

TITLE

Reversal of carbonate-silicate cation exchange in cold slabs in Earth's lower mantle

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ABSTRACT

The stable forms of carbon in Earth's deep interior control storage and fluxes of carbon through the planet over geologic time, impacting the surface climate as well as carrying records of geologic processes in the form of diamond inclusions. However, current estimates of the distribution of carbon in Earth's mantle are uncertain, due in part to limited understanding of the fate of carbonates through subduction, the main mechanism that transports carbon from Earth's surface to its interior. Oxidized carbon carried by subduction has been found to reside in MgCO₃ throughout much of the mantle. Experiments in this study demonstrate that at deep mantle conditions MgCO₃ reacts with silicates to form CaCO₃. In combination with previous work indicating that CaCO₃ is more stable than MgCO₃ under reducing conditions of Earth's

lowermost mantle, these observations allow us to predict that the signature of surface carbon reaching Earth's lowermost mantle may include CaCO_3 .

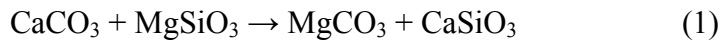
INTRODUCTION

Carbon is not only key to life and Earth's habitability, but also traces and modifies geological processes of subduction, partial melting, degassing, and metasomatism, providing valuable insights into Earth's evolution¹. Over the history of the planet, carbon transport between surface and deep reservoirs has impacted the atmospheric, oceanic and crustal CO_2 budgets in tandem with the composition and redox state of the Earth's mantle^{2, 3}. Carbon is transported from Earth's surface to its interior mainly as carbonate minerals in subduction zones, and is returned in carbon-bearing gas/fluid through volcanic degassing^{2, 3}. These processes leave signatures in the mantle including depletion of incompatible elements^{4, 5}, diamond formation (and inclusions)^{6, 7}, and isotopic abundances^{8, 9}. Carbon flux via subduction to the deep mantle remains uncertain, with estimated magnitudes ranging from 0.0001 to 52 megatons/year^{3, 10}. The wide range of these estimates is due in part to limited understanding of the physical and chemical responses of carbonates to mantle pressures, temperatures, and compositional environments.

The dominant carbonates carried into the mantle by subducting slabs, dolomite $\text{CaMg}(\text{CO}_3)_2$, magnesite MgCO_3 , and calcite CaCO_3 ¹¹, undergo changes in crystal structure or state and chemical reactions at depth. Carbonates are likely to be retained as solid minerals in subducting ocean crust until/unless the solidus of carbonated peridotite^{12, 13} or eclogite^{14, 15} intersects with mantle geotherms, initiating melting. These slab-derived carbonatite melts will segregate to the overlying mantle due to low viscosity and density¹⁶, or be reduced to diamonds at depths greater than ~250 km via redox freezing^{7, 15, 17}. However, carbonates are present in

transition zone and possibly lower mantle depths in some regions, based on direct evidence provided by carbonate minerals found in deep-sourced diamond inclusions^{18, 19}. Additional evidence from thermodynamic modeling of devolatilization of carbonate-bearing subducting slab^{20, 21}, and melting experiments on carbonates in the MgCO₃-CaCO₃ system up to 80 GPa²² supports preservation of solid carbonates along low-temperature geotherms in subducting slabs in the lower mantle. However, temperature is not the only control on the fate of subducted carbonates: carbonates may also interact chemically with the major phases of the ambient mantle or basalt-rich subducted crust. In these compositions in the lower mantle, the silicates potentially reacting with carbonates are bridgmanite (bdg), post-perovskite (pPv), and Ca-perovskite (Ca-Pv).

The presence of the end-member carbonates, MgCO₃ and CaCO₃ (note that (Mg,Ca)(CO₃)₂ dolomite breaks down to these end-members above 5 GPa and 1200 K²³), together with lower mantle silicates depends on the thermodynamics and kinetics of the carbonate-silicate exchange reaction:



Previous experiments^{24, 25} indicate CaCO₃ reacts with silicates to form MgCO₃ via the forward reaction up to 80 GPa and 2300 K, i.e. at least to the mid-lower mantle. Theoretical studies further predict that MgCO₃ + CaSiO₃ are enthalpically favored over CaCO₃ + MgSiO₃ throughout the lower mantle pressure and temperature regime^{26, 27, 28, 29, 30}. However, although many studies have addressed the stability of individual carbonates up to higher pressures^{31, 32, 33}, no experiments examined the carbonate-silicate cation exchange reaction up to core-mantle boundary conditions.

In this work, to assess the stability of MgCO_3 and CaCO_3 coexisting with lower mantle silicates, we conduct a series of experiments on the carbonate-silicate reaction along the lower mantle geotherm. Thin disks of carbonates and silicates were loaded together in laser-heated diamond-anvil cells (Table S1, see Methods for details). Laser heating at 1600-2800 K and 33-137 GPa was applied for 10-400 mins. Run products were examined by in-situ synchrotron X-ray diffraction (XRD) and ex-situ energy-dispersive X-ray spectroscopy (EDX) analysis with a scanning transmission electron microscope (STEM, see Methods for details).

RESULTS

Experiments assessed thermodynamic stability by using as reactants either $(\text{Mg,Ca})\text{CO}_3 + (\text{Mg,Fe})\text{SiO}_3$ (reactants for the forward reaction, hereafter referred to CaC-to-MgC) and $(\text{Mg,Fe})\text{CO}_3 + \text{CaSiO}_3$ (reactants for the reverse reaction, hereafter referred to MgC-to-CaC). For reaction CaC-to-MgC, the criterion for determining whether the reaction takes place is the presence of newly-synthesized CaSiO_3 -perovskite in the run product. For reaction MgC-to-CaC, newly-synthesized MgSiO_3 and CaCO_3 indicate the reaction is favorable. The silicate reaction products are easier to observe through diffraction than carbonates due to higher diffraction intensity.

