

Phase Stability and Reactions of Subducting CaCO₃ under Upper Mantle Conditions



GUI Weibin¹, SHEN Kewei^{1,*} and LIU Jin^{2,*}

¹ Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China

² Center for High Pressure Science, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei 066004, China

Abstract: CaCO₃ is an important component of marine sediments and one of the major deep-carbon carriers at subduction zones. Some subducted CaCO₃ can be dissolved in subduction fluids and recycled back to the surface via arc volcanoes degassing. At the same time, there still remain large amounts of CaCO₃ and its reaction products, which could be further transported into Earth's deep interior. These internal processes link atmosphere, hydrosphere and biosphere with the deep solid Earth, modifying the environments of our planet. In this review, we summarize current understanding from high pressure-temperature experiments and field petrological observations on the physical and chemical properties of CaCO₃. In particular, the phase stability and reactions of CaCO₃ largely control the migration and reservation of oxidized carbon in subducting slabs. Finally, we present several critical but unsolved questions on CaCO₃ subducting in the deep mantle.

Key words: calcium carbonates, phase stability, subducting carbon, upper mantle, subduction zone

Citation: Gui et al., 2023. Phase Stability and Reactions of Subducting CaCO₃ under Upper Mantle Conditions. Acta Geologica Sinica (English Edition), 97(1): 309–315. DOI: 10.1111/1755-6724.15040

1 Introduction

Subduction zone is the most active tectonic boundary on Earth and a major carbon cycle pathway between the surface and the deep interior. As predominant carbon hosts in subducting slabs, carbonates play a pivotal role in linking surface and deep carbon reservoirs (Plank and Manning, 2019). Beneath subduction arcs, some of the carbonates can be dissolved or melted, then recycled back to the atmosphere via arc volcanoes degassing (Facq et al., 2016; Farsang et al., 2021). Substantial quantities of carbonates may further be transported into the deep mantle (i.e., the mantle transition zone and the lower mantle), even reaching the core-mantle boundary (Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015; Lee et al., 2019). The migration and stability of carbonates dictate the conversion between surface and deep carbon, thus influencing the long-term CO₂ content of the atmosphere, modulating climate change and fundamentally shaping the habitability of our planet (Walker et al., 1981; Tang et al., 2022).

The carbon fluxes in subduction zones attract significant attention from a substantial number of researchers from interdisciplinary fields; however, this long-term quest is still under debate (Dasgupta and Hirschmann, 2010; Plank and Manning, 2019). The global carbon flux into the mantle via subduction was once proposed to be 24–48 Mt/yr, with 18–37 Mt/yr carbon released through arc volcanoes degassing (Dasgupta and Hirschmann, 2010). More recently, based on estimates by Plank and Manning (2019),

the global carbon flux into the mantle via subduction has been revised to ~82 Mt/yr, with 21–24 Mt/yr carbon being released by arc volcanoes degassing (Plank and Manning, 2019). Those data indicate a lower recycling efficiency in subduction zones, with respect to the model by Dasgupta and Hirschmann (2010). Notably, calcium carbonate (CaCO₃) is the most abundant form of oxidized carbon in marine sediments, altered oceanic crusts and serpentinized mantle peridotites within subducting slabs (Plank and Manning, 2019). Thus, to investigate the magnitude and pattern of carbon flux in subduction zones, we need to clarify the physical and chemical behaviors of CaCO₃ under the high pressure-temperature conditions of the upper mantle.

In this review, we summarize the phase stability and reactions of CaCO₃ under high pressure and temperature, which dictate the fundamental behaviors of CaCO₃ during subduction. Then we introduce major migration processes of CaCO₃, such as dissolution by subduction fluids and dissolving in carbonatite melts. Moreover, the interactions between CaCO₃ and silicate minerals likely improve the stability of carbonaceous substances, delivering carbon into the deep mantle. Ultimately, we present several important, pressing questions that deserve further investigation.

2 High *P-T* Phase Diagram of CaCO₃

Various polymorphs of CaCO₃ exist in oceanic sediments under Earth's surface conditions, including anhydrous CaCO₃ (e.g., calcite, aragonite and vaterite),

* Corresponding authors. E-mail: kewei.shen@hpstar.ac.cn; jinliu@ysu.edu.cn

amorphous CaCO_3 and hydrated CaCO_3 (e.g., monohydrocalcite $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ and ikaite $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) (Cölfen and Antonietti, 2005; Deer et al., 2013). Calcite is the dominant phase of CaCO_3 at ambient conditions, originating from the precipitation of supersaturated seawater and the biomineralization of organisms (Dunne et al., 2012; Hayes et al., 2021; Janjuhah et al., 2021). Aragonite is another common metastable phase of CaCO_3 in marine shelled creatures and corals, but it usually transforms into calcite due to its lower thermal stability under ambient conditions (Berner and Honjo, 1981; Sulpis et al., 2022). This phase transition is also reversible under high pressure-temperature conditions and aragonite, instead of calcite, becomes the principal form of CaCO_3 under extreme conditions relevant to subduction zones (Salje and Viswanathan, 1976; Suito et al., 2001; Zhang et al., 2003). Moreover, under water-saturated conditions, hydrated ikaite may exist in cold subducting slabs within a narrow temperature range of 313–373 K at 1.0–1.5 GPa in the hydrated upper mantle (Zhao et al., 2020).

