Fate of Carbonates in the Earth’s Mantle (10-136 GPa)

Jing Gao1*, Xiang Wu2, Xueyin Yuan3 and Wen Su1

1State Key Laboratory of Lithospheric Evolution, Institutions of Earth Science, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China, 2State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China, 3MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China

Earth carbon cycle shapes the evolution of our planet and our habitats. As a key region of carbon cycle, subduction zone acts as a sole channel transporting supracrustal carbonate rocks down to the mantle, balancing carbon budget between the Earth’s surface and the interior, and regulating CO2 concentration of the atmosphere. How carbonates evolve at depth is thus, a most fundamental issue in understanding carbon flux and carbon sequestration mechanism in the Earth. This study reviews prominent progresses made in the field of crystal chemistry of carbonates along subduction geotherms. It clearly finds that, in addition to common carbonates in the Earth’s crust, several new polymorphs of carbonates have been discovered to be stable under high-pressure and high-temperature conditions. This opens possibilities for oxidized carbon species in the deep Earth. However, metamorphic decarbonatation and reduction reactions restrict subducting carbonates to the top-mid region of the lower mantle. Specifically, subsolidus decarbonatation in the form of carbonates reacting with silicates has been proposed as an efficient process releasing CO2 from slabs to the mantle. Besides, carbonate reduction in the metal-saturated mantle likely results in generation of super-deep diamonds and a considerable degree of carbon isotope fractionation. Review of these novel findings leads us to consider three issues in the further studies, including 1) searching for new chemical forms of carbon in the mantle, 2) determining the reduction efficiency of carbonates to diamonds and the accompanying carbon isotope fractionation and 3) concerning carbon cycle in subduction of continental crust.

Keywords: phase relation, crystal chemistry, diamond, graphite, decarbonatation

INTRODUCTION

Carbon is a basic element that forms the Earth and the biosphere. Earth carbon cycle ties closely with the global climate, the origin and evolution of life and the carbon-based energy resources. The present review focuses on the carbon cycle in subduction zones. The crustal carbon is carried down to the Earth’s interior via subduction processes, modifying the redox state of the mantle, and the deep carbon exchanges with the crustal carbon via volcanism or metamorphic decarburization over geological timescales (Dasgupta and Hirschmann, 2010; Plank and Langmuir, 1993). This process is responsible for the recycling of a great amount of carbon and consequently, exerts profound influence upon the terrestrial ecosystem functions. In recent decades, the carbon balance between the Earth’s surface and the interior is wrecked. It has become our urgent desire to examine carbon sequestration capacity of different reservoirs and strive for a balance of carbon income and outcome.
Extensive studies have been carried out on carbon flux from the Earth’s surface to the interior but obtained totally different results (Gorman et al., 2006; Johnston et al., 2011). Estimation on the removal amount of the subducted carbon from slabs varies from 35 to 100% (Kelemen and Manning, 2015). The large inconsistency is due mainly to our limited knowledge on behaviors of carbonates in subduction zones.

Carbonates (e.g. calcite CaCO₃, magnesite MgCO₃, and dolomite (Ca, Mg)CO₃) are predominantly carbon species in the Earth’s crust. Their structural stability in subduction zones is a key to measuring carbon flux. On the one hand, with the increase of the subduction depth, the pressure-temperature and the oxygen fugacity conditions become more and more favorable for reduced carbon species. In this respect, carbonates would be overtaken by diamond or graphite at mantle depths in excess of ~250 km where the redox state begins to be buffered by iron-wüstite equilibrium due to disproportionation of Fe²⁺ to Fe³⁺ and metallic Fe⁰ (Frost et al., 2004). At greater depths, Fe²⁺ disproportionation to Fe³⁺ and Fe⁰ progressively increases, which likely results to diamond domains in the deep Earth (Rohrbach and Schmidt, 2011). On the other hand, however, the possibilities of crustal carbonates in the upper-mid mantle have been suggested by thermodynamic calculations (Sun et al., 2018) and experiments (Ghosh et al., 2009; Litvin et al., 2014). Besides, carbonate associations have been frequently discovered as inclusions in the transition-zone and the lower-mantle diamonds (e.g. Brenker et al., 2007; Kaminsky, 2012; Kaminsky et al., 2013; 2016). This indicates that the crystal chemistry of carbonates and the carbon sequestration mechanism in the deep Earth are far more complicated than previously thought.

In this study, we systematically review the high-pressure behaviors of carbonates along from cold to the hottest subduction geotherms, aiming at three scientific issues: 1) Establishing a comprehensive phase relation of main carbonates in the Earth’s mantle. Our first concern is whether carbonates will melt and breakdown at high-pressure and high-temperature conditions, or preserve to greater depths even approaching the core-mantle boundary (CMB). 2) Next, close attention are paid upon the reduction mechanism of carbonates in reactions with the metallic mantle during subducting processes, as that would be an impenetrable barrier to carbonate subduction. 3) Meanwhile, decarbonization of carbonated peridotites and eclogites (including mid-ocean ridge basalt, MORB) by the surrounding silicates should also be examined, as these processes exhibit the possibility of CO₂ release as an equilibrium phase in the deep mantle, which sets fundamental control on mantle metasomatism.

