

Saturated decomposition of calcium carbonate at high pressure and implication for deep carbon cycle

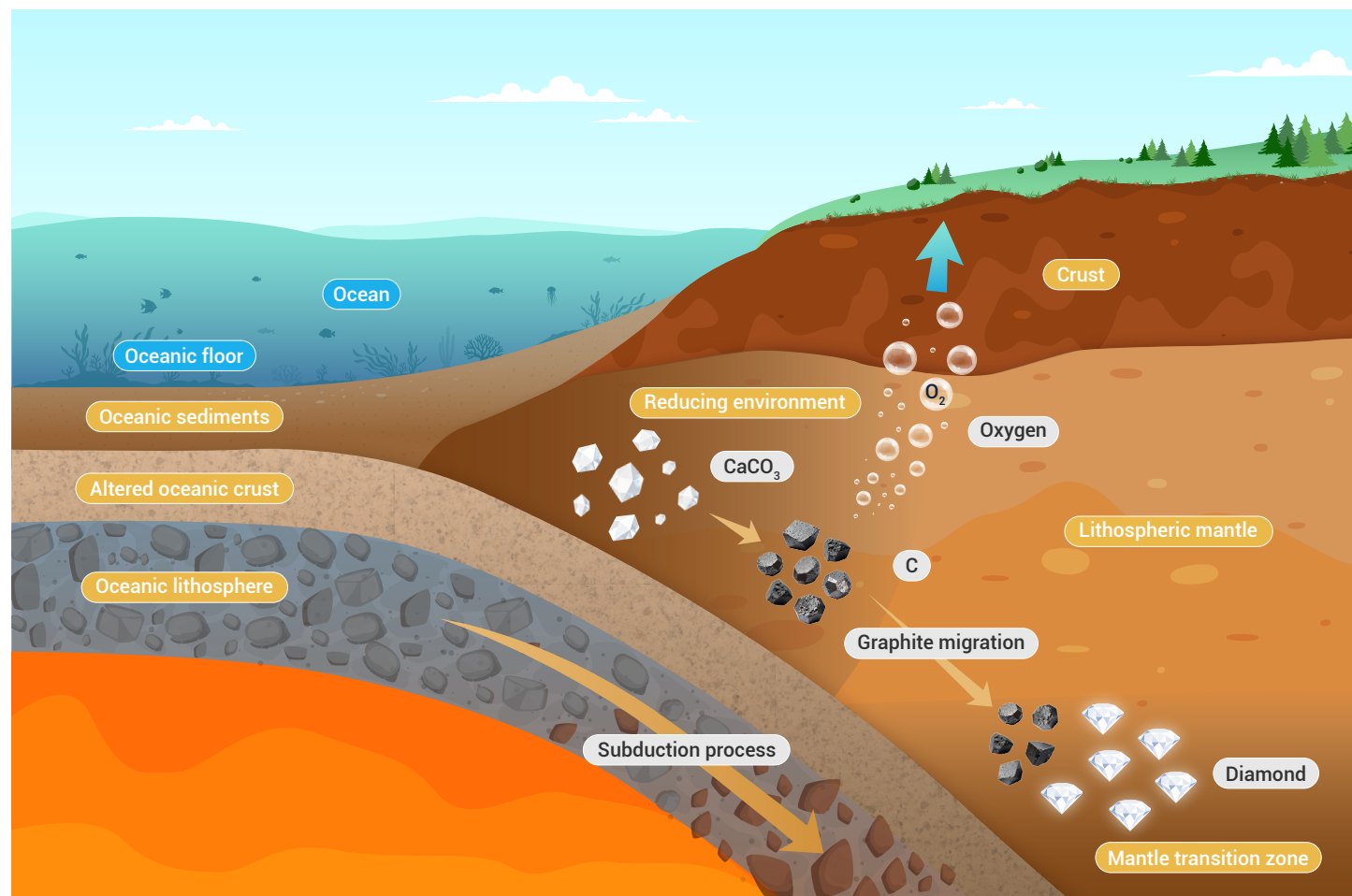
Jun Hu,¹ Chaojia Lv,^{1,*} Ao Deng,¹ Penghui Sun,¹ Jin Liu,^{1,*} and Yongjun Tian¹

*Correspondence: lvchaojia@ysu.edu.cn (C.L.); jinliu@ysu.edu.cn (J.L.)

Received: March 18, 2025; Accepted: January 29, 2026; Published Online: February 2, 2026; <https://doi.org/10.59717/j.xinn-geo.2026.100201>

© 2026 The Author(s). This is an open access article under the CC BY license (<https://creativecommons.org/licenses/by/4.0/>).

GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Effects of crystal structure and pressure on CaCO_3 decomposition are investigated under reducing conditions.
- Graphite formation out of CaCO_3 is instantaneous nucleation at 2.5 GPa and 950°C.
- Deep carbonate may undergo saturated decomposition under reducing conditions of the upper mantle.

Saturated decomposition of calcium carbonate at high pressure and implication for deep carbon cycle

Jun Hu,¹ Chaojia Lv,^{1,*} Ao Deng,¹ Penghui Sun,¹ Jin Liu,^{1,*} and Yongjun Tian¹

¹Center for High Pressure Science (CHIPS), State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

*Correspondence: lvchaojia@ysu.edu.cn (C.L.); jinliu@ysu.edu.cn (J.L.)

Received: March 18, 2025; Accepted: January 29, 2026; Published Online: February 2, 2026; <https://doi.org/10.59717/j.xinn-geo.2026.100201>

© 2026 The Author(s). This is an open access article under the CC BY license (<https://creativecommons.org/licenses/by/4.0/>).

Citation: Hu J., Lv C., Deng A., et al. (2026). Saturated decomposition of calcium carbonate at high pressure and implication for deep carbon cycle. *The Innovation Geoscience* 4:100201.

The evolution of calcium carbonate at subduction zones can significantly influence the Earth's long-term climate dynamics and planetary habitability. Here we report the effects of high pressure on carbonate decomposition kinetics for the first time. The oxygen fugacity-controlled experiments on CaCO_3 were carried out at 1.0–3.0 GPa and 650–1,050°C using a large volume cubic press. CaCO_3 is stable at 1.0 GPa, 800°C and relatively reducing conditions, but it decomposes to produce graphite with increasing pressure to 2.5–3.0 GPa at high temperature. The graphite formation via carbonate decomposition was initially controlled by instantaneous nucleation with diffusion-controlled growth according to the classical Avrami model. The nano-sized graphite encapsulated residual samples and then precluded further decomposition of calcium carbonate. This result suggests the unexpected evolution of the graphitization and saturated decomposition of calcium carbonate at 2.5–3.0 GPa under relatively reducing conditions relevant to the Earth's upper mantle.

