Evidence for amorphous calcium carbonate originated mid-lithospheric discontinuities

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Abstract

Cratonic lithosphere is a vast host for deep recycled carbon, trapping up to several weight percent CO\(_2\) among its compositions\(^1\) at depths overlapping the seismic mid-lithospheric discontinuities (MLDs)\(^3\)\(^-\)\(^5\). However, the role of carbonates, especially for the latest discovered amorphous calcium carbonate (CaCO\(_3\))\(^6\), is underestimated in forming MLDs. Using the pulse-echo-overlap method in a Paris-Edinburgh press coupled with X-ray diffraction, we explored the acoustic velocities of CaCO\(_3\) under high pressure-temperature (\(P\)-\(T\)) conditions relevant to the cratonic lithosphere. Two anomalous velocity drops were observed associated with the phase transition from aragonite to amorphous phase as well as with pressure-induced velocity drop in amorphous phase around 3 GPa, respectively. Both drops are comparable with approximately 35% and 52% reductions for compressional (\(V_P\)) and shear (\(V_S\)) wave velocities, respectively. The \(V_P\) and \(V_S\) values of the amorphous CaCO\(_3\) above 3 GPa are about 1/2 and 1/3 of those of the major upper-mantle minerals, respectively, and they are the same with aragonite below 3 GPa. These velocity reduction by the presence of CaCO\(_3\) would readily cause MLDs at depths of 70–120 km dependent on the geotherm even if only 1-2 vol.% CaCO\(_3\) presents in the cratonic lithosphere. The CaCO\(_3\)-originated MLDs is weak so as to be expected to influence the stability, rifting, and delamination of the craton\(^7\).

Introduction

Cratons are the cores of tectonomagnetically quiescent continents for at least 2.5 Ga featured with multiple physicochemical peculiarities, amongst which MLDs are the most distinguished one besides cool geothermal gradient, strong Fe- and H\(_2\)O-depletions, and multiple metasomatisms\(^8\)\(^,\)\(^9\). The MLDs produce both positive and negative, but mostly negative, seismic velocity gradients at depths of 60–160 km (predominantly between 80–120 km) in cratonic lithospheres\(^3\)\(^-\)\(^5\),\(^10\)\(^-\)\(^13\). The 2-10% reduction in \(V_S\) has been attributed to several attractive origins as partial melting, elastically accommodated grain boundary sliding (EAGBS), layered composition, layered anisotropy, and enrichment of seismically slow metasomatic minerals\(^3\)\(^-\)\(^5\),\(^14\)\(^-\)\(^16\). Recent studies indicate that partial melting and EAGBS are less likely to account for the MLDs since the geotherm of most MLDs falls between approximate 1,000 K and 1,200 K, which is well below the occurrence threshold (>1,300 K) of partial melting or EAGBS\(^3\)\(^,\)\(^5\),\(^16\). MLDs appear insensitive to pressure because their depth range is pretty wide, which makes a phase transition origin unlikely\(^4\). On the other hand, there is no phase transition in the volumetrically dominated olivine shallower than ~410 km and the phase transition of the second abundant pyroxene occurs at ~300 km depths in the upper mantle\(^17\). All those clues exclude layered composition as the possible origins of MLDs. For layered anisotropy, the diverse ray geometries of these MLDs do not support it as a global genesis\(^3\)\(^,\)\(^5\).

As the understanding of the cratonic lithospheres is enriched, accumulation of seismically slow metasomatic minerals becomes a preferred origin\(^3\)\(^,\)\(^14\)\(^-\)\(^16\). Rader, et al. \(^4\) and Eeken, et al. \(^16\) pointed out that 5–10% hydrous minerals (e.g., amphibole and phlogopite) or 10–15% aragonite-form CaCO\(_3\) could
reproduce the observed seismic signatures of the MLDs. This is consistent with the analysis results of xenoliths which indicate a more melt-depleted shallow cratonic lithosphere than its deep root caused by recrystallization of volatile-rich melt at depths less than 150-200 km. Amphibole is stable below 3 GPa and 1,350 K and the enrichment of amphibole can only explain the MLDs at depths shallower than 90 km. At depths greater than 90 km, phlogopite would be the main geological origin of the MLDs. CaCO₃ may work in the same way as hydrous minerals. However, the high $P$-$T$ electrical conductivity measurements of amphibole indicate the maximum fraction of hydrous minerals should be less than 1.5% to reconcile the magnetolluric observations. Another consequence of the enrichment of hydrous minerals in the MLDs is the young-age rocks sandwiched by old rocks, while the global resetting of the age at these regions is not observed.