Calcium carbonate reaction to form magnesium carbonate

Experiments with CaC-to-MgC reactants indicate the forward reaction takes place in runs conducted below 83 GPa (runs #1-4), as determined via both EDX and XRD. For example, ex-situ electron microscopic analysis of the sample recovered from 33 GPa and 1650 K (run #1) (Fig.1a-c) reveals a $\sim 1\text{-}\mu\text{m}$ -thick layer of CaSiO_3 between the silicate layer and the carbonate

layer, coexisting with SiO_2 , FeO , MgSiO_3 , and MgCO_3 . These observations are consistent with in-situ XRD patterns of run products after heating (Supplementary Fig. 3b, Supplementary Fig. 5a), which exhibit several new sharp peaks compared to the pattern before heating (Supplementary Fig. 3a). The diffraction pattern of run products is consistent with the presence of Ca-Pv, magnesite, bdg, wüstite, stishovite, and monoclinic dolomite III (previously observed at pressure above 36 GPa³⁴). Ca-Pv can be observed in the run products of CaC-to-MgC up to 83 GPa (Supplementary Fig. 3c, Supplementary Fig. 4a-b), in agreement with previous experimental observations^{24, 25}.

At higher pressures from 91 to 137 GPa, however, we observe no evidence of carbonate-silicate exchange reaction in experiments with CaC-to-MgC reactants. Ca-Pv is not identified in the run products (runs #5-7) through either in-situ (Supplementary Fig. 3d-e, Supplementary Fig. 4c-d, Supplementary Fig. 5b) or ex-situ analysis. New, sharp peaks from bdg and pPv can be observed in-situ in XRD patterns (Supplementary Fig. 3d-e), indicating the sample was sufficiently heated to transform starting materials to high-pressure silicate structures, but no carbonate-silicate exchange reaction occurs. Two hypotheses can explain these observations: (1) in contrast to theoretical predictions that the reversal of the carbonate-exchange reaction takes place at higher pressures and lower temperatures^{26, 27, 28, 29, 30}, $\text{CaCO}_3 + \text{MgSiO}_3$ become more favorable than $\text{MgCO}_3 + \text{CaSiO}_3$ from 91-137 GPa and 2100-2800 K; (2) the reaction CaC-to-MgC is hindered by reaction kinetics, and metastable starting materials are observed.

Magnesium carbonate reaction to form calcium carbonate

In order to resolve the thermodynamically stable phase assemblage, three separate sets of experiments on the backward reaction (MgC-to-CaC, runs #8-11) were conducted at 35-133 GPa and 1800-2000 K. Elemental mapping of the run products of experiments at 88 GPa (run #10,

Fig. 1d-f) and 133 GPa (run #11, Fig. 1g-i) indicates that MgSiO_3 layers formed along the carbonate-silicate interface, and newly-formed CaCO_3 can be observed as well. At 35 GPa, neither EDX nor XRD shows MgSiO_3 formed from MgC-to-CaC reactants (run #8, Supplementary Fig. 9). Observations of the reversal of the reaction confirm that MgCO_3 is unstable and reacts with CaSiO_3 producing CaCO_3 and MgSiO_3 at pressures higher than 88 GPa along a lower mantle geotherm.

Our results agree with previous experimental constraints (Fig. 2) below 80 GPa showing: dolomite is unstable relative to CaCO_3 and MgCO_3 at lower mantle conditions^{23, 24, 25, 35}; neither CaO nor MgO are observed in run products, indicating no decomposition of CaCO_3 and MgCO_3 into oxides plus CO_2 ^{26, 27, 30}; MgCO_3 is more favorable in the lower mantle than CaCO_3 up to ~80 GPa due to the CaC-to-MgC reaction^{24, 25}. Since similar previous studies were limited to pressures below 80 GPa, they did not observe the reversal reaction (MgC-to-CaC). Combining our new results with previous results^{24, 25} and theoretical predictions indicating a positive Clapeyron slope for this reaction^{28, 29, 30}, we suggest a reaction boundary above 80 GPa with a positive slope (black dashed line in Fig. 2). We note that the experimental data allow for significant uncertainty in this boundary, but are inconsistent with theoretical predictions^{28, 29, 30} (yellow region, Fig. 2). This discrepancy may have been produced by theoretical approximations at higher temperatures. If density functional perturbation theory and quasi-harmonic approximation have misestimated the volumes of the carbonate phases expected to be stable at ~80 GPa and higher pressures, this could lead to the systematic overestimation of Gibbs free energy of $\text{CaCO}_3 + \text{MgSiO}_3$ relative to $\text{MgCO}_3 + \text{CaSiO}_3$ at higher temperatures.

DISCUSSION

The pressure/temperature conditions of the reversal reaction as constrained by these experiments are similar to those of polymorphic phase transitions associated with sp^2 - sp^3 bonding changes in both $MgCO_3$ and $CaCO_3$, which suggests these transitions are related to the stabilization of a $CaCO_3 + MgSiO_3$ assemblage. The transition from sp^2 - to sp^3 -bonds in $MgCO_3$ has been identified at ~ 80 GPa with the stabilization of the $C2/m$ structure^{32, 33, 36}, and the resulting densification of $MgCO_3$ supports the forward reaction to $MgCO_3 + CaSiO_3$. The transition in $CaCO_3$ from sp^2 - to sp^3 -bonds in the $P2_1/c$ -h structure was experimentally observed at ~ 105 GPa and 2000 K³⁷. Computational studies predicted this boundary at ~ 70 ²⁹ and ~ 100 GPa³⁸ at mantle-relevant temperatures (red shaded region in Fig. 3). While an earlier study that did not include the sp^3 $CaCO_3$ - $P2_1/c$ -h structure predicted a crossover in silicate-carbonate exchange reaction at 135 GPa and 0 K²⁶, a later study that predicted the sp^3 $CaCO_3$ - $P2_1/c$ -h structure found a silicate-carbonate reaction reversal at 84 GPa and 0 K³⁰. This would correspond to sp^2 - sp^3 crossover and stabilization of $CaCO_3 + MgSiO_3$ in the mid-lower mantle.