INTRODUCTION

Subduction zones, the most active tectonic boundaries on Earth, are the primary conduits for carbon cycling between the Earth's surface and deep interiors.¹ As the major carbon host at subduction zones, calcium carbonate (CaCO_3) plays a key role in linking surface and deep carbon reservoirs. Subducting carbonates would undergo a series of geological processes including dissolution in subduction-zone fluids, partial melting, graphitization (i.e., decarbonization), and decarbonation to release carbon dioxide, which may be finally recycled back into the atmosphere via the degassing of arc volcanoes.^{2,3} A good number of the remaining subducted carbonates may be transported further into the mantle transition zone and the lower mantle, even reaching the core-mantle boundary.^{4,5} The phase stability of carbonates under extreme conditions relevant to the deep mantle, to some extent, dictate the exchanging efficiency of carbon between the Earth's surface and deep reservoirs.⁶ Consequently, the long-term atmospheric carbon dioxide levels and global climate changes shall be linked with how carbonates evolve in subducting slabs, ultimately shaping the habitability of our planet.^{7,8}

Among all the subducting carbonate minerals, calcium carbonate (CaCO_3) is the prevailing carbon-bearing material, accounting for ~75% of carbon fluxes in subduction zones.^{9–11} Thus far, the phase stability of CaCO_3 has been extensively explored under high pressure and temperature (P - T) conditions.^{6,12,13} Calcite-structured CaCO_3 -I undergoes a series of phase transformations to CaCO_3 -II at ~1.5 GPa, CaCO_3 -III at ~2.0 GPa and CaCO_3 -VI at ~15 GPa and room temperature.^{12,14,15} As T rises, Ishizawa et al.¹⁶ reported that CaCO_3 enters the CaCO_3 -V phase through an intermediate phase CaCO_3 -IV approximately at 985–1240 K in a CO_2 atmosphere of ~4 bar and rapidly decomposes into the CaO solid and CO_2 gas at >1,275 K. Furthermore, at $P > 0.3$ –0.5 GPa, calcium carbonate may not decompose directly to produce CO_2 ; instead, it first transforms into an amorphous/disordered phase prior to congruent melting.^{17,18} In particular, Hou et al.¹⁷ proposed that aragonite-structured CaCO_3 transforms into the amorphous phase approximately at 3.9–7.5 GPa and >1,000 K; upon further heating, it melts at about 1,800–1,900 K. However, most previous studies focused on the effects of high P and high T on the phase stability of CaCO_3 without considering the influence of oxygen fugacities relevant to subduction zones and the upper mantle. Reduction of carbonate minerals at convergent plate boundaries produces graphite and/or hydrocarbons such as methane (CH_4), which modulates the conversion and distribution of subducting carbon.^{19,20} Graphite

formation through carbonate reduction in shallow depths could offer a potential mechanism to retain carbon in subducted slabs, which may facilitate carbon transport into the deep Earth.^{20,21} Additionally, the liberation of H_2 gas during serpentinization generally causes relatively reducing local environments in subduction zones.²² Therefore, it is crucial to explore the high P - T stability of CaCO_3 under oxygen fugacity-controlled conditions for decoding the fate of calcium carbonate (CaCO_3) in subduction zones and the Earth's upper mantle.

MATERIALS AND METHODS

In this study, we carried out oxygen fugacity-controlled experiments to investigate the phase stability of calcium carbonate at 1.0–3.0 GPa and 650–1,050°C. The experimental oxygen fugacities were primarily regulated by the use of hexagonal boron nitride (BN) crucibles. As reported in Wendlandt, et al.²³, the use of BN capsule can develop relatively reducing environments, for instance, reaching approximately IW-0.3 at 950–1,050°C and 2.5–3.0 GPa. Notably, calcium carbonate remains intact at the relatively low pressure of 1.0 GPa, 800°C and relatively reducing conditions; however, with increasing P to 2.5–3.0 GPa, it partially decomposes to produce graphite and CaO at high T (hereafter referred to as “saturated decomposition”; Figures 1, 3 & S1–S2). Further, we performed time-series experiments to study the high- P decomposition kinetics of CaCO_3 at 2.5 GPa and 950°C for the first time (Table S1). This result suggests a novel phenomenon of saturated decomposition of carbonate under reducing conditions, providing new insights into deep carbon cycling in shallow subduction zones.

Metallographic microscopy images were collected for the high P - T experimental run products (Figure 1B). It was clearly observed that there were some dark grains mostly distributed at the boundary between the recovered sample and the BN capsule, except run#130. These high P - T experimental run products were further characterized using laser Raman spectroscopy (Figure 2). At 1.0 GPa and 800°C (run#130), only the Raman peaks of calcite were observed, indicating that CaCO_3 in the calcite phase can withstand relatively reducing conditions (approximately IW-0.3). With increasing P to 2.5–3.0 GPa, on the contrary, CaCO_3 was decomposed to form graphite in all high P - T experimental run products in this study. The experimental T range was from 650 to 1,050°C at 2.5–3.0 GPa. This result suggests that the phase stability of CaCO_3 under relatively reducing conditions is extremely sensitive to P , especially at the range of 1.0–3.0 GPa. Notably, CaCO_3 undergoes the calcite-aragonite phase transition at ~1.5 GPa.⁶ Meanwhile, the Raman signals of graphite are enhanced from 650 to 950°C at a given P of 2.5 GPa for the same heating duration of 0.5 h, indicating that the degree of carbonate decomposition could increase as T rises. Namely, elevated T promotes the decarbonization reaction rate of CaCO_3 at 2.5 GPa.

RESULTS AND DISCUSSION

The characteristic Raman peaks approximately at 1,350 and 1,580 cm^{-1} correspond to the D and G bands of graphite (Figure 2). Their peak intensity ratios and positions have been proposed to constrain the concentration of sp^3 -hybridized carbon and graphite grain sizes.^{24,25} In Raman spectra of the recovered samples in this study, the peak positions of G band are at 1,580–1,600 cm^{-1} , indicating that the graphite particles forming from CaCO_3 decarbonization are nearly free of sp^3 -hybridized carbon. At the same time, the grain size of the graphite (L_g in the unit of nm) can be derived from the Raman peak intensity ratio between the G and D bands, $I(\text{D})/I(\text{G})$, using Eqn. (1) as follows:

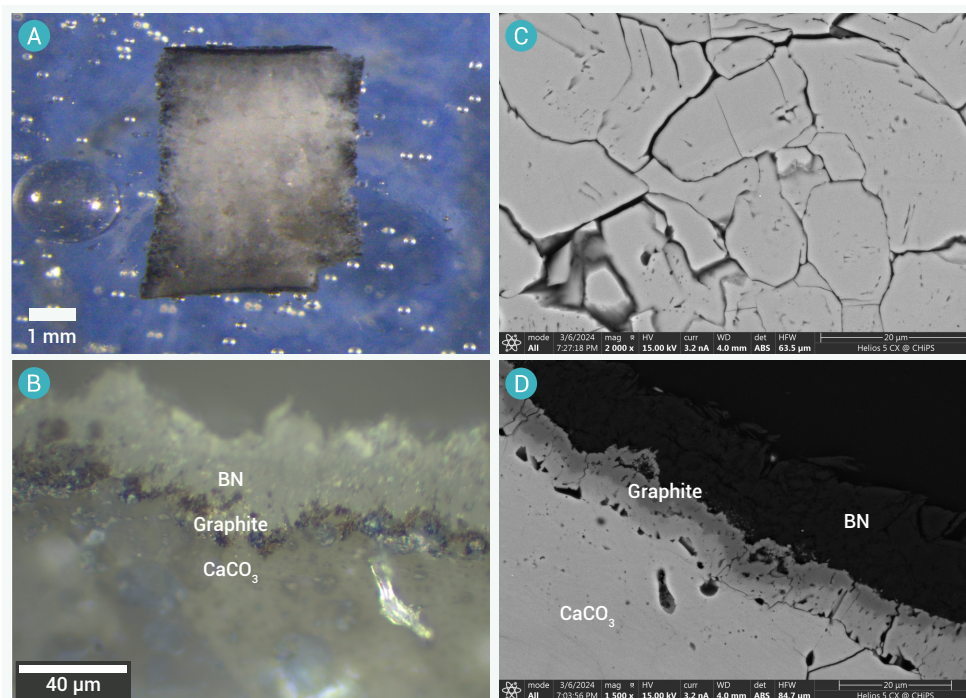


Figure 1. Representative optical and SEM images of the samples recovered from high P - T experiments at 2.5 GPa and 950°C (A) Optical image of the recovered sample placed in the resin epoxy. (B) Metallurgical image of the boundary between the BN capsule and the CaCO_3 sample. A graphite layer was evidently formed along the boundary. (C) The SEM image showing the recovered sample with the grain sizes of ~5-20 μm . (D) The SEM image showing the graphite layer along the boundary between the BN capsule and the CaCO_3 sample.

$$Lg = 4.4 \times \frac{I(G)}{I(D)} \quad (1)$$

The Raman peak intensity ratios of $I(D)/I(G)$ are between 0.1 and 1.0 for graphite in this study. Therefore, the average grain sizes of graphite particles range approximately from 0.4 to 4.4 nm in our high P - T recovered samples. This result is in good agreement with the lack of sharp diffraction lines of graphite particles in XRD patterns, evidencing that the grain sizes of graphite are a few nm and less (Figure 3).

One comparative experiment (run#261_MgO) was carried out to study the influence of different oxygen fugacity-controlled conditions on the high P - T stability of calcium carbonate. All the sample assemblies shared the same configuration, except for run#261_MgO in which the BN crucible was replaced by a magnesium oxide (MgO) crucible. Compared to the BN crucible, the MgO crucible would provide a relatively oxidized environment likely buffered by C-CO_2 , considering that the MgO powder separated the CaCO_3 sample from graphite heater. For run #261_MgO, the P - T conditions were set at 2.5 GPa and 950°C with a heating duration of 1.5 h, and the recovered carbonate sample was in the calcite phase based on its Raman and XRD characterizations. No detectable graphite was observed even at the boundary between the carbonate sample and the MgO crucible. In other words, CaCO_3 at 2.5 GPa and 950°C should not be subject to decomposition under relatively oxidizing conditions (e.g., the use of MgO crucible). Furthermore, the recovered CaCO_3 sample in run#261_MgO was in the calcite phase because the amorphous phase could not be preserved upon quenching to room temperature, consistent with the quenched phase by Hou et al.¹⁷ using graphite heaters. Hence, it can be concluded that the high P - T decarbonization of amorphous CaCO_3 is highly related to the relatively reducing environment. Compared with the previous study,¹⁷ our experimental results suggest the aragonite-amorphous transition temperatures are slightly greater, given that a trace amount of aragonite was observed in the recovered samples from 2.5 GPa and 950°C and that the aragonite has completely entered the amorphous phase as T increases to 1,050°C (run#240422).

Thermogravimetric analysis (TGA) measurements were performed on the primitive calcium carbonate as well as the samples recovered from 2.5 GPa and 650-950°C with varying heating durations (Tables S1-S2). As shown in Figure 4A, the primitive calcium carbonate samples were decomposed completely to CO_2 and CaO at 630°C within ~230 min and 650°C within ~120 min. Such a small incremental T of 20°C can significantly influence the decarbonization reaction rate of CaCO_3 at 1 bar. The measured weight loss (Δm) values were approximately at 43.9-44.9%. These Δm values slightly deviated from the theoretical Δm value of 44.0%, mostly reflecting the uncer-

tainties of TGA measurements (i.e., ~1.0%). On the other hand, the Δm values generally decreased with time until all the residual CaCO_3 completely decomposed in the TGA measurements on the samples recovered from high P - T experiments (Figure 4). For instance, the Δm value of the run #205-2 sample was ~8.0% (~10.0%) after TGA measurements for 0.5 h (1.5 h). The holding time of TGA measurements may affect the actual Δm values; hence, each TGA measurement was performed for 4-6 h until the Δm plateau was reached at least for 1 h.

The peak T and heating duration have distinct effects on the decarbonization reaction rate of

CaCO_3 at 2.5 GPa as the T rises. As shown in Figure 5, the decomposition fraction (X) of CaCO_3 was minimal for 30 min and marginally increased from 2.4 to 2.7% with T increasing from 650 to 750°C under reducing conditions. With T increasing to 850°C and doubling heating duration (run #201), the X value of CaCO_3 was comparable to those above. This is dramatically different from the trend of the decomposition rate of CaCO_3 at 630-650°C and 1 bar. We note that the CaCO_3 samples were in the aragonite phase at 650-850°C and 2.5 GPa, consistent with previous studies.^{17,18} This result suggests that the peak T and heating duration may have marginal effects on the decarbonization reaction rate of CaCO_3 in the aragonite phase. On the other hand, the decarbonization reaction rate of CaCO_3 in the amorphous phase is significantly greater than that in the aragonite phase. The calcium carbonate samples underwent the aragonite-amorphous phase transition from 650-850 to 950-1,050°C at 2.5-3.0 GPa, as evidenced by the changes in the recovered calcium carbonate changing from aragonite to calcite (Table S1). As the heating duration increased from 15 to 90 min, the X value of CaCO_3 changed from 8.5 to 22.5% at 2.5 GPa and 950°C. In particular, the X value of amorphous CaCO_3 was approximately 12.8% for the heating duration of 30 min, about 5 times that of aragonite-structured CaCO_3 within the same heating duration at 2.5 GPa.