Besides aragonite and ikaite, there are several other pressure- and temperature-induced phase transformations of CaCO_3 reported in previous experiments (Fig. 1). At room temperature, calcite transforms into monoclinic CaCO_3 -II at 1.5 GPa (Merrill and Bassett, 1975), triclinic CaCO_3 -III at 2.8 GPa, triclinic CaCO_3 -VI at 15 GPa and monoclinic CaCO_3 -VII at 30 GPa (Merlini et al., 2012; Bayarjargal et al., 2018). With increasing temperature at a low pressure of 0.4 MPa, calcite undergoes structural transitions into CaCO_3 -IV at 985 K and CaCO_3 -V at 1240 K (Ishizawa et al., 2013). Along the normal geothermal

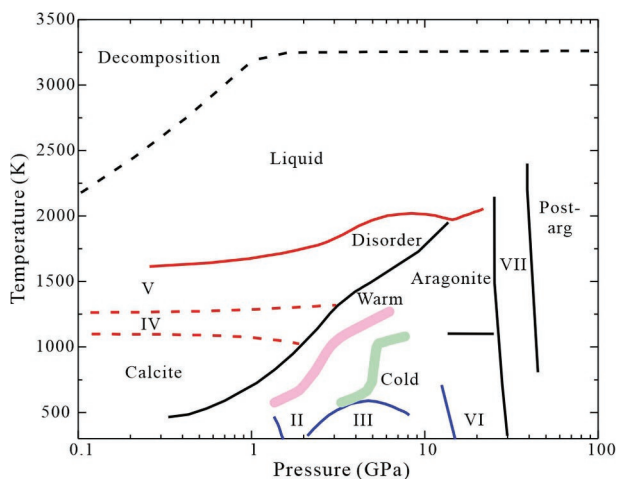


Fig. 1. Phase diagram of CaCO_3 under high pressure and temperature.

The blue lines show the boundaries of pressure-induced phase transitions (CaCO_3 -II, CaCO_3 -III and CaCO_3 -VI) (Merrill and Bassett, 1975; Merlini et al., 2012; Bayarjargal et al., 2018). The red dashed lines show boundaries of temperature-induced phase transitions (CaCO_3 -IV and CaCO_3 -V) (Ishizawa et al., 2013). The red solid lines show the experimental melting curves (Irving and Wyllie, 1975; Suito et al., 2001; Li et al., 2017). The black solid lines represent the boundaries of subducting phase transitions from calcite to aragonite, CaCO_3 -VII and post-aragonite (Bayarjargal et al., 2018). The black dashed line shows the decomposition curve of CaCO_3 from shock compression experiments (Ivanov and Deutsch, 2002). The pink and olive-green thick lines are geothermal gradients for warm and cold subducting slabs (Schmidt and Poli, 2014).

gradient of subduction zones, the aragonite phase of CaCO_3 transforms into a disordered or amorphous phase of CaCO_3 at 2–8 GPa and 1000–1600 K (Dove and Powell, 1989; Suito et al., 2001; Hou et al., 2019). As the pressure increases to 25 GPa, the CaCO_3 -VII phase is predicted to be the predominant phase; above 40 GPa, the post-aragonite phase is potentially the stable form of CaCO_3 under lower mantle conditions (Ono, 2005; Gavryushkin et al., 2017; Bayarjargal et al., 2018; Dorfman et al., 2018) (Fig. 1).

Pressure significantly affects the thermal stability of CaCO_3 , resulting in different high-temperature behaviors under different pressures. At 1 bar, CaCO_3 decomposes into CaO and CO_2 at 1175 K (Baker, 1962), but elevated pressures in excess of 0.5 GPa would suppress the dissociation, leading to CaCO_3 melting at 1600–1900 K and <4 GPa (Irving and Wyllie, 1975; Suito et al., 2001). According to multi-anvil melting experiments, the melting temperature of CaCO_3 increases from 1870 K at 3 GPa to 2000 K at 6 GPa. Between 8 and 13 GPa, the melting point of CaCO_3 descends slightly to 1950 K, but then increases to 2050 K from 13 to 21 GPa (Li et al., 2017). Note that the decomposition of liquid CaCO_3 finally occurs under extremely high temperatures at pressures greater than 0.5 GPa, the decomposition temperature of CaCO_3 dramatically increasing from 1175 K at 1 bar to 3000 K at 1 GPa. Interestingly, the decomposition temperatures of CaCO_3 remain almost constant at ~3300 K without obvious changes from 1 GPa to 200 GPa (Ivanov and Deutsch, 2002). Moreover, the CaCO_3 decomposition products can be altered under varying oxygen fugacity conditions. Laser-heated diamond-anvil cell experiments on CaCO_3 produced elemental carbon like graphite or diamond at 9–21 GPa and 3500 K, due to the disassociation of CO_2 under relatively low oxygen fugacities (Bayarjargal et al., 2010).

3 Migration of CaCO_3 via Dissolution and Melting

3.1 Dissolution of CaCO_3 in subduction fluids

Both marine sediments and hydrous minerals in subducting slabs contain massive quantities of water, some of which could be released at shallow depths in subduction zones (Zheng et al., 2016). Under high pressure and temperature above the critical point (647.35 K and 22.1 MPa), water transforms into supercritical fluids, which could dissolve much more substances than normal water (Bröll et al., 1999; Weingärtner and Franck, 2005; Liu and Zhang, 2022). Although the solubility of CaCO_3 in water is minimal under ambient conditions, its dissolution is greatly enhanced in supercritical subduction fluids. Besides pressure and temperature, the dissolution of CaCO_3 is also greatly influenced by other solutes in aqueous fluids. The low-density CaCO_3 -bearing subduction fluids could infiltrate and alter mantle wedges to form carbonatized peridotites. Finally, the carbon in these CaCO_3 -bearing domains could be returned to the surface by degassing CO_2 at arc volcanoes (Fig. 2) (Kawamoto et al., 2013).

The solubility of CaCO_3 in aqueous fluids changes with pressure and temperature (Pytkowicz and Connors, 1964). Under ambient and low-pressure conditions, the solubility of CaCO_3 decreases with increasing temperature (Segnit et

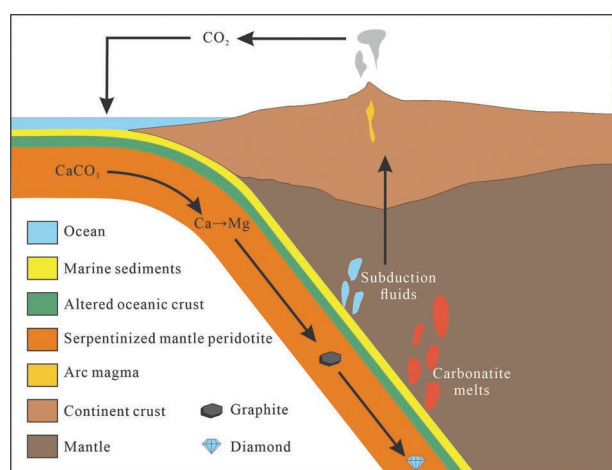


Fig. 2. Schematic diagram of subducting CaCO_3 in the global carbon cycle between Earth's surface and deep interiors.