Whether a crossover in the carbonate-silicate exchange reaction takes place in the deep Earth depends on whether carbonates are preserved in Earth's lower mantle to at least 1800 km depth. Previous studies have identified barriers to carbon subduction and stability in the lower mantle, particularly melting^{15, 39} and reduction^{40, 41, 42}. If carried in cold subducting slabs, $MgCO_3$ and $CaCO_3$ may avoid melting as their melting temperatures²² are higher than some predicted cold slab geotherms³⁶. Any solid carbonate in the mantle will be in contact and may equilibrate with silicates in all mantle environments and with free silica in basalt-rich compositions. $MgCO_3$ and $CaCO_3$ have been observed in experiments^{40, 41, 42} to undergo decarbonation reactions with free silica over a pressure range of ~ 40 to 60 GPa. However, the Clapeyron slope of $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ is positive and takes place at pressure/temperature conditions warmer

than the coolest slab geotherms⁴⁰. Observations that MgCO_3 is less thermally stable than CaCO_3 support the survival of CaCO_3 rather than MgCO_3 along a cold subducted slab geotherm to the lowermost mantle^{36, 41} (Fig. 3). In this study, we report a reversal in the Mg-Ca silicate-carbonate cation exchange reaction at ~ 90 GPa, making $\text{MgCO}_3 + \text{CaSiO}_3$ favorable in the upper part of the lower mantle, while $\text{CaCO}_3 + \text{MgSiO}_3$ is preferred in the lower part of the lower mantle (Fig. 3). However, the question of whether any carbonate persists to these depths in the coldest subducting slabs remains unresolved. If MgCO_3 remains present in cold slabs, and the reaction CaC-to-MgC proceeds throughout most of the mantle eliminating CaCO_3 , the reversal MgC-to-CaC reaction may transform MgCO_3 back to CaCO_3 in the lowermost mantle (Fig. 4). CaCO_3 could thus be found in the lowermost mantle coexisting with silicates and reduced iron.

The reduced nature of the Earth's mantle, with oxygen fugacity inferred to be near the iron-wüstite buffer in the transition zone and greater depths⁴³, stabilizes diamond or Fe-carbide as long-term hosts of carbon, owing to their chemical refractoriness and dynamic immobility⁴⁴. Similarly, our experimental observations support CaCO_3 as a refractory, stable host for oxidized carbon in the middle to lowermost mantle, in particular, the high-pressure polymorph of CaCO_3 ($\text{CaCO}_3\text{-}P2_1/c\text{-h}$) with tetrahedral bonds³⁷. Experimental observations also suggest CaCO_3 is more resistant to redox breakdown reaction with iron under reduced conditions than MgCO_3 ³⁵. In addition, due to the cation exchange between carbonate and silicate, the relative stability of MgCO_3 or CaCO_3 will change in the lowermost mantle, and depending on conditions one of these phases may buffer the redox state of the mantle through an influx of oxidized carbon in the form of solid carbonate⁴⁵.

The Mg-Ca silicate-carbonate exchange reactions along subduction pressure-temperature (P - T) conditions may impact observable signatures of Mg and Ca isotopes in mantle silicates

under certain special conditions, or in carbonate inclusions in diamonds. Subducting carbonates carry low- $\delta^{44/40}\text{Ca}$ and low- $\delta^{26}\text{Mg}$ signatures relative to the heavier mantle ratios, but although previous studies have observed heterogeneity in the Ca and Mg isotope signatures in basalts and mantle peridotites, these studies determined that lighter ratios cannot be simply interpreted as evidence of recycled marine carbonates^{46, 47}. The Mg-Ca silicate-carbonate exchange reactions along subduction P - T conditions may contribute to these variable Mg and Ca isotopic compositions. The reaction CaC-to-MgC in the transition zone and upper part of the lower mantle would transfer light Ca isotopes from subducted CaCO_3 to CaSiO_3 (Ca-Pv) (Supplementary Note, Supplementary Fig. 12). Isotopically light Ca-Pv can then be trapped in diamond inclusions and return to the surface⁴⁸, while the Ca isotopic signature of upwelling rocks would remain variable, as it undergoes continuous fractionation within peridotitic mantle lithologies^{46, 49, 50, 51}. The modification of carbonate-silicate phase equilibria observed in this study provides a new process that could alter Mg and Ca isotopic composition in such lithologies (Supplementary Note, Supplementary Fig. 12). While the isotope signature of MgSiO_3 produced by reaction MgC-to-CaC would not be observable due to the small masses involved relative to the vast lower mantle reservoir of MgSiO_3 , any CaCO_3 produced in the deep lower mantle by this reaction would carry a heavier deep mantle $\delta^{44/40}\text{Ca}$ signature that would distinguish it from surface-derived carbonate. If preserved in diamond inclusions and returned to the surface, heavy CaCO_3 could be used to trace the presence of oxidized carbon in the lowermost mantle. The potential of CaCO_3 to be a signature of an ultradeep carbon cycle reaching the core-mantle-boundary region may help to reveal other mysteries of the deep mantle, such as heat budget related to radioactive elements stored in Ca-bearing silicates⁵², and compositions of heterogeneities that may record Earth's early history^{48, 53}.