Further, the decomposition kinetics of calcium carbonate was studied using the classical Avrami equation for crystal nucleation and growth.²⁶ The decomposition fraction $X(t)$ against time t is given as follows:

$$X(t) = 1 - \exp(-kt^n) \quad (2)$$

$$\ln \ln[1/(1-X(t))] = \ln(k) + n \ln(t) \quad (3)$$

where k is the reaction rate and n the time exponent indicating the crystal growth mechanism. In the plot of $\ln \ln[1/(1-X(t))]$ as a function of $\ln(t)$, the linear fit gives the slope for n and the intercept for $\ln(k)$. The Avrami model takes into account that crystallization occurs by both nucleation and crystal growth with some assumptions. It is the most commonly used model in the kinetics study of chemical reactions, though the assumption of linear growth kinetics may sometimes not be maintained throughout the entire reaction. In other words, the growth rate and mechanism of the new phase may not only depend on temperature, but also change with time. As shown in Figure 4 and Table S2, the $X(t)$ was split into the two sections because the relatively large deviation was obtained using a single fit to the entire reaction with the $X(t)$ at 0-100%. The single fit resulted in the n value of about 1.1-1.2 for the decomposition of CaCO_3 at 1 bar and 630-650°C. For the two-segmented fits, the n

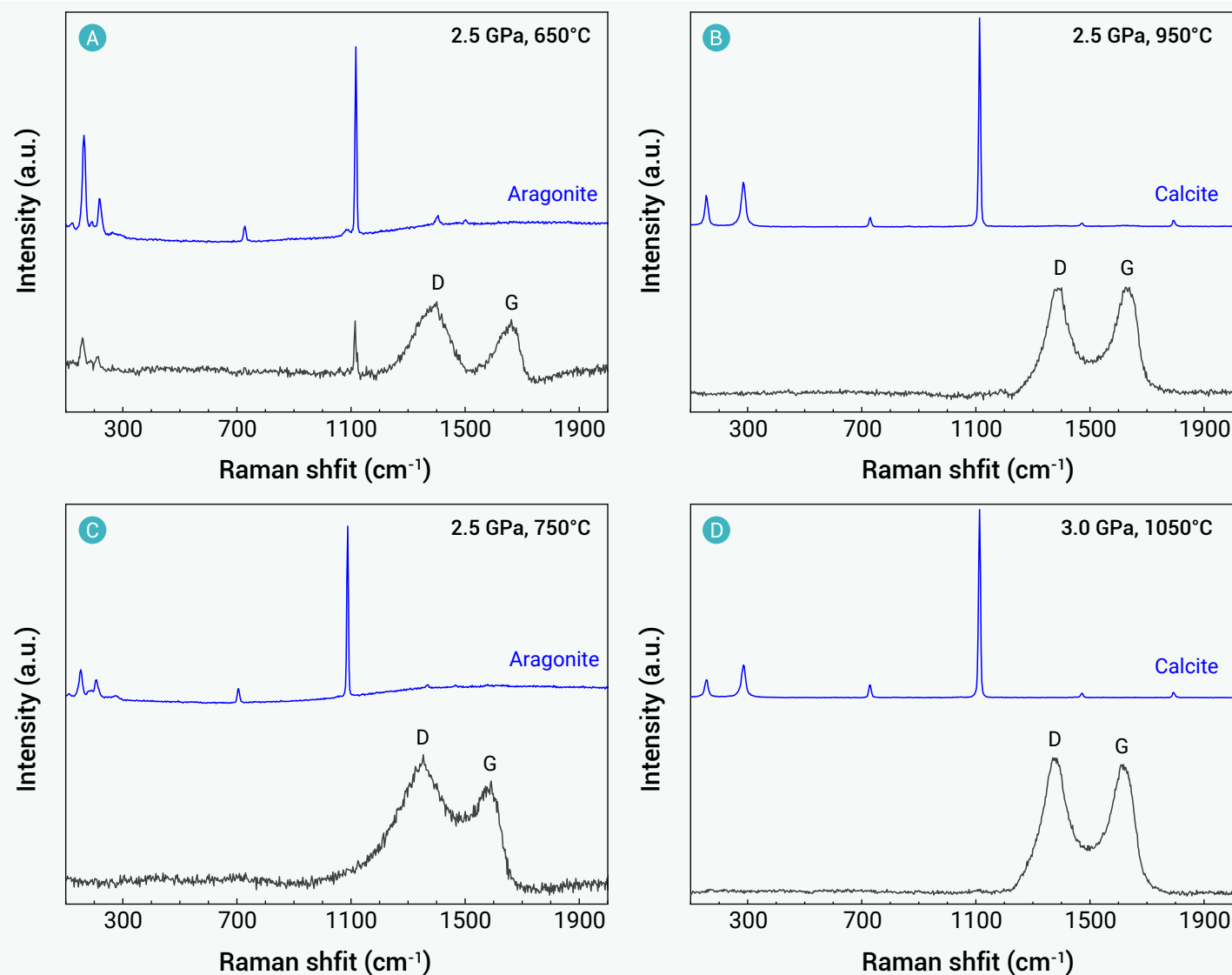


Figure 2. Representative Raman spectra of the recovered samples from high *P-T* experiments The blue curves represent the Raman spectra collected from the calcium carbonate region in the recovered samples. The black curves represent the Raman spectra collected from the graphite-forming region in the recovered samples.