**PHASE DIAGRAM OF CARBONATES IN THE MANTLE**

CaCO₃, MgCO₃, (Ca,Mg)CO₃ are three main inorganic carbon substances in the Earth’s crust. They are also dominant carbon species recovered in sublithospheric diamonds. Carbonates show versatile behaviors such as phase transition, dissolution, melting, decomposition and decarburization at mantle conditions. For example, CaCO₃ exhibits exceeding solubility in aqueous fluids and may extract a considerable portion of carbon from slabs. But Ca²⁺ in carbonates would be replaced by Mg²⁺ upon sinking, and the solubility of dolomite reduces significantly if carbonates become Mg-rich (Farsang et al., 2021). Naturally Fe²⁺ substituting Mg²⁺ forms a complete MgCO₃-FeCO₃ solid solution, and a minor addition of Fe²⁺ significantly affect the phase boundary of carbonates especially at lower-mantle pressures (Liu et al., 2015; Tao et al., 2014). The following section presents a summary of phase relation of CaCO₃, MgCO₃ and (Ca,Mg)CO₃ and their ferrous series at depths.
Calcite CaCO$_3$

The stable polymorph of CaCO$_3$ at ambient conditions is calcite (R-3c, Z = 6) where [CO$_3$]$^{2-}$ species form parallel layers and Ca$^{2+}$ are six-fold coordinated by O$^{2-}$. Upon pressures above ~2 GPa, calcite reconstructively converts to aragonite (Pmcn, Z = 4) with [CaO$_6$]-octahedra turning into [CaO$_9$]-polyhedra. Aragonite has long been considered as the dominant CaCO$_3$-structure in the Earth’s interior from the upper mantle to the top of the lower mantle. Yet its density is lower than the principle constituents of the mantle (Listov et al., 2007), which casts doubts on the presence of CaCO$_3$ in the deep Earth. Accumulations of experimental and theoretical data lately, however, create a whole new landscape of CaCO$_3$ inside the Earth. One significant finding is CaCO$_3$-VII (P2$_1$/c-l, Z = 4), which was put forward by Gavryushkin et al. (2017) as favorable in the pressure range of 30–50 GPa below1200 K (Figure 1). Bayarjargal et al. (2018) and Li et al. (2018) subsequently expanded its temperature scope to the melting point and suggest CaCO$_3$-VII as a predominant candidate at mantle depths of 690–1010 km. Increasing temperature would lower the pressure of aragonite → CaCO$_3$-VII transformation (Zhang ZG. et al., 2018). CaCO$_3$-VII is characterized with non-planar [CO$_3$]$^{2-}$ units that are rotated by ~45° relative to those in calcite/aragonite and are tilted ~90° to one another. It is considered as an intermediate in the aragonite → post-aragonite transformation wherein the [CO$_3$]$^{2-}$ units undergo a ~90° rotation (Pickard and Needs, 2015; Smith et al., 2018). Conversion of aragonite to CaCO$_3$-VII is accompanied by an uprush of 2% for density, and an increase of 9, 2 and 8% for shear, longitudinal and average sound velocities. The difference in wave velocities increase by ~6% when 10% CaCO$_3$ is present with respect to a pure pyrolitic composition (Bayarjargal et al., 2018). Therefore, the potential preferred orientation of CaCO$_3$-VII may contribute to seismic discontinuities at ~700 km in the vicinity of slabs (Kaneshima, 2013; Yang and He, 2015; Bayarjargal et al., 2018).

In the meanwhile, Gavryushkin et al. (2017) took the initiative in observing the occurrence of aragonite-II (P2$_1$/c), another model structurally relevant to aragonite at 35 GPa and its absence at 50 GPa. The phase domain of aragonite-II was reproduced by Bayarjargal et al. (2018) under non-hydrostatic pressures of 30–38 GPa. Yet never aragonite-II was a pure phase in both studies. By contrast, at pressures of 23–38 GPa, Li et al. (2018) observed only CaCO$_3$-VII generation at temperatures up to 2300 K. Zhang ZG. et al. (2018) provided thermodynamic arguments for the marginal metastability of aragonite-II at 30–40 GPa, and with temperature rising, aragonite-II became increasingly unfavorable. It is open to question for the presence and stability of aragonite-II, which is subjected to kinetic barriers of equilibrium phase transformations in experiments and uncertainties in calculations.

At 42 GPa and 1400 K, a further phase transition occurs from CaCO$_3$-VII to post-aragonite (Pmmm, Z = 2) with the Clapeyron slope of the phase boundary being -233 K/GPa (Bayarjargal et al., 2018; Li et al., 2018). Post-aragonite exhibits much higher wave velocity anisotropies than major silicates and other carbonates (Huang et al., 2017). This reconstructive transformation leads to measurable decreases in shear (~7.0%) and longitudinal (~4.7%) wave velocities around 1010 km in consideration of the pyrolytic mantle composition with 10% CaCO$_3$ (Li and Yuen, 2014; Niu, 2014; Bayarjargal et al., 2018). Post-aragonite was once believed as the best host structure for CaCO$_3$ in the bulk of the lower mantle and it transformed to a pyroxene-like structure C222$_2$ at the CMB (Oganov et al., 2008). This notion, however, should be deliberated. Another pyroxene-phase P$_2$/c-h as recommended above ~65 GPa, which was evolved from collapse of P$_2$/c-l without energy barriers (Pickard and Needs, 2015; Huang et al., 2017; Zhang ZG. et al., 2018). Both P$_2$/c-h and C22$_2$ are featured with [CO$_3$]$^{3-}$ species, but the former is made up of pyroxene chains stacked out-of-phase while the latter of parallel chains. In spite of pyroxene-phases, Lobanov et al. (2017) insisted that post-aragonite perseveres until ~105 GPa, afterwards it undergoes the lowest-enthalpy path to become P$_2$/c-l along with conversion of sp$^2$-to sp$^3$-hybridized carbon. But Smith et al. (2018) documented that CaCO$_3$-VII itself is capable of sp$^2$-sp$^3$ hybridization exchange and rather than any known CaCO$_3$-polymorphs, an entirely new phase came in at above ~50 GPa. There exist remarkable discrepancies as to the stability of CaCO$_3$-polymorphs under mid-mantle pressures as well as the phase boundaries, due likely to the unquenchable character of CaCO$_3$-V.

