modulus lies in between those of the two end-member carbonates: 67(2) GPa for CaCO\(_3\) calcite,\(^{49} \) 66.5(7) GPa (\( B'_0 = 5.0(1) \)) for CaCO\(_3\) aragonite,\(^{50} \) and 48(1) GPa for BaCO\(_3\) witherite,\(^{51} \) and it is comparable to the 62.7(6) GPa of SrCO\(_3\) strontianite.\(^{51,52} \) In other words, our data evidences that BaCa(CO3)\(_2\) alstonite is more compressible than all of the

![Figure 3](https://doi.org/10.1021/acsearthspacechem.1c00032)
divalent metal carbonates and silicate-carbonates except witherite.\textsuperscript{12,48,52–54}

Taking into account the good agreement found between experimental and theoretical data in (i) lattice parameters and atomic positions at ambient conditions (see Tables 2 and 3) and (ii) the unit-cell compressibility behavior within the 0–9 GPa pressure range, we use data from our DFT simulations to study the variation of bond distances and polyhedral compressibilities with pressure. The Ba- and Ca-centered polyhedral volumes of BaCa(CO₃)₂ alstonite vary smoothly with pressure in that range (see Figure 7) and give the bulk moduli shown in Table 4. It can be seen that the bulk moduli of both the Ba-centered and Ca-centered O polyhedra are similar (ranging from 60.5 to 68.2 GPa), but the $B''_0$ values are higher for [CaO₈]. This means that these polyhedra become progressively more incompressible with increasing pressure.

Above 9 GPa, the diffraction peaks of the XRD patterns could also be roughly explained with the trigonal unit-cell of alstonite. The $a$ lattice parameter would become almost incompressible (see Figures 5 and 6), whereas the O–O contacts between two neighboring [CO₃] units parallel to the $ab$ plane increase their stiffness. As it occurs in other common layered materials, it is most compressible along the stacking axis than along a perpendicular direction. No volume discontinuities were observed in the studied pressure range.

It is noticeable however that the width of several diffraction peaks, particularly those at higher 2$\theta$ angles, increases significantly above this pressure in the XRD pattern profiles. This fact could be due to the presence of nonhydrostatic stresses that could lead to the formation of a lower symmetry phase via a second-order symmetry-reduction phase transition, consequence of a lattice dynamical instability.

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**Figure 5.** Pressure dependence of the $a$ (top) and $c$ (bottom) lattice parameters of BaCa(CO₃)₂ alstonite. Upstroke experimental data are depicted as solid squares, whereas the data of the recovered sample are depicted with empty squares. Fits to experimental P321 data in the pressure ranges 0–9 and 9–19 GPa are represented as solid and dashed black lines, respectively. Lattice parameters from monoclinic C2 indexations are depicted in dark and light gray symbols. DFT data are represented as solid orange lines.

**Figure 6.** Pressure dependence of the unit-cell volume of BaCa(CO₃)₂ alstonite. Upstroke experimental data are depicted as solid squares, whereas the data point corresponding to the recovered sample is depicted with an empty square. Fits to experimental data in the pressure ranges 0–9 and 9–19 GPa (P321 and C2 unit-cells yield similar volumes per formula unit) are represented as solid and dashed black lines, respectively. DFT data are represented as solid orange lines. Inset: Evolution of the $a/c$ axes ratio as a function of pressure.

**Table 3. Atomic Coordinates of P321 BaCa(CO₃)₂ Alstonite at Ambient Pressure from DFT Calculations ($a = 17.4419$ Å and $c = 6.1030$ Å)**

| atom | $x$   | $y$   | $z$   |
|------|-------|-------|-------|
| Ba01 | 0.1552| 0.5028| 0.9967|
| Ba02 | 0.3370| 0.3370| 0.0000|
| Ba03 | 0.1584| 0.1584| 0.5000|
| Ca01 | 0.1821| 0.6842| 0.4965|
| Ca02 | 0.0000| 0.1794| 0.0001|
| Ca03 | 0.0000| 0.3264| 0.5001|
| O01  | 0.0714| 0.9946| 0.7561|
| O02  | 0.2310| 0.4047| 0.7145|
| O03  | 0.1603| 0.4117| 0.6288|
| O04  | 0.9958| 0.4298| 0.7412|
| O05  | 0.7372| 0.4110| 0.1826|
| O06  | 0.0820| 0.3268| 0.6172|
| O07  | 0.2372| 0.3404| 0.6441|
| O08  | 0.9264| 0.5085| 0.7460|
| O09  | 0.0746| 0.5780| 0.7377|
| O10  | 0.1587| 0.2560| 0.1399|
| O11  | 0.0880| 0.2642| 0.6668|
| O12  | 0.6614| 0.4049| 0.6451|
| C01  | 0.6667| 0.3333| 0.1857|
| C02  | 0.9990| 0.5055| 0.7349|
| C03  | 1.0000| 0.3383| 0.6504|
| C04  | 0.6667| 0.3333| 0.6491|
| C05  | 0.1580| 0.3297| 0.1639|
| C06  | 0.0000| 0.0000| 0.7628|
The lengths of the suggest that the dynamically than the initial alstonite structure above 15 GPa, and \( \beta \) following axes transformation:

\[
\begin{align*}
\alpha' & \sim a + b, \quad b' \sim b, \quad c' \sim c \quad \text{and an } \beta \text{ angle that could differ from 90°.} \\
\end{align*}
\]

Calculations predict that this distorted phase would be slightly more stable thermodynamically than the initial alstonite structure above 15 GPa, and suggest that the \( \beta \) angle barely varies around 90° up to 50 GPa. The lengths of the \( \alpha' \) and \( b' \) axes progressively change their ratio above that pressure but the difference between the length of the pseudotrigonal axes \( b-a \) is relatively small (for instance, \( a \) and \( b \) differ in 0.05 Å at 21.3 GPa). According to our calculations, the dominant deformation mechanism under hydrostatic pressure involves slightly correlated tilts of \( [\text{CO}_3] \) units located at \( y/a' \sim 0, \) 0.25, 0.5, and 0.75 with respect to the \( c' \) axis and small shifts of these units along \( \alpha' \). These atomic displacements cause the appearance of 12 different environments around the Ba and Ca atoms in the C2 phase (coming from only three environments for each type of atom in the initial P321 phase), which evolve independently under compression. This fact produces that the polyhedral volumes slightly diverge above 15 GPa. DFT calculations also predict a second phase transition to a different monoclinic C2 phase at 24 GPa. Above this pressure, in addition to the \( [\text{CO}_3] \) tilting movements, 1/3 of the carbonate units shift considerably in the \( c' \) direction (see Figure 8), which produces a change in the

\[
\begin{align*}
\end{align*}
\]

Phonon frequencies were calculated using the frozen-phonon method (implemented in Phonopy\textsuperscript{55}) for the P321 alstonite phase at nine points between zero and 20 GPa. The appearance of imaginary phonon frequencies indicates that a dynamical instability develops in this phase at around 15 GPa. The eigenvector corresponding to one of the imaginary-frequency modes at 20 GPa was used to perturb the P321 structure and a subsequent fixed-volume geometry relaxation was carried out, which resulted in a broken-symmetry C2 phase with lower enthalpy than the P321 phase at high pressure. The C2 phase converges to the same structure as P321 alstonite at low pressure, while it diverges from it in the pressure range between 15 and 20 GPa.

This C2 monoclinic unit-cell comes from a translationen gleiche subgroup of the initial trigonal P321 unit-cell, with the following axes transformation: \( \alpha' \sim 2a + b, \) \( b' \sim b, \) \( c' \sim c \) and an \( \beta \) angle that could differ from 90°. HP powder XRD data show a splitting of the pseudohexagonal \( a \) and \( b \) axes or a very small deviation of the \( \beta \) angle from 90° of the monoclinic cell would produce the apparent widening of the diffraction peaks experimentally observed above 10 GPa. Unfortunately, the huge monoclinic unit-cell generates a large number of reflections that overlap, not allowing the accurate determination of the lattice parameters. The monoclinic lattice parameters that best describe the experimental patterns at different pressures are shown in Table S2. The lattice parameters of the C2 phase inferred from our limited quality HP powder XRD data show a splitting of the pseudotrigonal axes above 9 GPa \( (b-a \sim 0.08 \text{ Å}) \). Between 9 and 12 GPa, the \( \beta \) angle is approximately 90°, but further compression increases the value to \( \sim 90.6° \) at \( P > 15 \) GPa. This monoclinic C2 unit-cell was previously proposed by Dickens (in an unpublished study, according to Roberts\textsuperscript{55}56) for the ambient conditions alstonite structure. Unfortunately, the crystal structure could only be partially refined and the location of the \( [\text{CO}_3] \) groups was uncertain.\textsuperscript{56} However, Dickens’ study provided lattice constants very similar to those of the high-pressure phase found in the present work, i.e., \( a = 30.163(9) \) Å, \( b = 17.413(5) \)