al., 1962). At one atmosphere pressure, the solubility of CaCO_3 decreases from 2.25×10^{-3} mol/L at 373 K to 8.4×10^{-5} mol/L at 573 K (Ellis, 1959) and at 0.2 GPa, the CaCO_3 solubility decreases from 8.13×10^{-4} mol/L at 622 K to 8.13×10^{-5} mol/L at 895 K (Fein and Walther, 1987). However, the dissolving behavior dramatically changes with increasing pressure. At 0.6 GPa, the CaCO_3 solubility increases from 6.4×10^{-3} mol/L at 773 K to 2.06×10^{-2} mol/L at 973 K. Pressure has positive effects on the solubility of CaCO_3 . For instance, with pressure increasing from 0.6 to 1.6 GPa at 973 K, the solubility of CaCO_3 increases from 2.06×10^{-2} to 4.04×10^{-2} mol/L (Caciagli and Manning, 2003).

NaCl can increase the solubility of CaCO_3 under high pressure and temperature by forming CaCl^+ and NaCO_3^- ions. At 1073 K and 1 GPa, CaCO_3 solubility increases from around 0.1 mol/L in pure H_2O to near 4.0 mol/L under halite saturation (Newton and Manning, 2002). This indicates that the halide-bearing seawater can dissolve more CaCO_3 than pure water during subduction. Moreover, the dissolved CO_2 in subduction fluids can also affect the solubility of CaCO_3 . Under 0.2 GPa and 673–823 K, a lower concentration of CO_2 ($X_{\text{CO}_2} < 0.05$) in aqueous fluids can increase the solubility of CaCO_3 because of pH decreasing, while a higher concentration of CO_2 ($0.05 < X_{\text{CO}_2} < 0.15$) will decrease due to the CO_2 hydration effects (Fein and Walther, 1987).

3.2 Molten CaCO_3 and formation of carbonatite melts

Based on experimental measurements, the melting curve of pure CaCO_3 lies above the normal geothermal gradient of subduction, which means that CaCO_3 could remain in a subsolidus state during subduction. However, calcium carbonatite magmatism has been reported in both subduction zone and intraplate settings, indicating that the melting of subducting CaCO_3 happens in the deep Earth (Korsakov and Hermann, 2006; Tsuno et al., 2012; Liu et al., 2015; Thomson et al., 2016). At shallow depths, the addition of water can decrease the melting point of CaCO_3 under high pressures. The melting point of CaCO_3 decreases from 1583 to 918 K at 1 GPa under water-

saturated conditions (Wyllie and Tuttle, 1960; Durand et al., 2015). At greater depths, cation substitution and interactions with silicate minerals could also decrease the melting point of CaCO_3 even under anhydrous conditions, attributed to the formation of carbonatite melts (Fig. 2) (Buob et al., 2006; Shatskiy et al., 2013, 2015).

As a common Ca–Mg substitution in nature, Mg^{2+} decreases the melting point of CaCO_3 under high pressures. At 6 GPa, the melting of the CaCO_3 – MgCO_3 binary system occurs at 1623 K, which reduces the melting point of CaCO_3 by over 400 K (Buob et al., 2006; Zhao et al., 2022). Na^+ substitution more efficiently effects a decrease in the melting point of CaCO_3 . At 6 GPa, the melting of the CaCO_3 – Na_2CO_3 binary system occurs at 1473 K, which is 550 K lower than pure CaCO_3 (Shatskiy et al., 2013). K^+ substitution has a similar effect to Na^+ substitution and the melting of the CaCO_3 – K_2CO_3 binary system occurs at 1448 K (Shatskiy et al., 2015). These alkali-rich CaCO_3 -bearing carbonatite melts are consistent with the high alkali contents of deep carbonatite originating from the mantle (Weidendorfer et al., 2017).

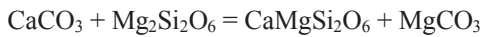
Besides substitution of cations, the presence of other oxides can also decrease the melting point of CaCO_3 and generate carbonatite melt under upper mantle conditions. The CaO – MgO – Al_2O_3 – SiO_2 – CO_2 system has been utilized to simulate the carbonated peridotite assemblages in high pressure-temperature experiments. The appearance of CaCO_3 -bearing carbonatite melts occurs at 1693 K and 2 GPa, which indicates the formation of carbonate liquids from alkali-poor anhydrous carbonated mantle at approximately 60 km depth (Keshav and Gudfinnsson, 2013; Novella et al., 2014). On the other hand, the presence of mafic and ultramafic minerals also affects the melting point of CaCO_3 (Poli, 2015). At 1.3–2.7 GPa, the addition of dunite decreases the melting temperatures of pure CaCO_3 from 1748–1878 K to 1198–1298 K (Chen et al., 2021). The solidus of carbonated eclogite has been explored experimentally over a range from 2 to 10 GPa (Hammouda, 2003; Dasgupta et al., 2004; Yaxley and Brey, 2004). Experimental results show that the melting points of carbonated eclogite are above 1200 K at 3 GPa and 1400 K at 6 GPa, indicating that even in hot subduction zones, carbonates could be preserved in carbonated eclogite and be stable in the upper mantle. At around 13 GPa, which is equivalent to the bottom of the upper mantle, the melting temperature of carbonated eclogite dramatically drops over a narrow pressure interval by ~ 200 K and forms sodium-rich carbonatite melts (Thomson et al., 2016).