Melting of CaCO$_3$ was observed at ~1880 K at 3 GPa (Irving and Wylie, 1975) and monitored using Raman Spectroscopy above ~1900 K at 10 GPa (Litvin et al., 2014), with a smoother slope by conductivity measurement (Li et al., 2017). The melting curve derived from First-principles calculations shifted slightly to lower temperatures, where a knee point occurred at 13 (1) GPa and 1970 (40) K that was attributed to conversion between CaCO$_3$-V and aragonite. Aragonite was detected in the recovered products in the pressure-temperature region where CaCO$_3$-V is supposed to be stable (Zhang and Liu, 2015; Li et al., 2017) due likely to the unquenchable character of CaCO$_3$-V. CaCO$_3$ had a broad area of congruent melting up to ~3500 K, above which, it started to decompose. Decomposition of CaCO$_3$ resulted in generation of graphite that transformed to diamond if annealed to lower temperatures of 700–2700 K (Bayarjargal et al., 2010; Spivak et al., 2011). All these studies pointed out that melting and decomposition of CaCO$_3$ were realized at temperatures above most subduction geotherms. That is, almost the whole mantle falls into the solid regime of CaCO$_3$ polymorphs.

CaCO$_3$ with complex structural chemistry can be understood from the following two perspectives. 1) In calcite-members (CaCO$_3$, CdCO$_3$, MnCO$_3$, FeCO$_3$, ZnCO$_3$, MgCO$_3$, etc), CaCO$_3$ has the largest ionic radius of Ca$^{2+}$ that can bear various pressures by adjusting coordination numbers (Oganov et al., 2008). 2) In aragonite-family (CaCO$_3$, SrCO$_3$, PbCO$_3$, BaCO$_3$, etc), CaCO$_3$ contains the closest matching in distance between Ca$^{2+}$ and [CO$_3$]$^{2-}$ species that results to the most variation in C-O bond lengths and deviation from [CO$_3$]$^{2-}$-coplane (Antao and Hassan, 2009). The great variety of CaCO$_3$ polymorphs opens possibilities of stable CaCO$_3$ component in the deep mantle. According to the results
above, we plot Figure 1 for to obtain an overview of phase evolution of CaCO₃ to be aragonite ($\sim$25 GPa) $\rightarrow$ CaCO₃-VII (25–42 GPa) $\rightarrow$ post-aragonite (42–80 GPa) $\rightarrow$ P₂/c-h or C222₁ (80–137 GPa), which is dominantly affected by pressure.

**Magnesite MgCO₃ and Ferromagnesite**

MgCO₃ maintained its rhombohedral structure (R-3c; $Z = 6$) up to at least $\sim$80 GPa and $\sim$2300 K, thereafter it turned into MgCO₃-II (C2/m; $Z = 6$) until the CMB (Ishikawa et al., 2004; Maeda et al., 2017) (Figure 1). MgCO₃-II is featured with [CO₃]$^-$-rings that consists of three [CO₃]$^{4-}$-tetrahedra with asymmetric C-O bonds, and Mg$^{2+}$ are in eight- or ten-fold coordination (Oganov et al., 2008; Boulard et al., 2011). Another silicate-like polymorph C222₁ was once proposed as the most thermodynamically favorable for MgCO₃ above $\sim$102 GPa (Panero and Kabbes, 2008), but it was dismissed later. By calculations, Pickard and Needs (2015) suggested a new phase of P-1 to be the best candidate at pressures of 85–101 GPa in a limited temperature regime that is slightly lower than the coldest subduction geotherm. That is the reason why in most attempts we observed MgCO₃ directly transformed to MgCO₃-II (Boulard et al., 2011; Maeda et al., 2017; Martiro syan et al., 2018). The stability of C2/m was also confirmed in Fe$^{2+}$-rich MgCO₃ (Ferromagnesite-II) above 80 GPa between 1850 and 2500 K. Ferromagnesite-II has a higher density and was temperature quenchable. Especially it could accommodate a considerable amount of Fe$^{2+}$ (magnesite FeO₂ and/or a new phase of Fe₂(CO₃)₃) that resulted from self-redox reaction between Fe$^{2+}$ and [CO₃]$^{2-}$ (Boulard et al., 2011, 2012, 2015; Chen et al., 2018). Special attention has been paid on spin transition of Fe$^{2+}$ that drives a prior-transformation of ferromagnesite from R-3c to Pmm2 at $\sim$50 GPa and 1400 K (Liu et al., 2015), along with an abrupt volume collapse. The phase boundary of ferromagnesite from high spin to low spin state was tightly constrained around 60 GPa for temperatures above $\sim$1000 K (Liu et al., 2015). There might be a possible correlation between the Fe$^{2+}$-content and the spin transition pressure (Spivak et al., 2014). Or there is just a negligible compositional effect due to the long Fe$^{2+}$-Fe$^{2+}$ distances in the structure separated by [CO₃]$^{2-}$ species (Lin et al., 2012; Hsu and Huang, 2016; Weis et al., 2017). Some doubts remain regarding the presence of intermediate-spin state (Hsu and Huang, 2016; Weis et al., 2017).

MgCO₃ melt congruently at temperatures above the Mantle Geotherm (Litvin et al., 2014; Solopova et al., 2015). An increasing separation in melting points between CaCO₃ and MgCO₃ with pressure was expected to partially account for the majority of carbonatitic melt found on the Earth’s surface being highly calcic (Hammouda et al., 2015; Li et al., 2017). MgCO₃ decomposed to oxides and diamond above $\sim$3000 K (Spivak et al., 2013; Litvin et al., 2014; Solopova et al., 2015), and the energy cost for CaCO₃ is much higher (Santos et al., 2019). Melting curve of ferromagnesite deviated seriously from that of pure MgCO₃. Similar to FeCO₃, melting loop of ferromagnesite was asymmetrical and had a thermal minimum for Fe$^{2+}$-rich compositions (Tao et al., 2014; Kang et al., 2015). At mantle conditions, ferromagnesite was energetically advantageous over decomposition (Boulard et al., 2011; 2012), which generated magnetite-magnesioperovskite solid solution, graphite and CO₂ (Kang et al., 2016). So melting and decomposition of CaCO₃-MgCO₃ series bounded the phase fields of these carbonates, and that cast doubts on releasing free CO₂ in the deep Earth.