METHODS

To investigate phase equilibria in the carbonate-silicate system in Earth's lower mantle and control for effects of reaction kinetics, both CaC-to-MgC and MgC-to-CaC experiments were carried out in symmetric diamond anvil cells with flat-top double-sided laser heating⁵⁴. For CaC-to-MgC, natural dolomite with homogeneous composition of $(\text{Mg}_{0.38}\text{Ca}_{0.59}\text{Fe}_{0.03})\text{CO}_3$ was used as a carbonate reactant, the composition and structure of which has been characterized by X-ray fluorescence spectroscopy and X-ray diffraction, respectively³⁵. Fe-bearing enstatite synthesized at École Polytechnique Fédérale de Lausanne with a composition of $(\text{Mg}_{0.5}\text{Fe}_{0.5})\text{SiO}_3$ was used as a silicate reactant⁵⁵. For MgC-to-CaC, natural ferromagnesite (sample from Princeton University) was used as a carbonate reactant, with composition determined to be $(\text{Mg}_{0.87}\text{Fe}_{0.13})\text{CO}_3$ by wavelength dispersive X-ray spectroscopy in a Cameca SX100 Electron Probe Microanalyzer at University of Michigan. Pure calcium silicate (CaSiO_3 , Alfa Aesar) was used as a silicate reactant. The chief advantages to the abovementioned starting compositions are that recognition of a carbonate-silicate exchange reaction only requires identification of the presence of newly synthesized silicates in quenched run products, i.e., Ca-perovskite (Ca-Pv) in CaC-to-MgC and bridgmanite (bdg) in MgC-to-CaC; and Fe-bearing enstatite and ferromagnesite can serve as laser absorber during forward CaC-to-MgC and reversal MgC-to-CaC experiments, respectively.

The dolomite, enstatite, and calcium silicate samples were separately ground under acetone in an agate mortar for ~2 hours each to achieve homogenous, finely powdered samples with grain size typically less than ~2 μm . A single ferromagnesite crystal was double-side polished to ~10-micron thickness. All starting materials were dried in an oven at 120 °C

overnight before loading, and the powder samples were subsequently pressed in a diamond anvil cell to form thin foils approximately $\sim 8\text{-}10\text{ }\mu\text{m}$ thick. The enstatite foils and ferromagnesite crystals were sandwiched between Fe-free dolomite and calcium silicate, respectively, serving as thermal insulators in symmetric diamond anvil cells for CaC-to-MgC and MgC-to-CaC (Supplementary Fig. 1-2). No other pressure standard or medium was loaded to prevent reactions with other components and contamination of the chemical system. The sample sandwiches were loaded in sample chambers with diameters approximately halves of the anvil culet sizes drilled into Re gaskets pre-indented to a thickness of $\sim 30\mu\text{m}$, by using the laser drilling system at HPCAT (Sector 16) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL)⁵⁶. Diamond anvils with flat culets of $300\text{ }\mu\text{m}$ were used for experiments under 60 GPa, beveled culets of $150/300\text{ }\mu\text{m}$ for experiments under 100 GPa, and beveled culets of $75/300\text{ }\mu\text{m}$ for experiments up to 140 GPa.

Before laser heating, each sample was compressed to the target pressure at 300 K, and after heating each sample was quenched to ambient pressure at 300 K to limit and preserve reactions at target conditions. Pressure was determined from the Raman shift of the singlet peak of the diamond anvil at the culet surface⁵⁷, and post-heating pressures were typically within 3% of the pre-heating pressure. Thermal pressure during heating may be estimated to be $\sim 10\%$ GPa higher than the pre-heating pressure at the modest temperatures^{58, 59}. High-temperature conditions were achieved by using a double-sided ytterbium fiber laser heating system at beamline 13-ID-D (GeoSoilEnviroCars) of APS, ANL⁵⁴, with two $1.064\text{ }\mu\text{m}$ laser beams focused down to a flat-top spot with a diameter of $10\text{-}12\text{ }\mu\text{m}$ on both sides of the sample. Temperatures of the heated samples were determined by fitting the measured thermal radiation spectra using the Planck radiation function under the graybody approximation⁵⁴. The temperature reported in

Table S1 is the temporal average of multiple temperatures measurements over the heating duration. Temperature fluctuations over this time scale were less than the specified uncertainty, which is derived from a standard deviation of temperature measurements from both sides of the laser-heated sample (typically ± 100 K below 2000 K and ± 150 K above 2000 K) (Supplementary Fig. 10, Supplementary Fig. 11). Experiments were held at temperatures between 1600 and 2800 K for ~ 30 min in CaC-to-MgC experiments and up to 400 min in MgC-to-CaC experiments.

Phases synthesized at high P/T and achievement of chemical steady-state were determined by in-situ angle-dispersive X-ray diffraction (XRD) measurements performed before, during and after heating at beamline 13-ID-D (GeoSoilEnviroCars) of APS, ANL. The incident X-ray beam was focused down to less than $3 \times 4 \mu\text{m}^2$ with a monochromatic wavelength $\lambda = 0.3344 \text{ \AA}$. Diffracted X-rays were recorded using a MAR 165 detector or Pilatus 1M CdTe pixel array detector. NIST standard LaB_6 was used to calibrate the detector distance, tilt angle, and rotation angle of the image plane relative to the incident X-ray beam. Exposure times were typically 30 s. The XRD patterns were integrated to produce 2θ plots using the software DIOPTAS⁶⁰.

After complete pressure release, each sample was recovered from the LHDAC, and then sectioned along the compression axis through the laser-heated spot and over the entire thickness of the DAC sample ($\sim 5\text{-}20 \mu\text{m}$), using a focused ion beam (FIB) coupled with a field emission scanning electron microscope (FE-SEM) at IPGP (Paris, France) or the Michigan Center for Materials Characterization at the University of Michigan (Ann Arbor, USA). A $\sim 30\text{-nm}$ -thick Au layer was coated on each sample to reduce charging in the scanning electron microscope, and a $2\text{-}\mu\text{m}$ -thick Pt layer was deposited across the center of each heated spot to protect the sample

from damage by the Ga⁺ ion beam. Thin sections of each heated spot were extracted and polished to electron transparency (~100 nm thickness).