4 CaCO_3 Reaction and Reduction with Silicate Minerals

At ambient conditions, CaCO_3 could coexist with mafic and ultramafic silicate minerals in altered oceanic crusts and serpentinized mantle peridotite (Plank and Manning, 2019). With increasing pressure and temperature in subduction zones, metamorphic reactions occur between CaCO_3 and silicates (Zheng, 2021). The cation-exchanging reactions between CaCO_3 and Mg-silicates produce Mg-bearing carbonates like dolomite and magnesite. Some reductive substances in the mantle will

also reduce CaCO_3 into elemental carbon and/or carbides. These carbonaceous products of CaCO_3 -silicate reactions are more stable under relatively reducing mantle conditions and may be subducted into the mantle transition zone and even the lower mantle (Fig. 2) (Liu et al., 2022).

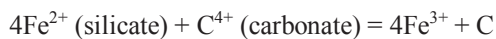
Mg-carbonates, including dolomite ($\text{CaMg}(\text{CO}_3)_2$) and magnesite (MgCO_3), are rare in the initial carbonates of subduction slabs (Plank and Manning, 2019). Their phase stability is higher than CaCO_3 at depths greater than ~100 km, Mg-carbonates becoming the major forms of carbonates and successors of CaCO_3 in subduction zones (Kato et al., 1997; Zhang et al., 2003). Enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) is a common mafic mineral in upper mantle peridotite. It can react with CaCO_3 at 2.3–7.7 GPa and 1073–1673 K, forming diopside ($\text{CaMgSi}_2\text{O}_6$), dolomite and magnesite as follows (Kushiro, 1975):



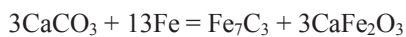
A similar Ca-Mg cation exchanging reaction also occurs between olivine (Mg_2SiO_4) and CaCO_3 in carbonated peridotites. At 3 GPa, CaCO_3 can react with olivine at 1373–1573 K, forming Ca-rich clinopyroxene and Mg-carbonates as follows (Wang X F et al., 2022):



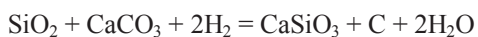
In the case of the existence of some reductive substances, CaCO_3 will be reduced to elemental carbon and/or carbides. Elemental carbon coexisting with variable-valence elements like Fe has been found in carbonated eclogites all over the world, e.g., from the Italian western Alps and southwestern Tianshan (Frezza et al., 2011; Tao et al., 2018). In high pressure-temperature experiments, Fe^{2+} in silicate can reduce CaCO_3 and produce elemental carbon at 6–14 GPa and 1373–1573 K as follows (Tao and Fei, 2021):



In addition to Fe^{2+} , metallic Fe is another efficient reductive agent for CaCO_3 beneath the metal-saturated depth in the deep mantle. At 4–16 GPa and 1073–1473 K, CaCO_3 can react with iron, forming iron carbides and Ca-wüstite as follows (Martirosyan et al., 2016):



The reductive fluids from the serpentinization of mantle peridotites in mantle wedges can also reduce CaCO_3 into elemental carbon (Liu et al., 2020). Highly crystalline graphite was discovered in an exhumed serpentinite-sediment contact in Alpine Corsica, France (Galvez et al., 2013). The graphite in this reaction zone has a carbon isotopic signature ($\delta^{13}\text{C}$) of up to 0.8‰, similar to that of the original calcite that composed the sediments, indicating that graphite should originate from calcite reduction by H_2 -rich fluids at 703 K and 0.9–1.5 GPa as follows:



More interestingly, dolomite marble with micro diamond inclusions from the Kokchetav Massif indicates ultra high-

pressure metamorphism above 7.85 GPa, which is equivalent to depths greater than 250 km (De Corte et al., 2000; Ogasawara et al., 2000; Zhu and Ogasawara, 2002). The transformation from graphite to diamond will improve the stability of carbonaceous substances. This indicates that the subducted carbonated eclogites could at least reach the base of the upper mantle and even the core-mantle boundary region.

5 Concluding Remarks and Perspectives

Thus far, considerable progress has been achieved over several decades of research involving phase stability, dissolution, melting and reduction of CaCO_3 under high pressure and temperature conditions. In this review, we have attempted to present a summary of the current state of understanding of the fate of subducting CaCO_3 in the upper mantle. However, there remain many important questions that require further research in the future.

Firstly, it is still a matter of debate whether or not CaCO_3 exists in the mantle transition zone and the lower mantle. The Ca-Mg exchanging metamorphic reactions at shallow depths indicate that Mg-carbonates should be the predominant oxidized form of carbon in subducting slabs in the upper and lower mantle (Seto et al., 2008). However, based on experimental stability under the lowest mantle conditions, CaCO_3 instead of MgCO_3 could be more stable above 90 GPa and 2100 K due to sp^2 - sp^3 bonding changes (Zhang et al., 2018; Lü et al., 2021). Consequently, CaCO_3 is proposed to be the principal form of carbonate at the core-mantle boundary.

Secondly, the Ca and Mg isotope signatures of intraplate carbonatite magmatism suggest a large-scale deep carbon cycle in the solid Earth (Liu et al., 2022; Uhlig et al., 2022). However, the formation mechanism of Ca-rich carbonatite magma is still unclear. A redox-melting mechanism has been proposed to explain the origin of carbon from the lower mantle and partial melting of carbonated peridotites to generate carbonatite magmas (Rohrbach and Schmidt, 2011). The migration of calcic components from subduction slabs to mantle plumes is not included in this mechanism. Notably, a mantle plume is absent from some carbonatite magmatism active areas such as the North China craton, which is also counter to the plume-driven redox-melting mechanism for calcic carbonatite (Wang X et al., 2022).

Thirdly, the formation of abiotic hydrocarbon during the reduction of subducting CaCO_3 has become a topic of great interest in recent years (Etiope and Sherwood Lollar, 2013; McCollom, 2016; Peng et al., 2021). The H_2 -bearing reductive fluids from the dehydration of hydrous silicates can react with CaCO_3 , forming methane and other hydrocarbons. The observation of subduction-related abiotic methanogenesis by reaction with reductive mantle fluids and Ca-carbonates has been reported in the Italian Alps by Vitale Brovarone et al. (2017). Talc and wüstite can also react with CaCO_3 in water-saturated conditions and produce methane in high pressure and temperature experiments (Holloway, 1984; Scott et al., 2004). In previous research, these abiotic hydrocarbons were neglected in estimates of deep carbon cycling fluxes.