The elastic behaviors of MgCO₃ associate closely to its structural chemistry, which besides, helps to locate the presence of subducted carbonates in the mantle. At mantle pressures, the shear wave velocities in MgCO₃ were smaller than those in silicates. Marcondes et al. (2016) thus associated the low-velocity zones near the bottom of the lower mantle with the presence of MgCO₃. In the light of the density reduction, Litasov et al. (2008) announced that MgCO₃ had a limited effect on seismic profiles of principle assemblages in the mantle, but Yang et al. (2014) proposed to detect its presence by regionally seismic anisotropies because of its unusual high compressional (Vp) and shear (Vs) anisotropies. Existence of minor Fe$^{2+}$ as well as the spin transition opened a new window on the elastic properties of ferromagnesite (Fu et al., 2017; Stekiel et al., 2017). For high spin state, the sound velocities decreased with Fe$^{2+}$-content, whereas the anisotropy of the sound velocities increased. Upon pressure, anisotropies of Vp and Vs increased until spin transition occurred and decreased afterwards. So a drastic softening of sound velocities across spin transition may occur in slabs enriched with ferromagnesite in the mid-lower mantle. Increases of both Vp and Vs velocities were observed after spin transition. Enrichment of Fe$^{2+}$ led to larger differences in sound velocities and velocity anisotropies for low spin state as well. In this regard, Fe$^{2+}$-rich MgCO₃ regions may show higher seismic contrast compared with principle minerals in the deep mantle.

To sum up (Figure 1), along subduction geotherms MgCO₃ maintains initial R-3c structure up to $\sim$80 GPa and hereafter converts to C2/m, with $sp^2$- $sp^3$ transition further upholding the phase in the lowermost mantle. Ferromagnesite undergoes spin transition in the mid-mantle and changes to Pmm2-structure subsequently. The drop in the unit-cell and the accordingly uprush of the density expand the stability field of ferromagnesite to higher pressures, yet disproportionation of Fe$^{2+}$ could highly disintegrate the structure at lower-mantle conditions. Temperature exerts a greater impact on phase relations of ferromagnesite relative to MgCO₃. Neither melting nor decomposition occurs in MgCO₃ or ferromagnesite over the entire mantle.

**Dolomite (Ca,Mg)CO₃ and Ankerite**

Dolomite-(Ca,Mg)CO₃ is a common carbonate mineral in marine sediments, carbonated eclogite and ophiolite (Tao et al., 2020; Shatskii et al., 2021). At the topmost of the upper mantle, dolomite broke down into a mixture of magnesiota-MgCO₃ and aragonite-CaCO₃, the field of the coexistence opening towards higher temperature with pressure (Tao et al., 2014). A monoclinic phase (dolomite-II) set in driven by rotation of [CO₃]$^{2-}$ groups at 14–20 GPa under ambient temperature (Santillán et al., 2003; Merlini et al., 2019; Stekiel et al., 2019). This new phase was expected to enhance the thermodynamic
stability of (Ca,Mg)CO₃ up to 40 GPa over MgCO₃+CaCO₃. Above 41 GPa, a triclinic structure (dolomite-III, Z = 8) formed (Merlini et al., 2019).

Naturally Fe²⁺ substitutes Mg³⁺ in dolomite with various contents. Incorporation of Fe²⁺ strongly decreased the order degree of the structure (Tao et al., 2014) and helped maintain its stability to higher pressures and temperatures (Stekiel et al., 2019). A trigonal → orthorhombic transformation was firstly observed in (Ca,Mg)₁₋ₓFeₓ(CO₃)₂ at ~17 GPa and 300 K (Mao et al., 2011). This new orthorhombic phase persisted in upon laser-heating to ~1600–1700 K at 27–31 GPa. At 36–83 GPa, it further transformed to a monoclinic structure. The pressure-induced spin transition of Fe²⁺ was manifested by a drop in the unit-cell volume at ~47 GPa. This observation, however, was not reproduced in Fe-richer counterparts. A similar experimental study on a Fe²⁺- richer crystal CaMg₀.₆Fe₀.₄(CO₃)₂, suggested formation of two triclinic structures under pressures (Merlini et al., 2012). One was Fe-dolomite-II (P-I; Z = 4), a distortion of the dolomite structure associated by rotation of [CO₃]²⁻ groups, existing between 17 and 35 GPa. The coordination number of Ca²⁺ increased from six in Fe-dolomite to eight in Fe-dolomite-II. The other was Fe-dolomite-III that adopted the same P-1 symmetry but had eight formula units in the primitive cell. It exhibited structural relations to CaCO₃-III, as the [CO₃]²⁻ units are non-planar with carbon partly in four-fold coordination, some of which edge-shared with Ca²⁺ and Fe²⁺ polyhedra. Fe-dolomite-III had a broad stability domain to 43 GPa and the melting point (~2600 K). Its density was demonstrably comparable to that of the mixture MgCO₃+CaCO₃ if taking into account the FeCO₃ component. The second-order transformation from Fe-dolomite to Fe-dolomite-II was similar to that of dolomite → dolomite-II, and it had been strongly confirmed by Merlini et al. (2019). But above 36 GPa, Merlini et al. (2019) suggested a first-order transition to a rhombohedral symmetry (R3) (Fe-dolomite-IIIb). In the pressure range of 70–120 GPa and at 2500 K, Fe-dolomite-IV with an orthorhombic symmetry (Pnma) was formed. It was characterized with corner-sharing [CO₃]¹⁻ units in three-fold rings, similar to MgCO₃-C₂/m (Oganov et al., 2008). Different Fe²⁺ contents could be responsible for the disagreement. Previously, Solomatova and Asimow (2016) predicted a monoclinic phase C2/c as the stable structure for more Fe²⁺-enriched samples Ca(Mg₀.₅Fe₀.₅)(CO₃)₂ and CaFe(CO₃)₂ up to 60 GPa. The C2/c phase cannot be achieved experimentally due to the large energy barrier and the correspondingly large volume collapse, resulting in conversion from dolomite to metastable structures.