Thus far, seeking the geological origin of the MLDs has been trapped in a dilemma. Notably, the pressure-induced $V_P$ and $V_S$ shrinks in amorphous phases occurred at 2–5 GPa and it is likely a common phenomenon in amorphous phases due to polymerization at relatively pressures. Then the newly discovered amorphous CaCO₃ phase stable above 2 GPa and 1,000 K may shed new light on the formation of MLDs. CaCO₃ is believed to be stable in cratonic lithosphere according to melting experiments of carbonated peridotite and eclogite below 5 GPa, and the Ca/(Ca+Mg) in quenched carbonate melts would approach 0.96-0.99 as pressure decreases because of the reaction of dolomitic parental melts with clinopyroxene. Consequently, most of the carbonates observed in xenoliths originated from 30–60 km depths are pure CaCO₃. Another theory for the CaCO₃-rich carbonatites in Earth's crust is that they originate from the recycled sediment-bearing oceanic crusts. CaCO₃ is a crystallizing phase over a large composition and temperature range in the ascending carbonatitic melt and it would be stable under the $P$-$T$ conditions of the cratonic lithosphere. That could be the reason why aragonite-form CaCO₃ was employed as a modeled candidate carbonate in explaining the formation of MLDs.

Bearing these in minds, we conducted high $P$-$T$ experiments using the pulse-echo overlap technique in a Paris-Edinburgh press. The acoustic velocities of aragonite and amorphous CaCO₃ were measured at 2.0-5.5 GPa up to 1,373 K. The representative radiograph, ultrasonic signals, and acoustic velocities as a function of frequency are presented in Fig. 1. We note that the large volume expansion in aragonite-amorphization phase transition assured the sample length ($l$) sufficient to avoid the overlapping of R1 and R2 signals reflected at the upper and lower interfaces of the sample, respectively, above 1,000 K (Fig. 1b). At the same time, a wide range of frequencies from 12 to 45 MHz with a step of 1 MHz were employed to obtain the travel time ($t$) of longitudinal ($V_P$) and transverse ($V_S$) ultrasonic signals in the sample on the basis of their different frequency sensitivities. High-quality R1 and R2 waveforms (Fig. 1c and 1d) were obtained to determine the $t$ up to 1,373 K at high pressure. The acoustic velocities calculated from varying frequencies agree with each other within experimental uncertainties, indicating the reliability of the measured $V_P$ and $V_S$ values in this study.
The measured acoustic velocities of calcite, aragonite and amorphous CaCO$_3$ are shown in Fig. 2. At 300–373 K and 3.0(1)–4.5(1) GPa, CaCO$_3$ is in the calcite-III phase$^{30}$ and its $V_P$ and $V_S$ values are about 6.2 and 3.2 km s$^{-1}$, respectively. They are in good agreement with previously published literature values$^{31}$. At 473(100) K, the calcite-III transforms into aragonite$^{6}$. The $V_P$ and $V_S$ values of aragonite are in the range of 6.00(7)–6.51(8) km s$^{-1}$ and 3.08(4)–3.48(4) km s$^{-1}$, respectively, at 473–973 K and 3.0(1)–5.0(1) GPa. Pressure dependences of the $V_P$ and $V_S$ for aragonite are 0.14(7) and 0.09(3) km s$^{-1}$ GPa$^{-1}$, respectively, whereas the temperature dependencies are very small if not negligible. It is noted that no abrupt changes were observed in acoustic velocities across the calcite-III to the aragonite phase transition.