Throughout Earth's geological history, these hydrocarbons may have played a critical role in Earth's paleoclimate.

Last but not least, in order to determine the evolution and fate of deep CaCO_3 , interdisciplinary and integrated methods should be introduced into high pressure and temperature researches. For instance, it is conventionally held that the metal-saturated lower mantle should maintain a very low oxygen fugacity, whereas recent research into hydrous minerals at the core-mantle boundary suggest an at least locally oxygen-rich lower mantle (Liu et al., 2017, 2021; Mao and Mao, 2020). Similarly, carbon embraces varying valence states, allowing CaCO_3 to be oxidized on the surface and reduced in the deep Earth. This makes CaCO_3 a major oxygen fugacity modulator between Earth's surface and interior, revealing a more critical role for CaCO_3 in the dynamics and evolution of our blue planet.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2019YFA0708502) and the National Natural Science Foundation of China (42072052).

Manuscript received Oct. 27, 2022

accepted Jan. 28, 2023

associate EIC: ZHANG Lifei

edited by Jeffery J. LISTON and FANG Xiang

References

- Baker, E.H., 1962. The calcium oxide–carbon dioxide system in the pressure range 1–300 atmospheres. *Journal of the Chemical Society*, 165: 464–470.
- Bayarjargal, L., Shumilova, T.G., Friedrich, A., and Winkler, B., 2010. Diamond formation from CaCO_3 at high pressure and temperature. *European Journal of Mineralogy*, 22(1): 29–34.
- Bayarjargal, L., Fruhner, C.J., Schrodt, N., and Winkler, B., 2018. CaCO_3 phase diagram studied with Raman spectroscopy at pressures up to 50 GPa and high temperatures and DFT modeling. *Physics of the Earth and Planetary Interiors*, 281: 31–45.
- Berner, R.A., and Honjo, S., 1981. Pelagic sedimentation of aragonite: Its geochemical significance. *Science*, 211(4485): 940–942.
- Bröll, D., Kaul, C., Krämer, A., Krammer, P., Richter, T., Jung, M., Vogel, H., and Zehner, P., 1999. Chemistry in supercritical water. *Angewandte Chemie International Edition*, 38(20): 2998–3014.
- Buob, A., Luth, R.W., Schmidt, M.W., and Ulmer, P., 2006. Experiments on CaCO_3 – MgCO_3 solid solutions at high pressure and temperature. *American Mineralogist*, 91(2–3): 435–440.
- Caciagli, N.C., and Manning, C.E., 2003. The solubility of calcite in water at 6–16 kbar and 500–800°C. *Contributions to Mineralogy and Petrology*, 146(3): 275–285.
- Chen, C., Förster, M.W., Foley, S.F., and Liu, Y., 2021. Massive carbon storage in convergent margins initiated by subduction of limestone. *Nature Communications*, 12(1): 4463.
- Cölfen, H., and Antonietti, M., 2005. Mesocrystals: Inorganic superstructures made by highly parallel crystallization and controlled alignment. *Angewandte Chemie International Edition*, 44(35): 5576–5591.
- Dasgupta, R., and Hirschmann, M.M., 2010. The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters*, 298(1–2): 1–13.
- Dasgupta, R., Hirschmann, M.M., and Withers, A.C., 2004. Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite under upper mantle conditions. *Earth and Planetary Science Letters*, 227(1–2): 73–85.
- De Corte, K., Korsakov, A., Taylor, W.R., Cartigny, P., Ader, M., and De Paepe, P., 2000. Diamond growth during ultrahigh-pressure metamorphism of the Kokchetav Massif, northern Kazakhstan. *Island Arc*, 9(3): 428–438.
- Deer, W.A., Howie, R.A., and Zussman, J., 2013. An introduction to the rock-forming minerals. London: The Mineralogical Society.
- Dorfman, S.M., Badro, J., Nabiei, F., Prakapenka, V.B., Cantoni, M., and Gillet, P., 2018. Carbonate stability in the reduced lower mantle. *Earth and Planetary Science Letters*, 489: 84–91.
- Dove, M.T., and Powell, B.M., 1989. Neutron diffraction study of the tricritical orientational order/disorder phase transition in calcite at 1260 K. *Physics and Chemistry of Minerals*, 16(5): 503–507.
- Dunne, J.P., Hales, B., and Toggweiler, J.R., 2012. Global calcite cycling constrained by sediment preservation controls. *Global Biogeochemical Cycles*, 26(3): GB3023.
- Durand, C., Baumgartner, L.P., and Marquer, D., 2015. Low melting temperature for calcite at 1000 bars on the join CaCO_3 – H_2O —Some geological implications. *Terra Nova*, 27(5): 364–369.
- Ellis, A.J., 1959. The solubility of calcite in carbon dioxide solutions. *American Journal of Science*, 257(5): 354–365.
- Etioppe, G., and Sherwood Lollar, B., 2013. Abiotic methane on Earth. *Reviews of Geophysics*, 51(2): 276–299.
- Facq, S., Daniel, I., Montagnac, G., Cardon, H., and Sverjensky, D.A., 2016. Carbon speciation in saline solutions in equilibrium with aragonite at high pressure. *Chemical Geology*, 431: 44–53.
- Farsang, S., Louvel, M., Zhao, C., Mezouar, M., Rosa, A.D., Widmer, R.N., Feng, X., Liu, J., and Redfern, S.A.T., 2021. Deep carbon cycle constrained by carbonate solubility. *Nature Communications*, 12(1): 1–9.
- Fein, J.B., and Walther, J.V., 1987. Calcite solubility in supercritical CO_2 – H_2O fluids. *Geochimica et Cosmochimica Acta*, 51(6): 1665–1673.
- Frezza, M.L., Selverstone, J., Sharp, Z.D., and Compagnoni, R., 2011. Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nature Geoscience*, 4(10): 703–706.
- Galvez, M.E., Beyssac, O., Martinez, I., Benzerara, K., Chaduteau, C., Malvoisin, B., and Malavieille, J., 2013. Graphite formation by carbonate reduction during subduction. *Nature Geoscience*, 6(6): 473–477.
- Gavryushkin, P.N., Martirosyan, N.S., Inerbaev, T.M., Popov, Z.I., Rashchenko, S.V., Likhacheva, A.Yu., Lobanov, S.S., Goncharov, A.F., Prakapenka, V.B., and Litasov, K.D., 2017. Aragonite-II and CaCO_3 -VII: New high-pressure, high-temperature polymorphs of CaCO_3 . *Crystal Growth & Design*, 17(12): 6291–6296.
- Hammouda, T., 2003. High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and storage in the mantle. *Earth and Planetary Science Letters*, 214(1–2): 357–368.
- Hayes, C.T., Costa, K.M., Anderson, R.F., Calvo, E., Chase, Z., Demina, L.L., Dutay, J.C., German, C.R., Heimbürger-Boavida, L.E., Jaccard, S.L., Jacobel, A., Kohfeld, K.E., Kravchishina, M.D., Lippold, J., Mekik, F., Missiaen, L., Pavia, F.J., Paytan, A., Pedrosa-Pamies, R., Petrova, M.V., Rahman, S., Robinson, L.F., Roy-Barman, M., Sanchez-Vidal, A., Shiller, A., Tagliabue, A., Tessin, A.C., van Hulten, M., and Zhang, J., 2021. Global ocean sediment composition and burial flux in the deep sea. *Global Biogeochemical Cycles*, 35(4): e2020GB006769.
- Holloway, J.R., 1984. Graphite– CH_4 – H_2O – CO_2 equilibria at low-grade metamorphic conditions. *Geology*, 12(8): 455.
- Hou, M., Zhang, Q., Tao, R., Liu, H., Kono, Y., Mao, H., Yang, W., Chen, B., and Fei, Y., 2019. Temperature-induced amorphization in CaCO_3 at high pressure and implications for recycled CaCO_3 in subduction zones. *Nature Communications*, 10(1): 1963.
- Irving, A.J., and Wyllie, P.J., 1975. Subsolvus and melting