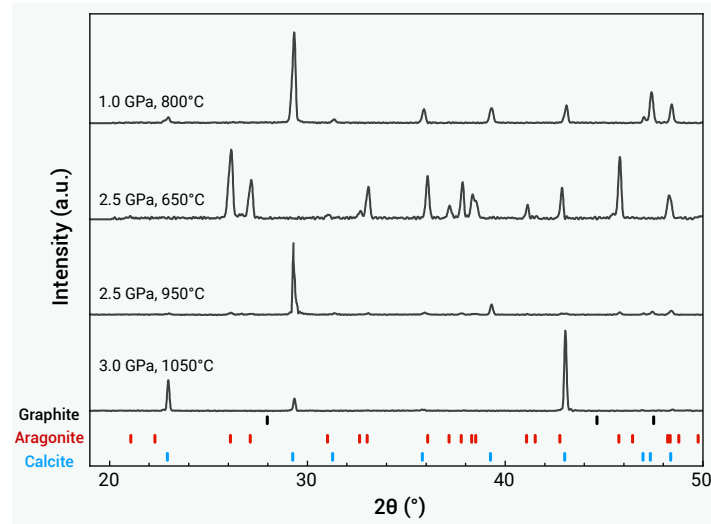


Figure 3. Representative x-ray diffraction patterns of the recovered samples from high *P-T* experiments Black, red and blue ticks: graphite, aragonite and calcite, respectively. The Cu K α radiation with 45.0 kV and a beam current of 200 mA was used and the x-ray beam was focused to ~ 300 μ m in diameter at the sample position.

value changed approximately from 0.8 to 1.4 at the $X(t)$ of $\sim 30\%$. This likely reflect the changes in the nature of crystal growth and nucleation at 1 bar and 630–650°C when the $X(t)$ reaching ~ 25 –30%. Meanwhile, the reaction rate k changed approximately from 3.01×10^{-4} to $1.29 \times 10^{-5} \text{ s}^{-1}$ at the $X(t)$ of 30% for the decomposition of CaCO_3 at 1 bar and 630°C. With T increasing to 860–870°C at 1 bar, the decarbonation kinetics of calcite was investigated using synchrotron radiation XRD with the n values approximately at 1.9–2.1.²⁴ The k values are significantly increased by one to three orders of magnitude from 630–650 to 860–870°C at 1 bar (Table S2).

As shown in Figure 4, the n and k values were determined to be ~ 0.6 and $\sim 1.8 \times 10^{-3} \text{ s}^{-1}$ for the CaCO_3 decomposition with the $X(t)$ up to 46.9% under 2.5 GPa, 950°C and relatively reducing conditions. This decomposition rate is comparable to that at 1 bar and 860–870°C, but they featured different nucleation processes. At 2.5 GPa and 950°C, the initial decomposition of calcium carbonate into graphite may be mainly controlled by instantaneous nucleation with diffusion-controlled growth according to the classical Avrami model.²⁶ This nucleation and crystal growth mechanism is also consistent with the observed grain sizes of 0.4 to 4.4 nm for graphite recovered in our high *P-T* samples. At 1 bar, the n values were around 1.0 for the decomposition of calcium carbonate into CO_2 gas at 630–650°C, which was also controlled by instantaneous nucleation; with T increasing to 860–870°C, however, the decarbonation reaction of calcium carbonate was mainly controlled by episodic nucleation.²⁷ In other words, the reaction mechanisms

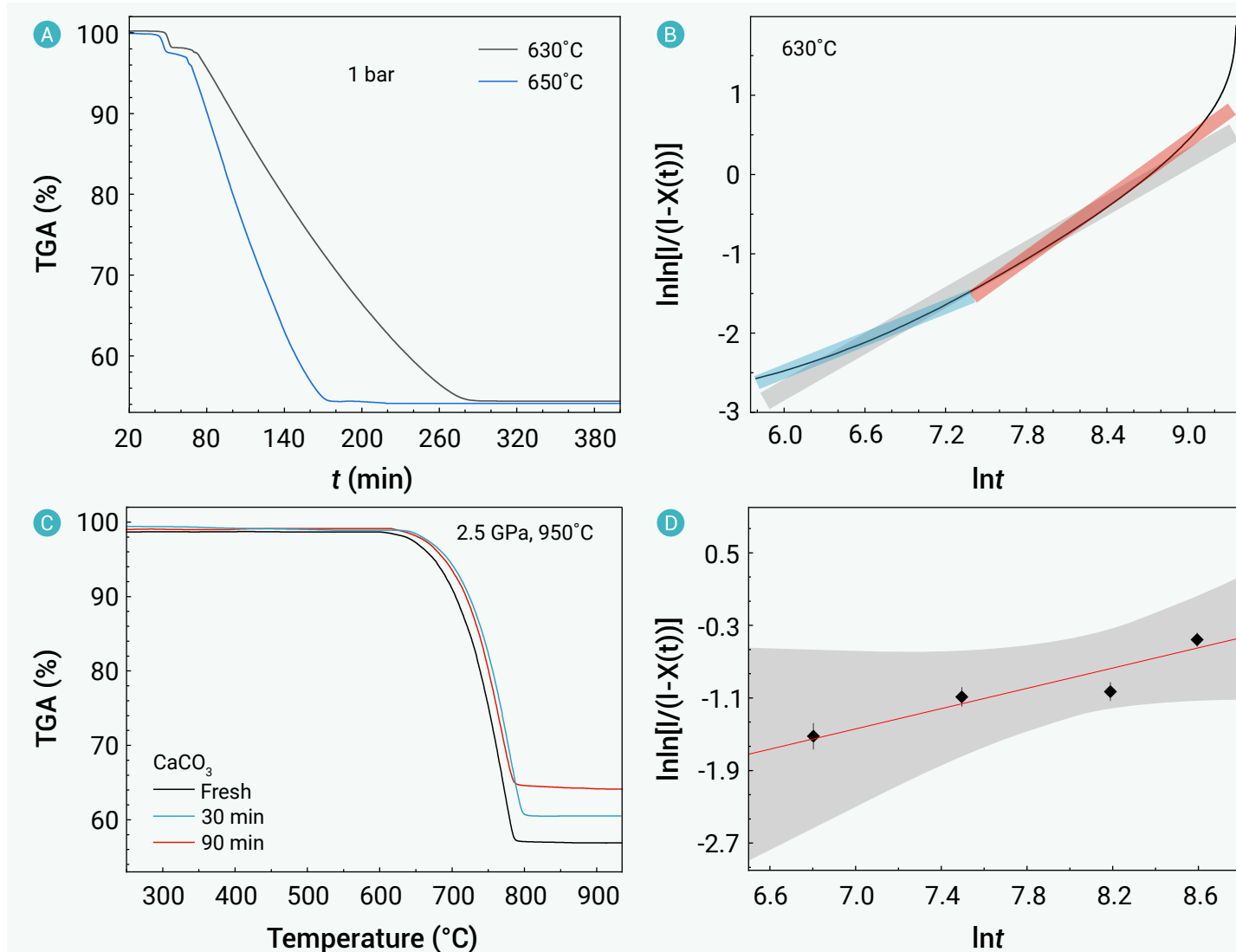


Figure 4. Representative weight loss curves from TGA measurements on (A) primitive CaCO_3 at 1 bar and 630–650°C and (C) the samples recovered from high P - T large volume cubic press experiments. (B) and (D): Avrami model for the decomposition of calcium carbonate under reducing conditions. Solid symbols (D): the measured decomposition fraction values corresponding to the heating durations at 15–90 min, this study. The shaded area represents the 95% confidence interval according to the linear regression fitting of the experimental data.