Existing data has revealed the high-pressure behaviors of dolomite, as is summarized in Figure 1, but it is limited to draw a full understanding of the structural evolution of Fe-dolomite at pressures and temperatures. Issues deserve evaluation with respect to the effect of Fe²⁺-content and its spin transition on the thermal and elastic properties and the stability fields (Tao et al., 2014; Merlini et al., 2016), and possibility of energetically competitive structures. Besides, there remains a large area uncovered for pressures above ~60 GPa. We now reach agreements on 1) a minor addition of Fe²⁺ stabilizes the rhombohedral structure of dolomite against decomposition and transformation under upper mantle conditions; 2) there stands a good chance for fine changes occurring at ~17 and ~35 GPa, and a decrease trend of crystal symmetry is expected with pressure.

**CARBONATES REDUCTION BY REDUCED MANTLE**

Given most subduction geotherms, CaCO₃, MgCO₃, (Ca,Mg) CO₃ and their ferrous series maintain solid polymorphs over a wide range of depths down to the CMB. But their presence in the mantle depends highly as well on oxygen fugacity, which is controlled by oxidation state of iron in minerals and melts (e.g. sulﬁdes and silicates) (Bataleva et al., 2017). A large part of the mantle below 250 km is thought to be Fe⁰-sufﬁcient and favorable for reductions of carbonates or carbonatitic melts, which is a potential barrier to carbonates further-subduction and a promising mechanism for sublithospheric diamond formation (Rohrbach and Schmidt, 2011; Stagno et al., 2011). Several carbon species uncovered from the lower-mantle diamonds, vary from oxidized phases (e.g. carbonates) to the reduced (e.g. methane, graphite and iron carbide) (Brenker et al., 2007; Kaminsky and Wirth, 2011; Kaminsky, 2012; Kaminsky et al., 2013, 2016; Smith et al., 2016). That strongly indicates that the redox reactions between subducted carbonates (oxidized) and metallic mantle (reduced) is responsible for sublithospheric diamond genesis (Figure 2).

Several studies have been conducted in petrologic context of subducted carbonate assemblages in contact with metallic mantle. One representative study (Palyanov et al., 2013) at 6.5–7.5 GPa and 1273–1873 K documented that (Mg₀.₉Ca₀.₁)CO₃·Fe⁰ interaction generated carbonatitic melts, magnesiowustite.
(Mg,Fe)O, cohenite Fe3C and metastable graphite. Increasing temperature led to a higher degree of partial melting but a decrease in Ca2+-component in carbonate melt. Diamonds nucleation from carbonatitic melts (≥1673 K) was expected with heavier carbon isotope relative to the initial carbonate and high concentrations of nitrogen (1000–1500 ppm). In contrast, at iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single subtitutional aggregration. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]

Thermodynamic calculations showed that over the entire mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. Thus, presence of residual carbides in the mantle pressure range, C+(Mg,Fe)O is more stable than MgCO3+Fe-C. At iron front where carbide (Fe-C) melt formed, diamond crystallized with lower δ13C value and only 100–200 ppm of nitrogen mostly in the form of single substitutional aggregation. These chemical characters are analogous to that of natural sublithospheric diamonds. Besides, the accompanying products, iron carbide, graphite and (Mg,Fe)O are characteristic inclusions in natural stones. For simplicity, at the topmost of the upper mantle, MgCO3 reduction by Fe0 is described as:

\[
\text{MgCO}_3 \text{(magnesite)} + \text{Fe}^0 \text{(metal)} \rightarrow (\text{Mg,Fe})\text{O} + \text{Fe}_3\text{C} + \text{C} \text{(diamond)} \quad (R3 - 1)
\]
presence of sulfur significantly lower the solubility of carbon and trigger carbon exsolution from the carbide (Zhang Z. et al., 2018). The discovery of a carbide+ sulfide+metal assemblage in sublithospheric diamonds shed lights on mechanism of diamond formation from Fe-C-S melt (Smith et al., 2016). Here we evaluate the phase relations of Fe-C-S systems in the mantle focusing on exsolution of diamond. Chemical reactions involving:

\[
2\text{Fe}_3\text{C} + 3\text{S}_2 \rightarrow 6\text{FeS} + 2\text{C}^0 \quad (R3 - 4)
\]

\[
\text{Fe}_3\text{C} + 3\text{FeS}_2 \rightarrow 6\text{FeS} + \text{C}^0 \quad (R3 - 5)
\]

Most studies on Fe-C-S systems were performed at pressures ≤8 GPa (Bataleva et al., 2017). These studies reported efficient capabilities of Fe\(_3\)C to generate graphite (1473–1873 K), diamond (1573–1873 K) and pyrrhotite (FeS) in the presence of sulfur-bearing metasomatic agents; further temperature increase led to higher efficiency of diamond crystallization. The established Fe-C-S model was applicable to Fe-Ni-C-S system, where Fe-Ni alloy showed a greater accommodation of dissolved carbon with temperature up to 2600 K but at lower pressures (≤20 GPa) (Narygina et al., 2011).