Textural and chemical characterization of recovered samples was performed with scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) in a JEOL 2200FS field emission TEM (Center for Advanced Microscopy, MSU), operated at 200 kV to image the sample in Bright-Field. EDX maps were scanned over 512 × 384 pixel areas with a pixel dwell time of 50 microseconds. Typical count rates were ~2,000 counts per second. Chemical mapping rather than point measurement approach prevents migration of elements due to damage by the electron beam. Uncertainties in compositions were determined from standard deviations of EDX measurements obtained from selected regions within multiple grains.

DATA AVAILABILITY

Additional diffraction and spectroscopy data and metadata are available in the supplementary materials and from the corresponding authors upon request.

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AUTHOR CONTRIBUTIONS

M. Lv: Conceptualization, Investigation, Formal analysis, Writing - Original Draft, Visualization; S. M. Dorfman: Conceptualization, Methodology, Investigation, Writing - Review & Editing, Supervision; James Badro: Conceptualization, Supervision, Writing - Review & Editing; S. Borensztajn: Investigation; E. Greenberg: Resources, Writing - Review & Editing; V. B. Prakapenka: Resources, Methodology, Writing - Review & Editing.

COMPETING INTERESTS

The Authors declare no competing interests.

FIGURES

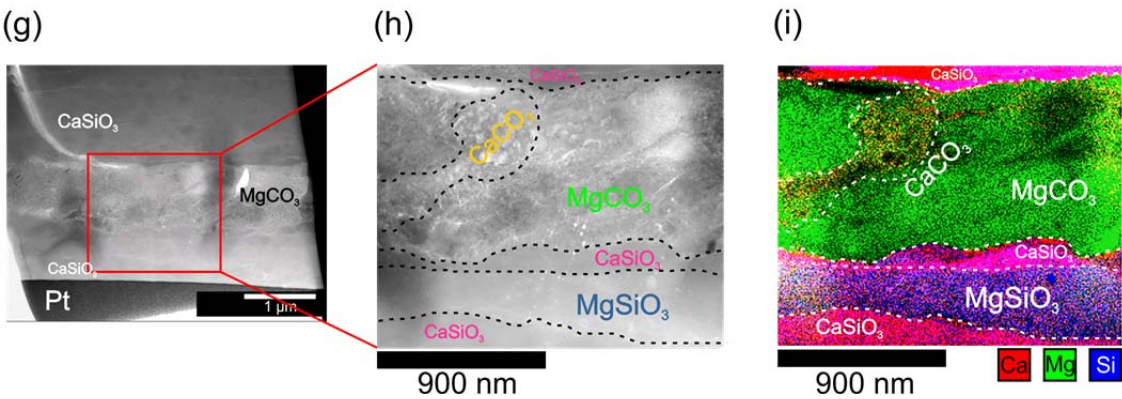
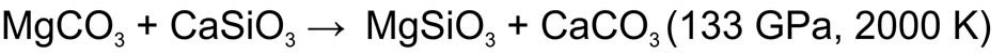
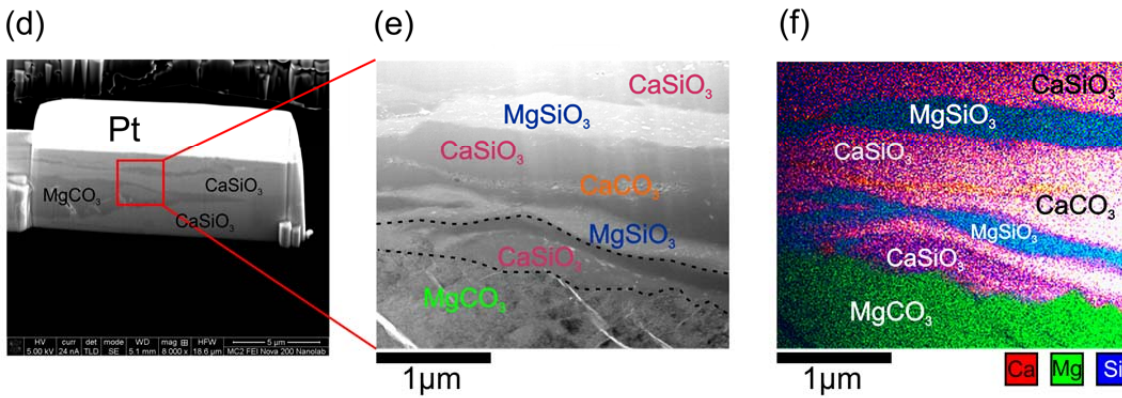
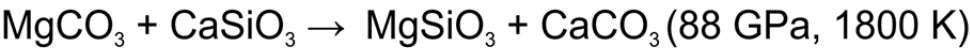
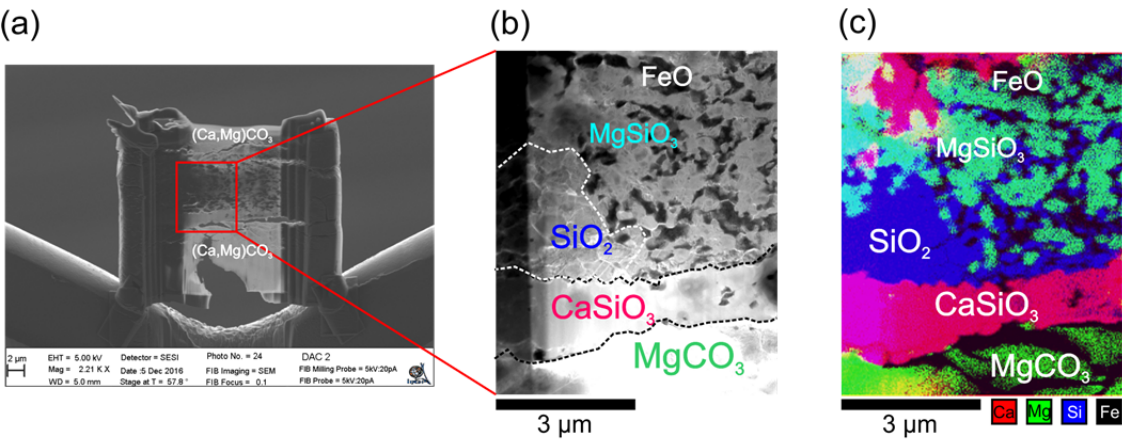
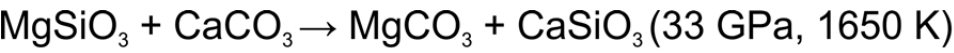
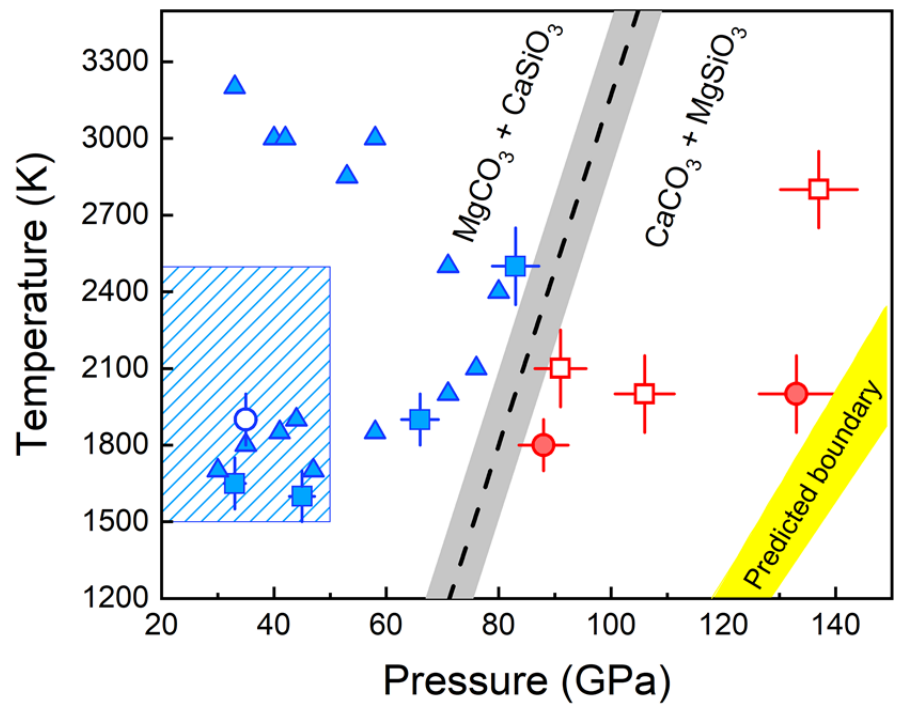