With further increasing temperature greater than 1,000 K, aragonite gradually transformed into an amorphous phase as reported previously$^{6}$, which could be clearly observed in the energy-dispersive x-ray diffraction (EDXRD) patterns of CaCO$_3$ samples (Extended Data Fig. 2). There are two distinct characters of the acoustic velocities of the amorphous CaCO$_3$. Below ~2.6 GPa, both $V_P$ and $V_S$ are comparable between the amorphous phase and aragonite. In other word, no obvious difference can be distinguished even if the data scattering is considered. As pressure increases, both $V_P$ and $V_S$ values of the amorphous CaCO$_3$ gradually drop in a narrow pressure range of ~1 GPa and then monotonically increase. The pressure-induced velocity reductions have been reported in amorphous SiO$_2$, MgSiO$_3$, (Fe,Al)-bearing silicate, and Icelandic basaltic glass at 2–5 GPa$^{22-24}$. Such pressure-induced acoustic velocity reductions appear to be a common character for amorphous phases due to changes in the degree of polymerization$^{22-24}$. The drops of $V_P$ and $V_S$ for the aforementioned amorphous phases are approximately 12% and 18% compared with their crystalline phases, respectively. Interestingly, the velocity reduction from crystalline aragonite to amorphous CaCO$_3$ reaches about 19–42% above 3.5 GPa. The $V_P$ dramatically decreases from 6.20(7) to 5.01(6) km s$^{-1}$ at 1,073 K, then to 4.63(5) km s$^{-1}$ at 1,373 K around 3.6(1) GPa, while the $V_S$ directly drops from 3.19(4) to 1.39(3) km s$^{-1}$ at temperatures above 1,073 K. The intermedia $V_P$ is caused by partial amorphization of CaCO$_3$, which can also be observed at 1073–1173 K and higher pressures. Moreover, at the maximum pressure of 5.2(1) GPa in this study, acoustic velocities greatly reduced from 6.25(8) to 4.19(5) km s$^{-1}$ and from 3.19(4) to 1.54(2) km s$^{-1}$ for the $V_P$ and $V_S$, respectively when CaCO$_3$ fully transforms into the amorphous phase from aragonite. The minimum $V_P$ value of CaCO$_3$ was 4.13(5) km s$^{-1}$ at 1,273–1,373 K and 4.0(1)–5.5(1) GPa (Fig. 2). Compared to the $V_P$, the $V_S$ is less sensitive to temperature and it varies within a relatively narrow range of 1.23(1)–1.76(2) km s$^{-1}$ at 1,173–1,373 K and 3.5(1)–5.2(1) GPa. Compared to aragonite, the velocity reductions of the amorphous CaCO$_3$ are as high as 35% and 52% for the $V_P$ and $V_S$, respectively.

Acoustic velocities of the amorphous CaCO$_3$ are far below those of the major upper mantle minerals. Clinopyroxenes, olivine, garnet, pyrolite, and mid-ocean ridge basalts (MORBs) exhibit about 8.4, 8.5, 9.5, 8.5, and 8.0 km s$^{-1}$ for the $V_P$, respectively, and about 4.7, 4.8, 5.2, 4.8, and 4.3 km s$^{-1}$ for the $V_S$ respectively, under similar $P-T$ conditions of the current study$^{32-38}$. In comparison, acoustic velocities of
amorphous CaCO$_3$ are 47-56\% for the $V_P$ and 65-71\% for the $V_S$ lower than those of the common upper mantle components. Even for aragonite, its acoustic velocities are less by 8-35\% for the $V_P$ and 8-38\% for the $V_S$, respectively. The CaCO$_3$ likely possesses the lowest seismic velocities among all the common minerals and solid aggregates observed in the Earth's upper mantle. Both the crystalline-amorphization transition and pressure-induced velocity shrink above 3 GPa in CaCO$_3$ could induce low seismic velocity anomalies even if a small amount of CaCO$_3$ is present. The solidified CaCO$_3$ from melts would distribute in the interstitial sites of silicate matrix according to both high $P$-$T$ experiments\textsuperscript{26,39} and xenoliths\textsuperscript{40}, forming suitable phase equilibrium aggregates for seismic velocity averaging.

Pyrolite represents the composition of the Earth's ambient upper mantle\textsuperscript{41}. Here, we evaluate the effect of CaCO$_3$ on low seismic velocity anomalies by incorporating 5 vol.\% CaCO$_3$ in the pyrolite. The calculated seismic velocities are plotted in Fig. 3 and Extended Data Tables 1–3. The shaded regions in Fig. 3 are bounded by the Voigt and Reuss bounds\textsuperscript{42}, which denote the upper and lower limits of the seismic velocities, respectively. The strength of CaCO$_3$ phases, including the aragonite and amorphous CaCO$_3$ phase, is rheologically and elastically lower than the co-existing mantle silicates (e.g., olivine, pyroxene, and garnet)\textsuperscript{32-38}. The amorphous CaCO$_3$ phase is likely to be strongly dimensionally anisotropic, and the mineral matrix in these multi-phase aggregates cannot completely obey either the constant strain assumption for Voigt bound or the constant stress assumption for the Reuss bound. The Hill average, on the other hand, is likely to overestimate the elastic properties of this multi-phase rock matrix\textsuperscript{43}. The realistic elastic properties of pyrolite + 5.0 vol\% CaCO$_3$ would lie in between the Hill average and the lower Reuss bound. Below 3 GPa and 1,073 K, aragonite-form CaCO$_3$ is stable and the incorporation of 5 vol.\% aragonite can only lower down the seismic velocity of pure pyrolite by less than 2\%. However, at higher $P$-$T$ conditions (>3.5 GPa and >1073 K), aragonite will transform into the amorphous phase, which could significantly decrease the velocities of the CaCO$_3$-bearing pyrolite. At ~100 km depth, the seismic velocities ($V_P$ and $V_S$) of pyrolite + 5.0 vol\% amorphous CaCO$_3$ are 6.6–10.3\% and 11.4–19.7\% smaller than the pure pyrolite, respectively. If the geotherm is high enough to keep CaCO$_3$ in amorphous phase at pressure as low as 2 GPa, the pressure-induced velocity reduction in amorphous CaCO$_3$ would play the same role as crystalline-amorphization transition in producing the low seismic velocity anomalies. Thus, a small amount (e.g., 5.0 vol\%) of CaCO$_3$ can significantly reduce the seismic velocities of pyrolite along the geotherm of the cratonic lithosphere.