Redox reactions between subducted carbonates and Fe\(^{2+}\)-peridotites/eclogites can be taken as a simplified model of slab-mantle interactions processing in the deep zones. It was mainly controlled by low concentrations of carbonates and metallic iron at the CMB as well as low diffusion of chemical components (e.g. O\(^2-\), Fe\(^{2+}\)) among silicates and carbonates. This is a limited process and set constraints for carbon speciation and protections for carbonates from reduction (Figure 2). Likely that a significant amount of (Ca,Mg,Fe)-carbonates may survive from Fe\(^0\)-saturation boundary (Martirosyan et al., 2016) at the upper mantle and the transition zone. But at the top of the lower mantle due to stagnation of subducting slabs, carbonates accumulate and are heated up. Carbonates-Fe\(^0\) interaction would be more probable for diamond production. The rate of graphite-to-diamond transformation was higher in a FeNi system. Higher pressure appeared to favor growth of cubo-octahedral diamonds, whereas octahedral diamonds grow at lower pressure conditions (≤10 GPa in MgCO\(_3\) and ≤15 GPa in FeNi). The run products lacked the slip planes and lamination lines commonly associated with superdeep diamonds, and we may suggest that these deformation features are due to transport instead of growth conditions (Tomlinson et al., 2011). Accompanying with carbon freezing in the Earth, carbon isotope fractionation occurs. The carbon isotope composition in the mantle displays a well-defined peak around δ\(^{13}\)C = −5‰ in an extensive range to the lowest of ~−40‰. Subduction of organic carbon was advocated for the mantle regions with \(^{13}\)C depletion. Relatively, reduction of carbonates extracted \(^{12}\)C to a greater degree and it was more likely to contribute to the broad distribution of carbon in the mantle (Horita and Polyakov, 2015).

**CARBONATES DECARBONIZATION BY SILICATES**

In consideration of major minerals in basaltic plates and the mantle, carbonate stability should also be inspected by carbonates-silicates interactions under mantle conditions. This reaction sets fundamental control not merely on subduction limit of carbonate or CO\(_2\) release in the mantle, but on physicochemical properties of the mantle such as initiation of melting by lowering the mantle solidus, generation of alkaline magma in oceanic islands and carbonate metasomatism in cratonic mantle. Two typical chemical reactions are appraised here:

\[
\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2 \quad (R4 - 1)
\]

\[
\text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_2 \quad (R4 - 2)
\]

SiO\(_2\) is one of the abundant components in MORB. Along subduction geotherms, SiO\(_2\) changes to its high-pressure polymorphs as coesite, stishovite, CaCl\(_2\)-type and seifertite successively (Murakami et al., 2003; Grocholski et al., 2013). According to experimental and theoretical results, even for the temperature profiles in cold subduction slabs, CaCO\(_3\)-VII reacted with SiO\(_2\)-stishovite above 23 GPa and 1500 K to produce CaSiO\(_3\)-perovskite and possibly free CO\(_2\). High temperature greatly increased the tendency of partitioning Ca\(^{3+}\) from carbonates CaCO\(_3\) to silicates CaSiO\(_3\) (Zhang ZG. et al., 2018; Li et al., 2018), accounting for the observation of abundance of CaSiO\(_3\)-perovskite in sublithospheric diamonds compared to typical mantle mineralogy. Decarbonation of MgCO\(_3\) by SiO\(_2\)-coesite was confirmed beginning at 6–7 GPa and above 1600 K, and the decarbonatation temperature increased sharply with pressure (Palyanov et al., 2002; Kakizawa et al., 2015). An addition of alkali-component to MgCO\(_3\)-SiO\(_2\) system negligibly changed the reaction path, and the output diamond was close to the initial MgCO\(_3\) in terms of carbon isotopic composition (Palyanov et al., 2002). At 28–62 GPa and 1490–2000 K (770–1500 km), MgSiO\(_3\)-perovskite and solid CO\(_2\) (V or VI) formed from interactions between MgCO\(_3\) and SiO\(_2\)-stishovite (Takafuji et al., 2006). With this regard, both CaCO\(_3\) and MgCO\(_3\) was unstable and would release CO\(_2\) to the lower mantle for SiO\(_2\)-rich subducted basalts.

Calculations carried out at higher pressures of 50–200 GPa under static conditions (0 K) showed that CaCO\(_3\) (post-argonite) and MgCO\(_3\) (R-3c) maintained stable but react with SiO\(_2\) at closely the CMB (Oganov et al., 2008; Pickard and Needs, 2015; Santos et al., 2019). This was contradictory to the experimental observations (Maeda et al., 2017) where the reaction of MgCO\(_3\)-SiO\(_2\) occurred at mantle depth beginning from ~1000 km and that held true for all the mantle regions below. Different results could be due to different conditions in these studies. MgCO\(_3\)-R-3c reacted with SiO\(_2\)-stishovite for formation of MgSiO\(_3\)-bridgmanite and CO\(_2\)-VI (six-fold coordinated of carbon) at depths around 1700 km (83 GPa; 1780 K). Internal production of CO\(_2\) from MgCO\(_3\)-SiO\(_2\) system was thus, possible in the middle of the lower mantle (1700–1900 km) and at greater depths CO\(_2\)-VI would decompose.
to diamond. If survived, MgCO3-R-3c changed to C2/m and reacted with SiO2-seifertite to generate MgSiO3-post-perovskite and diamond at the lowermost mantle.