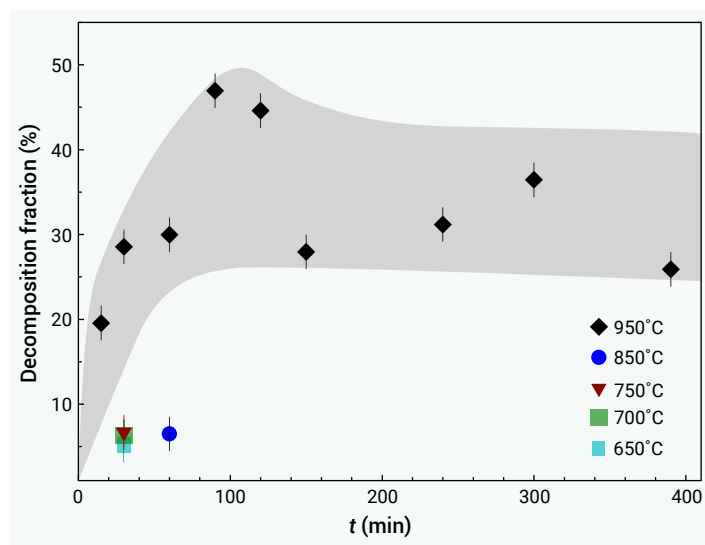


Figure 5. The evolution of decomposition fraction of calcium carbonate with time at 2.5 GPa and reducing conditions. Vertical ticks represent the uncertainties of TGA measurements ($\pm 1.5\%$). The shaded area is used to guide the eye.

of calcium carbonate decarbonation change with increasing T at ambient pressure.

At 2.5 GPa, 950°C and reducing conditions, the decomposition fraction (X) of calcium carbonate did not increase further when the heating duration exceeded 90–120 min (Figure 5). Intriguingly, it decreased approximately from 46.9% at 90 min to 27.9% at 150 min and remained almost constant at $\sim 30 \pm 2\%$ within the heating duration of 150–390 min. This phenomenon highlights the contradiction between intuitive inferences and experimental findings, especially considering that the amount of reducing crucible materials (BN) was inexhaustible with respect to the CaCO_3 sample. In other words, the decomposition of CaCO_3 was first terminated at the X value of $\sim 46.9\%$ and then the reversal reaction was activated to reform CaCO_3 at 2.5 GPa, 950°C and reducing conditions. Such an anomalous change in the decomposition of amorphous CaCO_3 at high P - T is likely due to the formation of graphite layer (i.e., dark bands as show in Figure 1) at the boundary between the BN capsule and the CaCO_3 sample. The nucleation and crystal growth of graphite particles may have preferentially occurred at the boundary and to some degree, the inner surface of the BN capsule could be completely covered by nano-sized graphite grains. From that point on (e.g., $X = \sim 46.9\%$), the reducing function of the BN capsule was disabled to cause further carbonate decomposition. As a matter of fact, the oxygen fugacity inside the sample capsule could have been increased enough to activate the reversal reaction of

reforming carbonate until the run products could thermodynamically coexist together, such as the aforementioned $X = \sim 30\%$ in this study.

The present study employs time-series analyses to reveal the intriguing phenomenon of saturated decomposition of calcium carbonate under very reducing, high P - T conditions. It is thus inferred that CaCO_3 could not undergo complete decomposition during the formation of nano-sized graphite when oxygen fugacities exceeds the IW buffer. More importantly, subduction-zone processes are complex, resulting in a broad spectrum of oxygen fugacity from relatively oxidizing to highly reducing environments within the mantle wedge, subducted slabs, and the deep mantle.²⁸⁻³⁰ Notably, during serpentinization, the production of H_2 can lead to local oxygen fugacity conditions below the IW buffer.³¹ In this study, unexpected observations of saturated carbonate decomposition are reported under relatively reducing conditions (with oxygen fugacity slightly higher than the aforementioned levels), thereby providing valuable insights into carbon cycling processes in subduction zones.

Saturated decomposition of CaCO_3 under relatively reducing conditions provides a new pathway for carbon sequestration. It can greatly decrease the amount of surface oxygen sinking further into the deep mantle. Through graphite formation, subducting carbon can be transported into the mantle transition zone in the form of elemental carbon (e.g., diamond). Diamond has been proposed to be lighter than lower-mantle materials, leading to its accumulation in the mantle transition zone.³² Further, it may be oxidized by upwelling mantle materials to form carbonates, potentially triggering partial melting in the deep mantle.³²⁻³⁴ Notably, mantle wedge peridotites generally record high oxygen fugacities, typically from FMQ+0.5 to +3.0; this may be mostly related to recycled subducting fluids and sediments.^{4,35-38} The oxygen-rich materials originated from carbonate decomposition could migrate upwards to oxidize mantle wedges. Recently, Duncan and Dasgupta³⁹ linked the immobilization and fixation of organic carbon in the deep mantle with the Great Oxidation Event.^{40,41} Compared to organic carbon, subducted carbonate is approximately four-fold,⁴² and calcium carbonate instability may be more efficient to control the oxygen level in the atmosphere. Therefore, saturated decomposition of calcium carbonate may be an important process, potentially impacting the global carbon and oxygen cycles.

The high buffering capacity and low solubility of graphite in both aqueous solutions and melts make it an important carrier for deep carbon transport.^{43,44} The metamorphosed sedimentary rocks from the Italian Alps demonstrate that greater than 75% of graphite in subduction zones can be preserved to depths of at least 100 km.⁴⁵ Furthermore, the coexistence of diamond inclusions with graphite indicates that graphite can be stabilized to depths in excess of 150 km, after which it is subject to conversion into diamond.⁴⁶ It is noteworthy that elemental carbon can also be precipitated from C-O-H fluids.⁴⁷ Some low-carbon species can be dissolved in C-O-H fluids at low temperatures and high pressures, which is beneficial for graphite preservation in subduction zones. High P - T experiments on the solubility of graphite under controlled oxygen fugacity conditions reported that graphite solubility reaches a maximum near the fayalite-magnetite-quartz (FMQ) buffer conditions; on the other hand, graphite solubility reaches a minimum either under extremely oxidizing (FMQ+4) or reducing (FMQ-7) conditions.⁴⁸ Therefore, the fate of graphite is complex due to mantle redox gradients, revealing the critical role of varying oxygen fugacities environments in subduction-zone carbon transport.