CaCO$_3$ is the major carbonate phase stable at the depths of MLDs (Fig. 4), which could be distributed in the interstitials of the grains of craton chemical compositions (peridotite, eclogite, and pyroxenites). As the molten carbonates percolate from the lithosphere-asthenosphere boundary (LAB) or the LAB retreats to greater depths because of the cooling of the Earth, carbonates would crystallize out. Although the primary melts contain significant magnesium (Mg), it would be consumed by the mantle wall rock during ascending upward and the carbonates will be enriched in CaCO$_3$. This is well confirmed by laboratory experiments and the CaCO$_3$ content in carbonates reach a maximum around 3–5 GPa\textsuperscript{25}. In the geological
time scale, the depths with noticeable accumulation of CaCO$_3$ would be expected at depths greater than 150 km. According to the phase diagram of CaCO$_3$ and the $P$-$T$ conditions of the cratonic lithosphere, the initial solidified CaCO$_3$ would be in the amorphous phase. At depths shallower than ~120 km, the seismic velocities of amorphous CaCO$_3$ are far below those of the main craton minerals and its crystalline phase. As CaCO$_3$ migrates upwards, it may transform to the high-velocity aragonite along a cold geotherm or to the high-velocity amorphous CaCO$_3$ at depths shallower than ~80 km along a warm/hot geotherm. Then a seismic velocity discontinuity would be present at depths of 80–120 km due to the crystalline-amorphization transition or the pressure-induced velocity reduction of the amorphous CaCO$_3$. Therefore, the observed 2–10% seismic reduction in the $V_S$ of the MLDs$^{3-5,10-13}$ would be readily explained by the presence of only 2 vol.% CaCO$_3$.

The enrichment and thermodynamically stabilization of the metasomatic CaCO$_3$ in the cratonic lithosphere make it a viable, competitive mechanism in forming the MLDs over other explanations. In addition, this mechanism could avoid constraining the CaCO$_3$ in a confined depth. Even if CaCO$_3$ distributes homogeneously from the surface to the depths of ~150 km, the crystalline-amorphization transition or pressure-induced velocity reduction could guarantee a seismic velocity discontinuity at depths of 80-120 km. This also meet the constraints of global resetting of the age at these regions$^{21}$ and magnetolluric observations$^{19,20}$.

**Methods**

*Experimental methods*

The starting material is reagent CaCO$_3$ powder (grain size: ~1µm) purchased from Alfa Aesar Company with a purity of 99.99% (CAS No.: 471-34-1). The CaCO$_3$ powder was pre-compressed to a cylinder with 0.8 mm in height and 2 mm in diameter using a tungsten steel compressor. Then the sample cylinder was loaded into a standard high-pressure and high-temperature Paris-Edinburgh (PE) cell assembly (see Supporting Materials) and compressed above 3GPa before measurement. The sample porosity should be extremely low due to the soft nature of the sample. The experiments were conducted using the PE press at 16-BM-B, High Pressure Collaborative Access Team (HPCAT) at the Advanced Phonon Source, Argonne National Laboratory, USA. The pulse-echo overlap technique was employed to obtain the ultrasonic $V_P$ and $V_S$ signals of the CaCO$_3$ sample. An ultrasonic excitation sine wave of 3-periods long, containing compressional and shear components, was generated using 10° Y-cut LiNbO$_3$ transducer. The wave was reflected at the buffer-rod/sample (R1) and sample/backing (R2) interfaces and the travel time ($t$) of the ultrasonic wave in the sample was determined by R1 and R2 signals. Ultrasonic reflection (echo) signals were collected with excitation waves varying from 12 to 45 MHz with a step of 1 MHz. The sample length ($l$) was measured by polychromatic X-ray radiography. The total uncertainties of the derived acoustic velocities are about 1.2% which originated from two parts: (1) uncertainties in determining the sample length and travel time ($t$) of signal in the sample (less than 0.5%) and (2) frequency-induced uncertainty
The pressure was determined by thermal EOS of MgO and pre-calibrated power-temperature relations with uncertainties of 0.2 GPa in pressure and of 100 K in temperature, respectively.