- relationships for calcite, magnesite and the join $\text{CaCO}_3\text{--MgCO}_3$, 36 kb. *Geochimica et Cosmochimica Acta*, 39(1): 35–53.
- Ishizawa, N., Setoguchi, H., and Yanagisawa, K., 2013. Structural evolution of calcite at high temperatures: Phase V unveiled. *Scientific Reports*, 3(1): 2832.
- Ivanov, B.A., and Deutsch, A., 2002. The phase diagram of CaCO_3 in relation to shock compression and decomposition. *Physics of the Earth and Planetary Interiors*, 129(1–2): 131–143.
- Janjuhah, H.T., Sanjuan, J., Alqudah, M., and Salah, M.K., 2021. Biostratigraphy, depositional and diagenetic processes in carbonate rocks from southern Lebanon: Impact on porosity and permeability. *Acta Geologica Sinica (English Edition)*, 95(5): 1668–1683.
- Kato, T., Enami, M., and Zhai, M., 1997. Ultra-high-pressure (UHP) marble and eclogite in the Su–Lu UHP terrane, eastern China. *Journal of Metamorphic Geology*, 15(2): 169–182.
- Kawamoto, T., Yoshikawa, M., Kumagai, Y., Mirabueno, M.H.T., Okuno, M., and Kobayashi, T., 2013. Mantle wedge infiltrated with saline fluids from dehydration and decarbonation of subducting slab. *Proceedings of the National Academy of Sciences*, 110(24): 9663–9668.
- Kelemen, P.B., and Manning, C.E., 2015. Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences*, 112(30): E3997–E4006.
- Keshav, S., and Gudfinnsson, G.H., 2013. Silicate liquid-carbonatite liquid transition along the melting curve of model, vapor-saturated peridotite in the system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2\text{--CO}_2$ from 1.1 to 2 GPa. *Journal of Geophysical Research: Solid Earth*, 118(7): 3341–3353.
- Korsakov, A.V., and Hermann, J., 2006. Silicate and carbonate melt inclusions associated with diamonds in deeply subducted carbonate rocks. *Earth and Planetary Science Letters*, 241(1–2): 104–118.
- Kushiro, I., 1975. Carbonate–silicate reactions at high pressures and possible presence of dolomite and magnesite in the upper mantle. *Earth and Planetary Science Letters*, 28(2): 116–120.
- Lee, C.T.A., Jiang, H., Dasgupta, R., and Torres, M., 2019. A framework for understanding whole-Earth carbon cycling. In: Orcutt, B.N., Daniel, I., and Dasgupta, R. (eds.), *Deep Carbon: Past to Present*. Cambridge: Cambridge University Press, 313–357.
- Li, Z., Li, J., Lange, R., Liu, J., and Militzer, B., 2017. Determination of calcium carbonate and sodium carbonate melting curves up to Earth's transition zone pressures with implications for the deep carbon cycle. *Earth and Planetary Science Letters*, 457: 395–402.
- Liu, F., Yang, J., Lian, D., Xiong, F., and Wu, W., 2020. Diamonds and other unusual minerals in global ophiolites. *Acta Geologica Sinica*, 94(9): 2588–2605 (in Chinese with English abstract).
- Liu, J., Hu, Q., Kim, D.Y., Wu, Z., Wang, W., Xiao, Y., Chow, P., Meng, Y., Prakapenka, V.B., Mao, H.K., and Mao, W.L., 2017. Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones. *Nature*, 551(7681): 494–497.
- Liu, J., Wang, C., Lü, C., Su, X., Liu, Y., Tang, R., Chen, J., Hu, Q., Mao, H.K., and Mao, W.L., 2021. Evidence for oxygenation of Fe–Mg oxides at mid-mantle conditions and the rise of deep oxygen. *National Science Review*, 8(4): nwa096.
- Liu, S.A., Qu, Y.R., Wang, Z.Z., Li, M.L., Yang, C., and Li, S.G., 2022. The fate of subducting carbon tracked by Mg and Zn isotopes: A review and new perspectives. *Earth-Science Reviews*, 228: 104010.
- Liu, Y., He, D., Gao, C., Foley, S., Gao, S., Hu, Z., Zong, K., and Chen, H., 2015. First direct evidence of sedimentary carbonate recycling in subduction-related xenoliths. *Scientific Reports*, 5(1): 11547.
- Liu, Y., and Zhang, L., 2022. Fluid immiscibility and evolution in subduction zones. *Acta Geologica Sinica*, 96(12): 4104–4130 (in Chinese with English abstract).
- Lü, M., Dorfman, S.M., Badro, J., Borensztajn, S., Greenberg, E., and Prakapenka, V.B., 2021. Reversal of carbonate–silicate cation exchange in cold slabs in Earth's lower mantle. *Nature Communications*, 12(1): 1712.