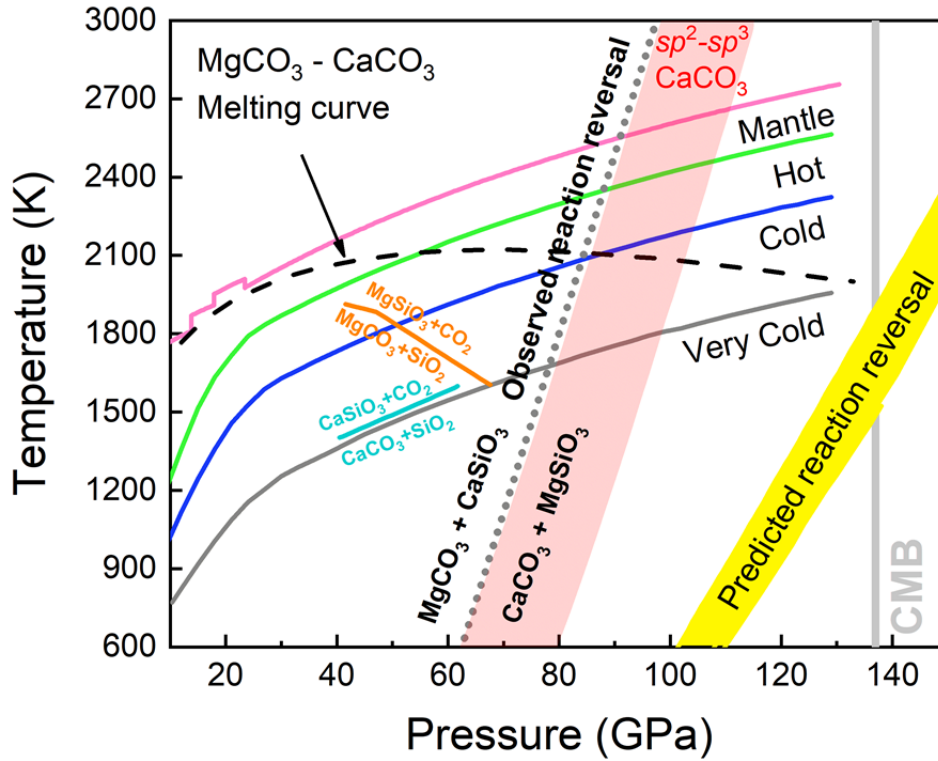
Figure 1. Images of selected recovered sample cross-sections obtained using backscattered scanning electron microscopy (a, d, g), scanning transmitted electron microscopy (b, e, h) and