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Representation of the evolution under compression of the different polyhedral unit volumes of BaCa(CO\textsubscript{3})\textsubscript{2} alstonite according to DFT calculations. Above 24 GPa, the Ba atoms increase their coordination numbers from 10 to 11 (17%) and 12 (83%).

| \( V_0 \) (Å\textsuperscript{3}) | \( B_0 \) (GPa) | \( B'_0 \) |
|-----------------|-------------|-------------|
| BaCa(CO\textsubscript{3})\textsubscript{2} experiment | 1608(2) | 60(3) | 4.4(8) |
| BaCa(CO\textsubscript{3})\textsubscript{2} theory | 1608.0(1) | 64.25(4) | 3.99(1) |
| [Ba(1)O\textsubscript{10}] | 45.53(6) | 63.8(3) | 4.37(5) |
| [Ba(2)O\textsubscript{10}] | 45.57(4) | 63.5(2) | 4.31(3) |
| [Ba(3)O\textsubscript{10}] | 46.50(3) | 66.4(2) | 4.43(3) |
| [Ca(1)O\textsubscript{8}] | 26.208(5) | 68.2(4) | 5.50(8) |
| [Ca(2)O\textsubscript{8}] | 25.773(4) | 60.5(3) | 4.71(6) |
| [Ca(3)O\textsubscript{8}] | 25.773(4) | 64.5(3) | 5.00(6) |

![Figure 8](https://example.com/figure8.png)

**Figure 8.** Projections along the \( c \) and \( b \) axes of the HP BaCa(CO\textsubscript{3})\textsubscript{2} C2 polymorph found to be stable above 24 GPa. Cyan, green, brown, and small red spheres represent Ba, Ca, C, and O atoms, respectively.
Å, c = 6.110(1) Å, and β = 90.10(1)°, and revealed pseudohexagonal symmetry normal to (001) and alternating Ba- and Ca-rich layers in the ...ABAB... sequence, just like the structure we report here.

A second-order BM-EoS fit to our experimental P–V data above 9 GPa yields a V0/Z = 127.4(6) Å3 and a bulk modulus of B0 = 128(7) GPa. The fact that the structure is considerably less compressible at high pressures is likely due to a combination of two factors: (i) the aforementioned structural behavior, which entails a progressive decrease in compressibility upon compression and (ii) the loss of the hydrostaticity of the pressure-transmitting medium above 10 GPa, which could lead to a change in the slope of the V–P experimental data. Alstonite appears to be extremely sensitive to non-hydrostatic stresses. We also note that our calculations do not reproduce the experimental compressibility above 9 GPa.

## CONCLUSIONS

In this work, we have first determined the BaCa(CO3)2 alstonite structure at ambient conditions from single-crystal XRD measurements. The unit-cell dimensions and atomic coordinates of the heavier metallic atoms coincide with those recently reported by Bindi et al., but the location of some of the carbonate groups is different. This entails different coordination environments in the Ba and Ca atoms despite being 10-fold and 8-fold coordinated, respectively, in both structural models. The atomic weight of the cations present makes a more stable carbonate than the single-cation end-members. This becomes clear from direct comparison of the free energies of formation from ions of CaCO3 calcite/aragonite, BaCO3 witherite, and BaCa(CO3)2 alstonite. The relative stability of the different BaCa(CO3)2 polymorphs, however, was never investigated. Our DFT calculations show that barytocalcite is the thermodynamically stable phase but different BaCa(CO3)2 polymorphs, which are small (<0.08 eV/formula unit), which suggests that either the coordination number of the Ba atoms increase to 11–12. This second high-pressure monoclinic (also C2) polymorph is an alstonite structural variant more stable than barytocalcite at high pressures.

Carbonates play a central role in the subduction transport of oxidized carbon from the earth’s surface to the mantle. Although at upper mantle conditions the chemistry of carbonates within subducting slabs is thought to be mainly restricted to the CaCO3-MgCO3-FeCO3 system, the study of the effect of the inclusion of larger cations in the carbonate structure is important. Our results provide information on the structural local environment of metal atoms in a double Ca–Ba carbonate, which affects the density and the solubility, and reports the phase stability and compressibility of this carbonate upon compression. More thorough structural analyses of carbonate minerals will give further insight into potential chemical substitution at inner earth conditions and the great mineralogical diversity found in nature.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00032.

Tables showing the experimental and calculated (static) lattice parameters and unit-cell volumes for BaCa(CO3)2 alstonite at different pressures (PDF)

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### Notes

The authors declare no competing financial interest.

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