- Mao, H., and Mao, W.L., 2020. Key problems of the four-dimensional Earth system. *Matter and Radiation at Extremes*, 5(3): 038102.
- Martirosyan, N.S., Yoshino, T., Shatskiy, A., Chanyshv, A.D., and Litasov, K.D., 2016. The CaCO_3 interaction: Kinetic approach for carbonate subduction to the deep Earth's mantle. *Physics of the Earth and Planetary Interiors*, 259: 1–9.
- McCullom, T.M., 2016. Abiotic methane formation during experimental serpentinization of olivine. *Proceedings of the National Academy of Sciences*, 113(49): 13965–13970.
- Merlini, M., Hanfland, M., and Crichton, W.A., 2012. $\text{CaCO}_3\text{--III}$ and $\text{CaCO}_3\text{--VI}$, high-pressure polymorphs of calcite: Possible host structures for carbon in the Earth's mantle. *Earth and Planetary Science Letters*, 333–334: 265–271.
- Merrill, L., and Bassett, W.A., 1975. The crystal structure of $\text{CaCO}_3\text{(II)}$, a high-pressure metastable phase of calcium carbonate. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, 31(2): 343–349.
- Newton, R.C., and Manning, C.E., 2002. Experimental determination of calcite solubility in $\text{H}_2\text{O--NaCl}$ solutions at deep crust/upper mantle pressures and temperatures: Implications for metasomatic processes in shear zones. *American Mineralogist*, 87(10): 1401–1409.
- Novella, D., Keshav, S., Gudfinnsson, G.H., and Ghosh, S., 2014. Melting phase relations of model carbonated peridotite from 2 to 3 GPa in the system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2\text{--CO}_2$ and further indication of possible unmixing between carbonatite and silicate liquids. *Journal of Geophysical Research: Solid Earth*, 119(4): 2780–2800.
- Ogasawara, Y., Ohta, M., Fukasawa, K., Katayama, I., and Maruyama, S., 2000. Diamond-bearing and diamond-free metacarbonate rocks from Kumdy-Kol in the Kokchetav Massif, northern Kazakhstan. *Island Arc*, 9(3): 400–416.
- Ono, S., 2005. Post-aragonite phase transformation in CaCO_3 at 40 GPa. *American Mineralogist*, 90(4): 667–671.
- Peng, W., Zhang, L., Tumiati, S., Vitale Brovarone, A., Hu, H., Cai, Y., and Shen, T., 2021. Abiotic methane generation through reduction of serpentinite-hosted dolomite: Implications for carbon mobility in subduction zones. *Geochimica et Cosmochimica Acta*, 311: 119–140.
- Plank, T., and Manning, C.E., 2019. Subducting carbon. *Nature*, 574(7778): 343–352.
- Poli, S., 2015. Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. *Nature Geoscience*, 8(8): 633–636.
- Pytkowicz, R.M., and Connors, D.N., 1964. High pressure solubility of calcium carbonate in seawater. *Science*, 144(3620): 840–841.
- 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(7342): 209–212.
- Salje, E., and Viswanathan, K., 1976. The phase diagram calcite–aragonite as derived from the crystallographic properties. *Contributions to Mineralogy and Petrology*, 55(1): 55–67.
- Schmidt, M.W., and Poli, S., 2014. Devolatilization during Subduction. *Treatise on Geochemistry*, 4: 669–701.
- Scott, H.P., Hemley, R.J., Mao, H., Herschbach, D.R., Fried, L.E., Howard, W.M., and Bastea, S., 2004. Generation of methane in the Earth's mantle: In situ high pressure-temperature measurements of carbonate reduction. *Proceedings of the National Academy of Sciences*, 101(39): 14023–14026.
- Segnit, E.R., Holland, H.D., and Biscardi, C.J., 1962. The solubility of calcite in aqueous solutions-I: The solubility of calcite in water between 75° and 200° at CO_2 pressures up to 60 atm. *Geochimica et Cosmochimica Acta*, 26(12): 1301–1331.
- Seto, Y., Hamane, D., Nagai, T., and Fujino, K., 2008. Fate of carbonates within oceanic plates subducted to the lower mantle, and a possible mechanism of diamond formation. *Physics and Chemistry of Minerals*, 35(4): 223–229.
- Shatskiy, A., Sharygin, I.S., Litasov, K.D., Borzdov, Y.M., Palyanov, Y.N., and Ohtani, E., 2013. New experimental data