energy-dispersive X-ray mapping (c, f, i) of the cross-section show the silicate layer sandwiched by two carbonate layers, with the reaction region along the contacting interface. (a-c) Ex-situ analysis of sample quenched from 33 GPa and 1650 K heated for 15 min (run #1) demonstrates reaction CaC-to-MgC: CaSiO_3 is not present in starting materials but is indicated in EDX map by colocation of Ca and Si, shown in magenta; (d-f) Ex-situ analysis of sample quenched from 88 GPa and 1800 K heated for 150 min (run #9) demonstrates reaction MgC-to-CaC: MgSiO_3 is not present in starting materials but is indicated in EDX map by colocation of Mg and Si, shown in blue-green. CaCO_3 also appears as red (Ca, but no Si) ribbon within CaSiO_3 starting material. (g-i) Ex-situ analysis of sample quenched from 133 GPa and 2000 K heated for 400 min (run #10) demonstrates reaction MgC-to-CaC: MgSiO_3 appears as Ca-depleted, Si-rich region (blue or blue-green) adjacent to CaSiO_3 starting material (magenta).



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534 **Figure 2.** Pressure-temperature conditions of carbonate-silicate exchange reaction (sketched as
535 black dashed line with gray shadow as uncertainty) inferred based on experimental observations
536 of CaC-to-MgC and MgC-to-CaC. Squares represent observations from this work starting with
537 (Ca,Mg)CO₃ and (Mg,Fe)SiO₃, looking for newly-synthesized CaSiO₃ to indicate the CaC-to-
538 MgC reaction takes place. Circle symbols represent observations from this work of experiments
539 starting with (Mg,Fe)CO₃ + CaSiO₃, looking for identification of newly-synthesized MgSiO₃ to
540 indicate the MgC-to-CaC reaction takes place. Open symbols indicate nonreaction and filled for
541 confirmed reaction, and blue and red colors correspond to the inferred stable phase assemblage
542 based on reaction products. Triangles indicate the *P-T* conditions for CaC-to-MgC taking place
543 reported by Seto et al.²⁵, and blue shaded region indicates approximate conditions of four
544 experiments conducted by Biellmann et al.²⁴ using indirect methods for pressure and temperature
545 calibration, which all produced the run products MgCO₃ + CaSiO₃. The error bars indicate
546 uncertainties of pressure and temperature measurements (see Methods for details).



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Figure 3. Pressure-temperature diagram showing reactions between carbonate, silicates, and silica in the subducted oceanic crust to the lower mantle. The grey dotted line indicates the reversal boundary of the carbonate-silicate exchange reaction proposed by this study, whereas previous theoretical predictions are illustrated by yellow shaded region^{28, 29, 30}. The cyan and orange lines indicate the decarbonation reactions of $\text{CaCO}_3 + \text{SiO}_2$ ⁴⁰ and $\text{MgCO}_3 + \text{SiO}_2$ ⁴¹, respectively. The black dashed line shows the melting curve of MgCO_3 - CaCO_3 system constrained by Thomson et al.²². Four typical mantle geotherms are modified from Maeda et al.³⁶. The red shaded region indicates the transition boundary of CaCO_3 from sp^2 - to sp^3 structure predicted by density functional theory computations^{29, 38}.

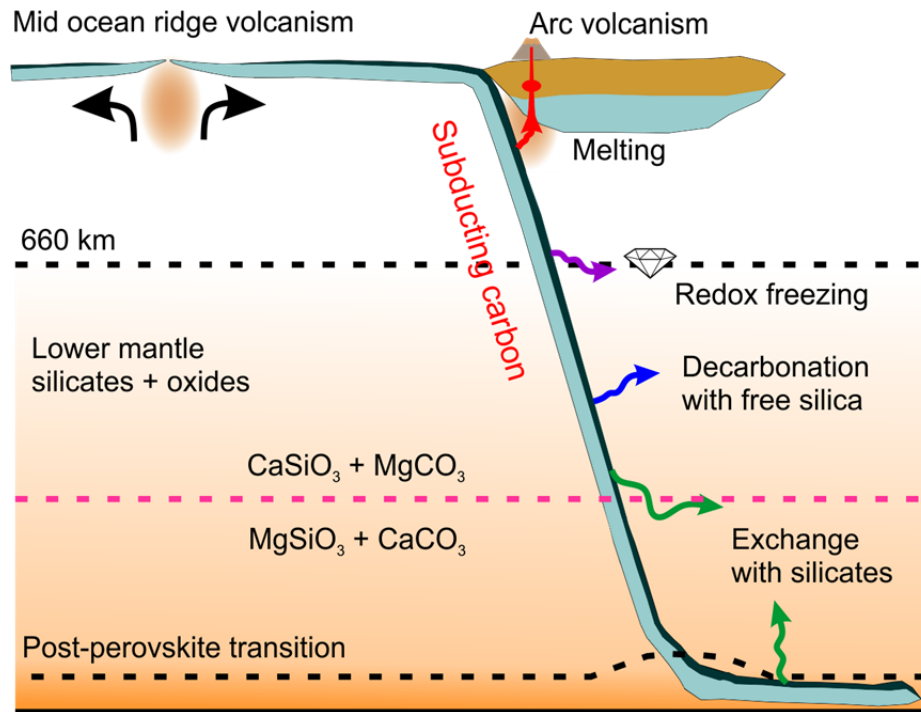
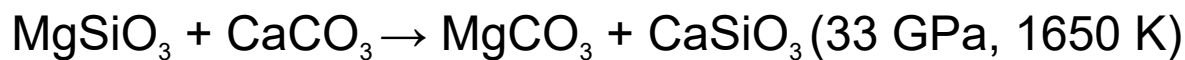
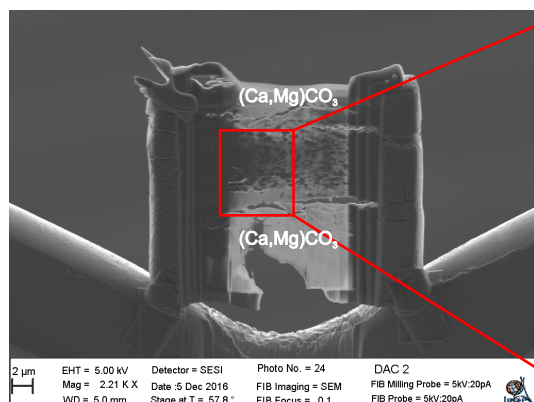