CONCLUSION

In summary, the phase stability and decomposition kinetics of calcium carbonate were investigated under oxygen fugacity buffered conditions at 1.0–3.0 GPa and 650–1,050°C using a large volume cubic press for the first time. The experimental results show distinct structural stability between calcite, aragonite, and amorphous CaCO_3 at high P - T . Namely, calcite-structured CaCO_3 is stable at 1.0 GPa, 800°C and relatively reducing conditions, but both aragonite-structured and amorphous CaCO_3 decompose to form graphite with increasing pressure to 2.5–3.0 GPa at high T . Intriguingly, the saturated decomposition of amorphous CaCO_3 were observed in our time-series experiments under IW-0.3 reducing conditions at 2.5 GPa and 950°C. It is worth noting that graphite particles are nano-sized and can encapsulate residual CaCO_3 inside the BN capsule, preventing carbonate from further decomposi-

tion. As to the formation of nano-sized graphite through CaCO_3 decomposition, it may be initiated by instantaneous nucleation and diffusion-controlled growth. The saturated decomposition of calcium carbonate provides new insights into the deep carbon cycling in subduction zones.

REFERENCES

- Plank T. and Manning C. (2019). Subducting carbon. *Nature* **574**:343–352. DOI:10.1038/s41586-019-1643-z
- Facq S., Daniel I., Montagnac G., et al. (2016). Carbon speciation in saline solutions in equilibrium with aragonite at high pressure. *Chem. Geol.* **431**:44–53. DOI:10.1016/j.chemgeo.2016.03.021
- Farsang S., Louvel M., Zhao C., et al. (2021). Deep carbon cycle constrained by carbonate solubility. *Nat. Commun.* **12**:4311. DOI:10.1038/s41467-021-24533-7
- Dasgupta R. and Hirschmann M. M. (2010). The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.* **298**:1–13. DOI:10.1016/j.epsl.2010.06.039
- Kelemen P. B. and Manning C. E. (2015). Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proc. Natl. Acad. Sci. USA* **112**:E3997–4006. DOI:10.1073/pnas.1507889112
- Gui W., Shen K. and Liu J. (2023). Phase stability and reactions of subducting CaCO_3 under upper mantle conditions. *Acta Geol. Sin.-Engl.* **97**:309–315. DOI:10.1111/1755-6724.15040
- Xu Y.-G., Huang X., Wang Q., et al. (2024). Earth's habitability driven by deep processes. *Chin. Sci. Bull.* **69**:169–183. DOI:10.1360/TB-2023-0816
- Liu J. and Mao H.-K. (2021). Yi-Gang Xu: The Earth's deep interior holds the key to habitability. *Natl. Sci. Rev.* **8**:nwab018. DOI:10.1093/nsr/nwab018
- Alt J., Schwarzenbach E., Früh-Green G., et al. (2013). The role of serpentinites in cycling of carbon and sulfur: Seafloor serpentinization and subduction metamorphism. *Lithos.* **178**:40–54. DOI:10.1016/j.lithos.2012.12.006
- Dutkiewicz A., Müller D., Cannon J., et al. (2018). Sequestration and subduction of deep-sea carbonate in the global ocean since the Early Cretaceous. *Geology.* **47**:91–94. DOI:10.1021/jacs.8b08298
- Li K., Li L., Pearson G., et al. (2019). Diamond isotope compositions indicate altered igneous oceanic crust dominates deep carbon recycling. *Earth Planet. Sci. Lett.* **516**:190–201. DOI:10.1016/j.epsl.2019.03.041
- Liu J., Caracas R., Fan D., et al. (2016). High-pressure compressibility and vibrational properties of $(\text{Ca,Mn})\text{CO}_3$. *Am. Mineral.* **101**:2723–2730. DOI:10.2138/am-2016-5742
- Santos S. M., Marcondes M. L., Justo J. F., et al. (2019). Stability of calcium and magnesium carbonates at Earth's lower mantle thermodynamic conditions. *Earth Planet. Sci. Lett.* **506**:1–7. DOI:10.1016/j.epsl.2018.10.030
- Merlini M., Hanfland M. and Crichton W. A. (2012). CaCO_3 -III and CaCO_3 -VI, high-pressure polymorphs of calcite: Possible host structures for carbon in the Earth's mantle. *Earth Planet. Sci. Lett.* **333**:265–271. DOI:10.1016/j.epsl.2012.04.036
- Pippinger T., Miletich R., Merlini M., et al. (2014). Puzzling calcite-III dimorphism: Crystallography, high-pressure behavior, and pathway of single-crystal transitions. *Phys. Chem. Minerals.* **42**:29–43. DOI:10.1007/s00269-014-0696-7
- Ishizawa N., Setoguchi H. and Yanagisawa K. (2013). Structural evolution of calcite at high temperatures: Phase V unveiled. *Sci. Rep.* **3**:2832. DOI:10.1038/srep02832
- Hou M., Zhang Q., Tao R., et al. (2019). Temperature-induced amorphization in CaCO_3 at high pressure and implications for recycled CaCO_3 in subduction zones. *Nat. Commun.* **10**:1963. DOI:10.1038/s41467-019-09742-5
- Suito K., Namba J., Horikawa T., et al. (2001). Phase relations of CaCO_3 at high pressure and high temperature. *Am. Mineral.* **86**:997–1002. DOI:10.2138/am-2001-8-906
- Giuntoli F., Vitale Brovarone A. and Menegon L. (2020). Feedback between high-pressure genesis of abiogenic methane and strain localization in subducted carbonate rocks. *Sci. Rep.* **10**:9848. DOI:10.1038/s41598-020-66640-3
- Malvoisin B., Chopin C., Brunet F., et al. (2012). Low-temperature wollastonite formed by carbonate reduction: A marker of serpentinite redox conditions. *J. Petrol.* **53**:159–176. DOI:10.1016/j.epsl.2011.10.040
- Galvez M. E., Beyssac O., Martinez I., et al. (2013). Graphite formation by carbonate reduction during subduction. *Nat. Geosci.* **6**:473–477. DOI:10.1038/ngeo1827
- Schrenk M. O., Brazelton W. J. and Lang S. Q. (2013). Serpentinization, carbon, and deep life. *Rev. Mineral. Geochem.* **75**:575–606. DOI:10.2138/rmg.2013.75.18
- Wendlandt R. F., Huebner J. S. and Harrison W. J. (1982). The redox potential of boron nitride and implications for its use as a crucible material in experimental petrology. *Am. Mineral.* **67**:170–174. <https://pubs.geoscienceworld.org/msa/ammin/article-abstract/67/1-2/170/104771/The-redox-potential-of-boron-nitride-and>
- Ferrari A. C. and Robertson J. (2004). Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Philos. Trans. A Math. Phys. Eng. Sci.* **362**:2477–2512. DOI:10.1098/rsta.2004.1452
- Tuinstra F. and Koenig J. L. (1970). Raman spectrum of graphite. *J. Chem. Phys.* **53**:1126–1130. DOI:10.1063/1.1674108
- Avrami M. (1939). Kinetics of Phase Change. I General Theory. *J. Chem. Phys.* **7**:1103–1112. DOI:10.1063/1.1750380
- Liu C., Han K. and Wang D. (2022). An in situ decarbonation kinetic study of calcite using synchrotron radiation XRD. *Can. Mineral.* **60**:687–698. DOI:10.3749/canmin.