- on phase relations for the system $\text{Na}_2\text{CO}_3\text{--CaCO}_3$ at 6 GPa and 900°C. *American Mineralogist*, 98(11–12): 2164–2171.
- Shatskiy, A., Borzdov, Y.M., Litasov, K.D., Sharygin, I.S., Palyanov, Y.N., and Ohtani, E., 2015. Phase relationships in the system $\text{K}_2\text{CO}_3\text{--CaCO}_3$ at 6 GPa and 900–1450°C. *American Mineralogist*, 100(1): 223–232.
- Suito, K., Namba, J., Horikawa, T., Taniguchi, Y., Sakurai, N., Kobayashi, M., Onodera, A., Shimomura, O., and Kikegawa, T., 2001. Phase relations of CaCO_3 at high pressure and high temperature. *American Mineralogist*, 86(9): 997–1002.
- Sulpis, O., Agrawal, P., Wolthers, M., Munhoven, G., Walker, M., and Middelburg, J.J., 2022. Aragonite dissolution protects calcite at the seafloor. *Nature Communications*, 13(1): 1104.
- Tang, H., Guo, T., Wu, K., Liu, Z., Xu, J., Lu, B., and Wang, P., 2022. Reassessment of the distribution of mantle CO_2 in the Bohai Sea, China: The perspective from the source and pathway system. *Acta Geologica Sinica (English Edition)*, 96(1): 337–347.
- Tao, R., and Fei, Y., 2021. Recycled calcium carbonate is an efficient oxidation agent under deep upper mantle conditions. *Communications Earth & Environment*, 2(1): 1–8.
- Tao, R., Zhang, L., Tian, M., Zhu, J., Liu, X., Liu, J., Höfer, H.E., Stagno, V., and Fei, Y., 2018. Formation of abiotic hydrocarbon from reduction of carbonate in subduction zones: Constraints from petrological observation and experimental simulation. *Geochimica et Cosmochimica Acta*, 239: 390–408.
- Thomson, A.R., Walter, M.J., Kohn, S.C., and Brooker, R.A., 2016. Slab melting as a barrier to deep carbon subduction. *Nature*, 529(7584): 76–79.
- Tsuno, K., Dasgupta, R., Danielson, L., and Richter, K., 2012. Flux of carbonate melt from deeply subducted pelitic sediments: Geophysical and geochemical implications for the source of Central American volcanic arc. *Geophysical Research Letters*, 39(16): L16307.
- Uhlig, D., Wu, B., Berns, A.E., and Amelung, W., 2022. Magnesium stable isotopes as a potential geochemical tool in agronomy—Constraints and opportunities. *Chemical Geology*, 611: 121114.
- Vitale Brovarone, A., Martinez, I., Elmaleh, A., Compagnoni, R., Chaduteau, C., Ferraris, C., and Esteve, I., 2017. Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps. *Nature Communications*, 8(1): 14134.
- Walker, J.C.G., Hays, P.B., and Kasting, J.F., 1981. A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *Journal of Geophysical Research: Oceans*, 86(C10): 9776–9782.
- Wang, X.F., Zhang, J., Wang, C., Zong, K., and Xu, H., 2022. Experimental constraint on Ca-rich carbonatite melt-peridotite interaction and implications for lithospheric mantle modification beneath the North China Craton. *Journal of Geophysical Research: Solid Earth*, 127(9): e2022JB024769.
- Wang, X., Zhu, W.B., and Zheng, Y.F., 2022. Geochemical constraints on the nature of Late Archean basaltic-andesitic magmatism in the North China Craton. *Earth-Science Reviews*, 230: 104065.
- Weidendorfer, D., Schmidt, M.W., and Mattsson, H.B., 2017. A common origin of carbonatite magmas. *Geology*, 45(6): 507–510.
- Weingärtner, H., and Franck, E.U., 2005. Supercritical water as a solvent. *Angewandte Chemie International Edition*, 44(18): 2672–2692.
- Wyllie, P.J., and Tuttle, O.F., 1960. The system $\text{CaO--CO}_2\text{--H}_2\text{O}$ and the origin of carbonatites. *Journal of Petrology*, 1(1): 1–46.
- Yaxley, G.M., and Brey, G.P., 2004. Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: Implications for petrogenesis of carbonatites. *Contributions to Mineralogy and Petrology*, 146(5): 606–619.
- Zhang, Z., Mao, Z., Liu, X., Zhang, Y., and Brodholt, J., 2018. Stability and reactions of CaCO_3 polymorphs in the Earth's deep mantle. *Journal of Geophysical Research: Solid Earth*, 123(8): 6491–6500.
- Zhang, L., Ellis, D.J., Arculus, R.J., Jiang, W., and Wei, C., 2003. 'Forbidden Zone' subduction of sediments to 150 km depth—The reaction of dolomite to magnesite + aragonite in the UHPM metapelites from western Tianshan, China. *Journal of Metamorphic Geology*, 21(6): 523–529.
- Zhao, S., Poli, S., Schmidt, M.W., Rinaldi, M., and Tumiati, S., 2022. An experimental determination of the liquidus and a thermodynamic melt model in the $\text{CaCO}_3\text{--MgCO}_3$ binary, and modelling of carbonated mantle melting. *Geochimica et Cosmochimica Acta*, 336: 394–406.
- Zhao, X., Zheng, Z., Chen, J., Gao, Y., and Sun, J., 2020. High P - T calcite-aragonite phase transitions under hydrous and anhydrous conditions. *Frontiers in Earth Science*, 10: 907967.
- Zheng, Y.F., 2021. Metamorphism in subduction zones. In: Elias, S., and Alderton, D. (eds.), *Encyclopedia of Geology*. Elsevier, 612–622.
- Zheng, Y., Chen, R., Xu, Z., and Zhang, S., 2016. The transport of water in subduction zones. *Science China Earth Sciences*, 59(4): 651–682.
- Zhu, Y., and Ogasawara, Y., 2002. Carbon recycled into deep Earth: Evidence from dolomite dissociation in subduction-zone rocks. *Geology*, 30(10): 947–950.

About the first author



GUI Weibin, male, born in 1993 in Laizhou, Shandong Province, China. Ph.D. candidate in high-pressure geochemistry at the Center for High Pressure Science and Technology Advanced Research. He is currently interested in the geochemical behavior of carbonates and hydrous minerals under high pressure and temperature conditions. E-mail: weibin.gui@hpstar.ac.cn.

About the corresponding authors



SHEN Kewei, female, born in 1993 in Xingtai, Hebei Province, China. Postdoctoral researcher at the Center for High Pressure Science and Technology Advanced Research. Her research interests focus on the physics and chemistry of minerals and rocks under high-pressure-temperature conditions. E-mail: kewei.shen@hpstar.ac.cn.



LIU Jin, male, born in 1984 in Jiangsu Province, China, Ph.D.; professor of mineral physics at Yanshan University. He has been focused on the physical and chemical properties of planetary materials under extreme conditions since 2007. E-mail: jinliu@ysu.edu.cn.