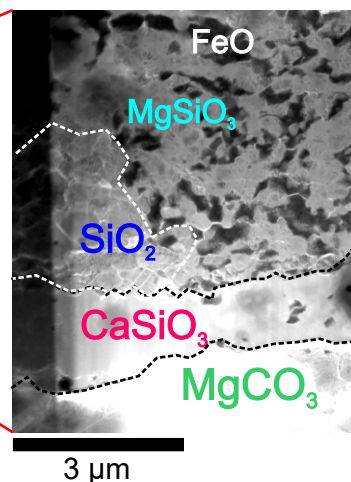
Figure 4. Schematic illustration of the fate of carbonates in the oceanic crust (dark blue) subducted to the lower mantle. Through subduction, the carbonates may undergo melting (red arrow), redox freezing with metallic iron (purple arrow), decarbonation reaction with free silica (blue arrow), and exchange reaction with lower mantle silicates (green arrow). Based on the observation of reversal of the carbonate-silicate cation exchange reaction at conditions relevant to cold subducted slabs at mid-lower-mantle depths, CaCO₃ is the potential stable phase that hosts oxidized carbon in the lowermost mantle.



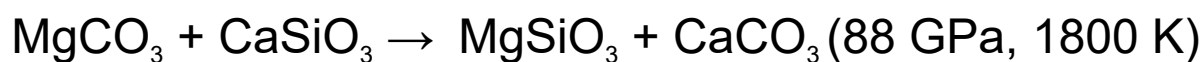
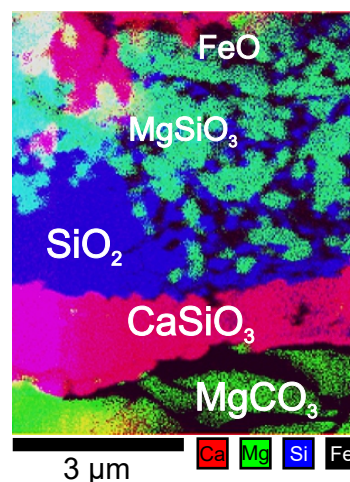
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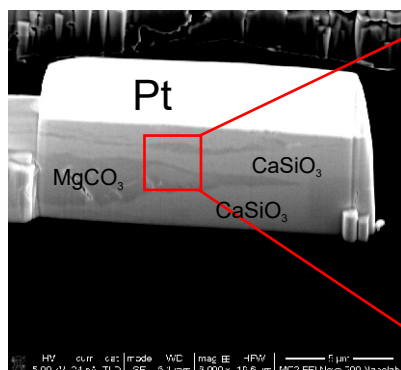
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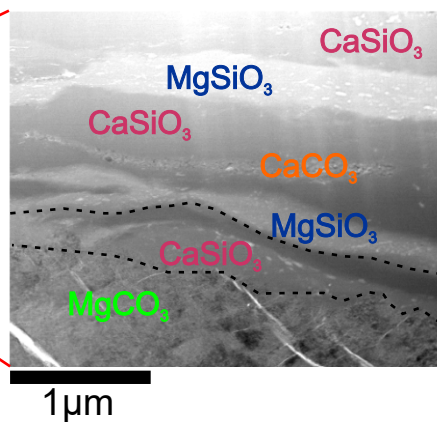
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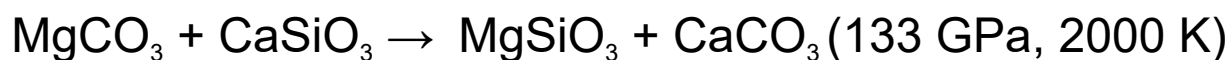
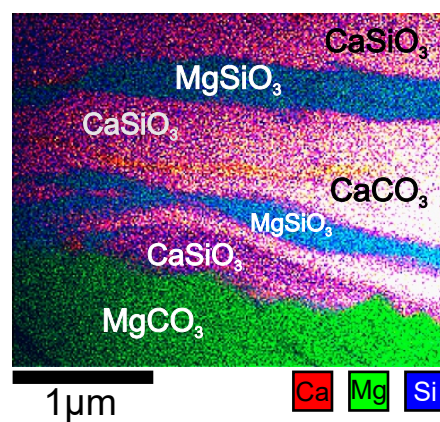
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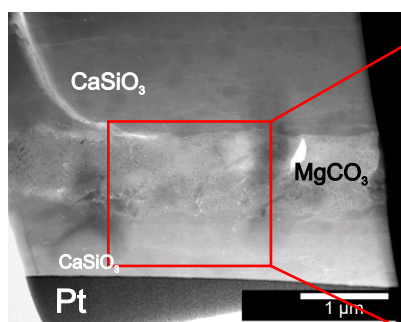
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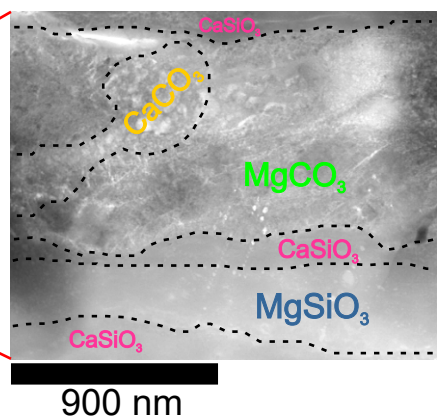
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(g)



(h)



(i)