- 2100063
28. Brounce M., Kelley K. A., Cottrell E., et al. (2015). Temporal evolution of mantle wedge oxygen fugacity during subduction initiation. *Geology*. **43**:775–778. DOI:10.1130/G36742.1
 29. Liu Y., Santos M., Yuan T., et al. (2016). Reduction of buried oxidized oceanic crust during subduction. *Gondwana. Res.* **32**:11–23. DOI:10.1016/j.gr.2015.02.014
 30. Chowdhury P., Dasgupta R., Phelps P. R., et al. (2022). Oxygen fugacity range of subducting crust inferred from fractionation of trace elements during fluid-present slab melting in the presence of anhydrite versus sulfide. *Geochim. Cosmochim. Acta*. **325**:214–231. DOI:10.1016/j.gca.2022.02.030
 31. Schrenk M. O., Brazelton W. J. and Lang S. Q. (2013). Serpentinization, carbon, and deep life. *Rev. Mineral. Geochem.* **75**:575–606. DOI:10.2138/rmg.2013.75.18
 32. Sun W.-d., Hawkesworth C., Yao C., et al. (2018). Carbonated mantle domains at the base of the Earth's transition zone. *Chem. Geol.* **478**:69–75. DOI:10.1016/j.chemgeo.2017.08.001
 33. Rohrbach A. and Schmidt M. W. (2011). Redox freezing and melting in the Earth's deep mantle resulting from carbon–iron redox coupling. *Nature* **472**:209–212. DOI:10.1038/nature09899
 34. Taylor W. R. and Green D. H. (1988). Measurement of reduced peridotite-C-O-H solidus and implications for redox melting of the mantle. *Nature* **332**:349–352. DOI:10.1038/332349a0
 35. Wood B. J. and Virgo D. (1989). Upper mantle oxidation state: Ferric iron contents of Iherzolite spinels by ⁵⁷Fe Mössbauer spectroscopy and resultant oxygen fugacities. *Geochim. Cosmochim. Acta*. **53**:1277–1291. DOI:10.1016/0016-7037(89)90062-8
 36. Parkinson I. and Arculus R. (1999). The redox state of subduction zones: Insights from arc-peridotites. *Chem. Geol.* **160**:409–423. DOI:10.1016/S0009-2541(99)00110-2
 37. Frost D. J. and McCammon C. A. (2008). The redox state of Earth's mantle. *Annu. Rev. Earth Planet. Sci.* **36**:389–420. DOI:10.1146/annurev.earth.36.031207.124322
 38. Eguchi J., Seales J. and Dasgupta R. (2020). Great Oxidation and Lomagundi events linked by deep cycling and enhanced degassing of carbon. *Nat. Geosci.* **13**:71–76. DOI:10.1038/s41561-019-0492-6
 39. Duncan M. S. and Dasgupta R. (2017). Rise of Earth's atmospheric oxygen controlled by efficient subduction of organic carbon. *Nat. Geosci.* **10**:387–392. DOI:10.1038/ngeo2939
 40. Canfield D. E. (2005). The early history of atmospheric oxygen: Homage to Robert M. Garrels. *Annu. Rev. Earth Planet. Sci.* **33**:1–36. DOI:10.1146/annurev.earth.33.092203.122711
 41. Papineau D., Mojzsis S. J. and Schmitt A. K. (2007). Multiple sulfur isotopes from Paleoproterozoic Huronian interglacial sediments and the rise of atmospheric oxygen. *Earth Planet. Sci. Lett.* **255**:188–212. DOI:10.1016/j.epsl.2006.12.015
 42. Clift P. (2016). A revised budget for Cenozoic sedimentary carbon subduction: Cenozoic carbon subduction. *Rev. Geophys.* **55**:97–125. DOI:10.1002/2016RG000531
 43. Frost B. R. (1979). Mineral equilibria involving mixed-volatiles in a C-O-H fluid phase; the stabilities of graphite and siderite. *Am. J. Sci.* **279**:1033–1059. DOI:10.2475/ajs.279.9.1033
 44. Lan C., Tao R., Huang F., et al. (2023). High-pressure experimental and thermodynamic constraints on the solubility of carbonates in subduction zone fluids. *Earth Planet. Sci. Lett.* **603**. DOI:10.1016/j.epsl.2023.117989
 45. Cook-Kollars J., Bebout G. E., Collins N. C., et al. (2014). Subduction zone metamorphic pathway for deep carbon cycling: I. Evidence from HP/UHP metasedimentary rocks, Italian Alps. *Chem. Geol.* **386**:31–48. DOI:10.1016/j.chemgeo.2014.07.013
 46. Frezzotti M. L., Selverstone J., Sharp Z. D., et al. (2011). Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nat. Geosci.* **4**:703–706. DOI:10.1038/ngeo1246
 47. Zhu J., Zhang L., Tao R. et al. (2020). The formation of graphite-rich eclogite vein in S.W. Tianshan (China) and its implication for deep carbon cycling in subduction zone. *Chem. Geol.* **533**:119430. DOI:10.1016/j.chemgeo.2019.119430
 48. Toffolo L., Tumati S., Villa A., et al. (2023). Experimental dissolution of carbonaceous materials in water at 1 GPa and 550°C: Assessing the role of carbon forms and redox state on COH fluid production and composition during forearc subduction of organic matter. *Front. Earth Sci.* **11**. DOI:10.3389/feart.2023.1013014

FUNDING AND ACKNOWLEDGMENTS

We thank Tao Shen and Kewei Shen for experimental assistance and constructive discussion. This work is supported by the National Key Research and Development Program of China (2023YFF0804100), Natural Science Foundation of Hebei (D2024203001, 253A7646D), and Science Research Project of Hebei Education Department (JZX2024017). Some experiments are supported by the Synergic Extreme Condition User Facility (SECUF). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

AUTHOR CONTRIBUTIONS

J. L. and Y. T. conceptualized the research. P. S. and A. D. assisted J. H. with the experiment. J. H., J. L. and C. J. analyzed the data. All authors contributed to the manuscript and approved the final version

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-geo.2026.100201>.