Figure 3 summarizes the phase relations of carbonate-silicate system at mantle conditions. The solidus lines representing CaCO3-SiO2 reaction is measured according to Li et al. (2018) and Zhang and Liu (2015). The dark-blue lines indicate phase boundaries for MgCO3-SiO2 system (solid: Maeda et al., 2017; dotted: Takahashi et al., 2009). Partial melting of MgCO3-SiO2 series produces a simple eutectic system (Kakizawa et al., 2015). Curve [2] represents solidus curve of carbonated peridotite (Litasov and Ohtani, 2009). Solidus curves of carbonated eclogites are plotted according to Litasov and Ohtani (2010) (Curve [3]) and Kiseeva et al. (2013) (Curve [4], [5]). The melting curve of carbonated MORB (Curve [6]) according to Thomson et al. (2016), Phase diagram for the stability of MgCO3+CaSiO3 versus CaCO3+MgSiO3 is referred to Santos et al. (2019). Phase boundaries of CaCO3- and MgCO3-polymorphs follow the references in Section 2.1. The phase diagrams of SiO2 (Murakami et al., 2003; Gurochko et al., 2015), CO2 (Litasov et al., 2011) and MgSiO3 (Komabayashi et al., 2008) are included with gray solid lines. Abbreviations: Gr., graphite; Dm., diamond; St., stishovite; CS., CaCO3-type SiO2; Se., seifertite; Brd., MgSiO3 bridmanite; Ppv., MgSiO3 post-perovskite.

CONCLUSIONS AND PROSPECTS

Carbonates play a key role in the recycling of carbon from the Earth’s crust to the interior via subduction processes, producing one of the carbon budgets in the entire Earth’s system. In light of the striking discoveries above, we now have a much clearer picture of behaviors of carbonates in the deep Earth.

First, several new polymorphs have been identified as stable of CaCO3, MgCO3 and (Ca,Mg)CO3 and their ferrous series (Figure 1), which improve our expectations for their possibilities in the mantle. Existence of carbonates and the occurrence of the phase transitions may correlate with the discontinuities in the Earth’s seismic profile. Carbonates of CaCO3-MgCO3-FeCO3 series remain in solid phases along with pressure in subducted MORB (Figure 3). However, higher pressure on subducted SiO2-seifertite to generate MgSiO3-post-perovskite and diamond at the lowermost mantle.

FIGURE 3 | Schematic reaction line of carbonate-silicate at the Earth’s mantle conditions. The black lines representing CaCO3-SiO2 reaction is measured according to Li et al. (2018) and Zhang and Liu (2015). The dark-blue lines indicate phase boundaries for MgCO3-SiO2 system (solid: Maeda et al., 2017; dotted: Takahashi et al., 2009). Partial melting of MgCO3-SiO2 series produces a simple eutectic system (Kakizawa et al., 2015). Curve [2] represents solidus curve of carbonated peridotite (Litasov and Ohtani, 2009). Solidus curves of carbonated eclogites are plotted according to Litasov and Ohtani (2010) (Curve [3]) and Kiseeva et al. (2013) (Curve [4], [5]). The melting curve of carbonated MORB (Curve [6]) according to Thomson et al. (2016), Phase diagram for the stability of MgCO3+CaSiO3 versus CaCO3+MgSiO3 is referred to Santos et al. (2019). Phase boundaries of CaCO3- and MgCO3-polymorphs follow the references in Section 2.1. The phase diagrams of SiO2 (Murakami et al., 2003; Gurochko et al., 2015), CO2 (Litasov et al., 2011) and MgSiO3 (Komabayashi et al., 2008) are included with gray solid lines. Abbreviations: Gr., graphite; Dm., diamond; St., stishovite; CS., CaCO3-type SiO2; Se., seifertite; Brd., MgSiO3 bridmanite; Ppv., MgSiO3 post-perovskite.
most modern subduction geotherms. So liberation of carbonatitic melts or CO2 owing to carbonate decomposition seems unlikely, with such possibility restricted merely for conditions in hot zones. However, decarbonization of CaCO3 and MgCO3 takes place in SiO2-rich subducted basalts under the lower-mantle conditions (Figure 3). CO2 decomposing to diamond is energetically favored in the region from the middle of the lower mantle to the CMB. Meanwhile, carbonates in slabs tend to be reduced to diamond at metal-saturation boundary at the topmost of the lower mantle (Figure 2). Diamonds produced from slab-mantle interactions are similar to natural stones in terms of chemical composition and inclusion characteristics. So far the existing data have covered almost the entire mantle conditions for decarbonization and reduction of carbonates and documented diamond nucleation. In this regard, carbonates reduction and decarbonization are effective mechanisms of carbon sequestration at the top-mid region of the lower mantle.

Researchers on carbon cycle throughout the Earth’s system have long represented an interesting frontier. One fundamental goal of carbon cycle research is to know the balance between income and outcome global carbon fluxes as well as the carbon fluxes change in space and time. But many details of the processes remain unclear for the lack of intensive monitoring. Three issues may be worth of particular considerations in the future work:

1. **Besides carbonates, CO2 and iron carbides mentioned above, there could exist other chemical forms of carbon in the mantle that has been uncovered, for example, a new carbon phase of Fe4(CO4)3 derived from decomposition of Fe-bearing carbonates (Bouard et al., 2015). So a critical and pressing task is to search for these undiscovered carbon. Given the scarcity of natural samples, we may gain insights by thermodynamic calculations and experiments. These efforts will shed new lights on our view on deep carbon reservoirs, for example, how they form and under what conditions are they stable for long.**

2. **Existing experiments have confirmed the possibility of redox reactions between subducted carbonates and metallic mantle to produce sublithospheric diamonds and other reduced carbon species. However, it is not yet clear whether carbonates-Fe0 processes generate significant amounts of diamonds. To what extent do carbonates turn into diamonds? And what role has the remaining carbonatitic melts played in deep carbon cycle and besides, in mantle metasomatism? These questions are basically related to the kinetics of carbonates-Fe0 interactions that set constraints on sequestration efficiency directly of deep carbon. Besides, carbon isotope fractionation during slab-mantle interactions is also an essential part in the study of deep carbon cycle. However, previous insights have been gained from theoretical calculations (Horita and Polyakov, 2015), as natural samples are too scarce. Experiments conducted at high-pressure and high-temperature conditions may be a favor to synthesize large samples.**

**AUTHOR CONTRIBUTIONS**

JG wrote the original draft. XW, XY, and WS were responsible for the review and modification.