**Voigt, Reuss, and Hill averaging methods**

The Voigt bound corresponds to a uniform strain scenario while the Reuss bound to a uniform stress scenario. In a multi-phase aggregate, they are defined as:

\[
\text{Voigt bound: } E^V = f_a E_a + f_b E_b
\]

\[
\text{Reuss bound: } E^R = \left(\frac{f_a}{E_a} + \frac{f_b}{E_b}\right)^{-1}
\]

\[
\text{Hill average: } E^{VRH} = \frac{E^V + E^R}{2}
\]

\[
V_p^2 = \frac{K}{\rho} + 4/3 \frac{G}{\rho}
\]

\[
V_s^2 = \frac{G}{\rho}
\]

where \(E^V, E^R,\) and \(E^{VRH}\) represent the aggregate material properties (bulk modulus \(K\), shear modulus \(G\), and density \(\rho\)) of Voigt bound, Reuss bound, and Hill average, respectively; \(E_a\) and \(E_b\) represent the properties of phase \(a\) and \(b\), respectively; \(f_a\) and \(f_b\) represent the volume fractions of phases \(a\) and \(b\), respectively. The average properties of a multi-phase aggregate shall lie in between the Voigt and Reuss bounds. The modeled seismic velocity values have been listed in Extended Data Tables 2-3.

**Declarations**

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Figures
Figure 1

**Acoustic velocity measurements of CaCO$_3$ at high pressure and temperature.** (a) Acoustic velocities as a function of frequency. Black squares: aragonite at 4.0 GPa and 873 K; blue circles: amorphous CaCO$_3$ at 3.6 GPa and 1,273 K. The uncertainties of the measured acoustic velocities are less than 1.2% and the error bars are within the symbols. (b) Polychromatic X-ray radiograph. The red dash lines denote the interfaces of the sample/buffering rod and sample/backing rod. The sample length ($l$) can be determined by the pixels between the two dash lines in the image. (c) and (d): The $V_P$ and $V_S$ signals (R1 and R2) of CaCO$_3$ at 3.6 GPa and 1,273 K as a function of acoustic frequency.
Figure 2

The acoustic velocities of aragonite/calcite (a) and amorphous CaCO$_3$ (b) at elevated pressures and temperatures. The solid lines in (a) are linear fits to the experimental $V_P$ and $V_S$ values and the curves in (b) are drawn by hand to guide eyes. Error bars are smaller than the symbol size and are not shown for clarity.
Figure 3

The seismic velocities of the pyrolite + 5 vol.% amorphous CaCO$_3$ along a typical craton geotherm with surface heat flux of 40 mW/m$^2$. The solid black and blue curves represent the seismic velocities of pyrolite and amorphous CaCO$_3$, respectively. The shaded blue areas are bounded by Voigt (up) and Reuss average of seismic velocities of pyrolite + 5 vol.% amorphous CaCO$_3$. The dash curve is obtained by Hill average. Red arrows denote the velocity reductions of Reuss bound and Hill average compared with the pure pyrolite.
The stability field of amorphous CaCO$_3$ constrained by its phase diagram$^6$, craton geotherms (surface heat flux of 35, 40 and 45 mW/m$^2$)$^{45}$, and the solidi of carbonated eclogites$^{39}$ and peridotite$^{26}$ (up) and the schematic of CaCO$_3$-originated seismic abnormalities in the cratonic lithosphere (down). The red dot curve represents the solidi of carbonated eclogite (Fe-Mg-Ca-Na-K carbonates) in Dasgupta, et al.$^{46}$ The
solidi of carbonated eclogite are significantly affected by Ca\# and Na\# in the system. When the carbonate phase is CaCO$_3$, the carbonated eclogite would melt at much higher temperatures\textsuperscript{39}.

**Supplementary Files**

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