**ACKNOWLEDGMENTS**

The authors are thankful to the reviewers.

**REFERENCES**

Antao, S. M., and Hassan, I. (2009). The Orthorhombic Structure of CaCO3, SrCO3, PbCO3 and BaCO3: Linear Structural Trends. Can. Mineral. 47 (5), 1245–1255. doi:10.3749/camin.47.5.1245

Bataleva, Y. V., Palyanov, Y. N., Borzov, Y. M., Bayukov, O. A., and Zdrokov, E. V. (2017). Iron Carbide as a Source of Carbon for Graphite and Diamond Formation Under Lithospheric Mantle P-T Parameters. Lithos 286-287, 151–161. doi:10.1016/j.lithos.2017.06.010

Bayarjargal, L., Fruhner, C.-J., Schrodt, N., and Winkler, B. (2018). CaCO3 Phase Diagram Studied with Raman Spectroscopy at Pressures up to 50 GPa and High Temperatures and DFT Modeling. Phys. Earth Planet. Interiors 281, 31–45. doi:10.1016/j.pepi.2018.05.002

Bayarjargal, L., Shumilova, T. G., Friedrich, A., and Winkler, B. (2010). Diamond Formation from CaCO3 at High Pressure and Temperature. ejm 22, 29–34. doi:10.1127/0935-1221/2010/0021-1986

Bouard, E., Menguy, N., Auzende, A. L., Benzerara, K., Bureau, H., Antonangeli, D., et al. (2012). Experimental Investigation of the Stability of Fe-Rich Carbonates in the Lower Mantle. J. Geophys. Res. 117, B02208. doi:10.1029/2011JB008733

Bouard, E., Gloter, A., Corgne, A., Antonangeli, D., Auzende, A.-L., Perrillat, J.-P., et al. (2011). New Host for Carbon in the Deep Earth. Proc. Natl. Acad. Sci. 108 (13), 5184–5187. doi:10.1073/pnas.1016934108

Bouard, E., Pan, D., Galli, G., Liu, Z., and Mao, W. L. (2015). Tetrahedrally Coordinated Carbonates in Earth’s Lower Mantle. Nat. Commun. 6, 6311. doi:10.1038/ncomms7311

Brenker, F. E., Vollmer, C., Vincze, L., Vekemans, B., Szymanski, A., Janssens, K., et al. (2007). Carbonates from the Lower Part of Transition Zone or Even the Lower Mantle. Earth Planet. Sci. Lett. 260, 1–9. doi:10.1016/j.epsl.2007.02.038

Bundy, F. P., Bassett, W. A., Weathers, M. S., Hemley, R. J., Mao, H. U., and Goncharov, A. F. (1996). The Pressure-Temperature Phase and Transformation Diagram for Carbon; Updated Through 1994. Carbon 34, 141–153. doi:10.1016/0008-6223(96)00170-4
Takafuji, N., Fujino, K., Nagai, T., Seto, Y., and Hamane, D. (2006). Decarbonation Reaction of Magnesite in Subducting Slabs at the Lower Mantle. Phys. Chem. Minerals 33, 651–654. doi:10.1007/s00269-006-0119-5

Tao, R., Zhang, L., Fei, Y., and Liu, Q. (2014). The Effect of Fe on the Stability of Dolomite at High Pressure: Experimental Study and Petrological Observation in Eclogite from Southwestern Tianshan, China. Geochimica Et Cosmochimica Acta 143, 253–267. doi:10.1016/j.gca.2014.02.031

Tao, R., Zhang, L., and Zhang, L. (2020). Redox Evolution of Western Tianshan Subduction Zone and its Effect on Deep Carbon Cycle. Geosci. Front. 11 (3), 915–924. doi:10.1016/gsf.2019.09.007

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, 76–79. doi:10.1038/nature16174

Tomlinson, E. L., Howell, D., Jones, A. P., and Frost, D. J. (2011). Characteristics of HPHT Diamond Grown at Sub-lithosphere Conditions (10-20GPa). Diamond Relat. Mater. 20, 11–17. doi:10.1016/j.diamond.2010.10.002

Yang, J., Mao, Z., Liu, X., Yuan, Z., and Prakapenka, V. B. (2014). Single-crystal Elasticity of the Deep Mantle Magnesite at High Pressure and Temperature. Earth Planet. Sci. Lett. 392, 292–299. doi:10.1016/j.epsl.2014.01.027

Yang, Z., and He, X. (2015). Oceanic Crust in the Mid-mantle Beneath West-central Pacific Subduction Zones: Evidence from Sto-Ponverted Waveforms. Geophys. J. Int. 203 (1), 541–547. doi:10.1093/gji/ggv314

Zhang, Z., and Liu, Z. (2015). High Pressure Equation of State for Molten CaCO3 from First Principles Simulations. Chin. J. Geochem. 34 (1), 13–20. doi:10.1007/s11631-015-0036-8

Zhu, F., Li, J., Liu, J. C., Lai, X. J., Chen, B., and Meng, Y. (2018). Kinetic Control on the Depth Distribution of Superdeep Diamonds. Geophys. Res. Lett. 46, 1984–1992. doi:10.1029/2018GL080740

Zhu, Y.-F., Massonne, H.-J., and Men-Fan Zhu, M. F. (2009). Petrology of Low-Temperature, Ultrahigh-Pressure Marbles and Interlayered Coesite Eclogites Near Sanqinjiao, Sulu Terrane, Eastern China. Mineral. Mag. 73 (2), 307–332. doi:10.1180/minmag.2009.073.2.307

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher’s Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Gao, Wu, Yuan and Su. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.