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## The deep carbon cycle and melting in Earth's interior

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## ABSTRACT

Carbon geochemistry of mantle-derived samples suggests that the fluxes and reservoir sizes associated with deep cycle are in the order of  $10^{12-13}$  g C/yr and  $10^{22-23}$  g C, respectively. This deep cycle is responsible for the billion year-scale evolution of the terrestrial carbon reservoirs. The petrology of deep storage modulates the long-term evolution and distribution of terrestrial carbon. Unlike water, which in most of the Earth's mantle is held in nominally anhydrous silicates, carbon is stored in accessory phases. The accessory phase of interest, with increasing depth, typically changes from fluids/melts → calcite/dolomite → magnesite → diamond/Fe-rich alloy/Fe-metal carbide, assuming that the mass balance and oxidation state are buffered solely by silicates. If, however, carbon is sufficiently abundant, it may reside as carbonate even in the deep mantle. If Earth's deep mantle is Fe-metal saturated, carbon storage in metal alloy and as metal carbide cannot be avoided for depleted and enriched domains, respectively. Carbon ingassing to the interior is aided by modern subduction of the carbonated oceanic lithosphere, whereas outgassing from the mantle is controlled by decompression melting of carbonated mantle. Carbonated melting at >300 km depth or redox melting of diamond-bearing or metal-bearing mantle at somewhat shallower depth generates carbonatitic and carbonated silicate melts and are the chief agents for liberating carbon from the solid Earth to the exosphere. Petrology allows net ingassing of carbon into the mantle in the modern Earth, but in the hotter subduction zones that prevailed during the Hadean, Archean, and Paleoproterozoic, carbonate likely was released at shallow depths and may have returned to the exosphere. Inefficient ingassing, along with efficient outgassing, may have kept the ancient mantle carbon-poor. The influence of carbon on deep Earth dynamics is through inducing melting and mobilization of structurally bound mineral water. Extraction of carbonated melt on one hand can dehydrate the mantle and enhance viscosity; the presence of trace carbonated melt on other may generate seismic low-velocity zones and amplify attenuation.

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### 1. Introduction

The CO<sub>2</sub> budget of Earth's atmosphere is critical for maintaining a habitable climate through geologic time. Fluxes of carbon between the mantle and the exosphere modulate Earth's atmosphere and climate on short to long time scales (Hayes and Waldbauer, 2006; Huybers and Langmuir, 2009). On time scales of millions of years, volcanic emissions of CO<sub>2</sub> are thought to have provided the negative feedback that allowed Earth to recover from the NeoProterozoic "snowball" conditions (Caldeira and Kasting, 1992; Kirschvink, 1992; Hoffman et al., 1998) and may also have influenced climate in more recent times, such as the Cretaceous warm period (Kerrick, 2001) and Paleocene–Eocene thermal maximum (Storey et al., 2007). At time scales of billions of years, subduction has the potential to transport the entire surface carbon budget to the interior (Sleep and Zahnle, 2001; Dasgupta et al., 2004), and so the persistence of the near-surface

carbon reservoir depends on return fluxes to the surface owing to volcanism.

Although it is clear that the surface carbon inventory has a key influence in building and sustaining a habitable planet (e.g., Zahnle et al., 2007), the specific petrologic and dynamical processes in the Earth's interior that maintain the surface carbon inventory have received concerted attention only in the last few years. For example, although it is commonly assumed that carbon is degassed from the Earth's mantle during volcanism, the extent and the efficiency of CO<sub>2</sub> degassing remained poorly constrained as they depend on both the depth and the extent of magma generation beneath volcanic centers. If melting initiates at shallow depths in the mantle, the efficiency of release of deep carbon will be poor, whereas if melting initiates deep (McKenzie, 1985), carbon outgassing can be comparatively efficient. In addition to the onset and extent of melting, carbon outgassing must also be strongly influenced by the carbon carrying capacity of magmas. This is a function of pressure, temperature, and melt composition. If the solubility of carbon (e.g., as CO<sub>2</sub> or CO<sub>3</sub><sup>2-</sup>) is low in certain magma type, associated eruptions may not account for significant fluxes of carbon from the deep Earth. Whereas, eruption of magmas with high CO<sub>2</sub> solubility could be extremely efficient

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in releasing deep carbon to the exosphere. Moreover, the oxidation state of the mantle may also influence the conditions of carbon-present melting. If conditions are reduced, carbon may partly remain in the residue as graphite or diamond, and CO<sub>2</sub> degassing could be less efficient (Holloway, 1998). On the other hand, if carbon exists in the form of carbonates, then the mantle could be readily fusible, leading to efficient extraction of carbon from the deep interior (Dasgupta and Hirschmann, 2006).

Ingassing of carbon also depends strongly on the petrology of subduction. For example, if slab top conditions are sufficiently hot and/or if carbon in the slab is hosted in easily fusible carbonate minerals such as siderite or ankerite (Laverne, 1993), carbon may be released in the mantle wedge. Alternatively, for cooler subduction environments and/or if carbon is stored as a refractory phase (e.g., calcite, diamond or graphite), carbon may survive shallow release and may enter deep mantle.

There is increasing recognition that on one hand carbon plays a critical role in processes in the Earth's interior and on the other the petrologic processes in the deep Earth modulate the carbon cycle. Perhaps the most important process in the Earth's interior that can be affected by carbon is partial melting of mantle lithologies. Recent experimental works suggest that carbon may be responsible for causing the deepest melting in the Earth's mantle and consequent generation of carbonatitic melt may contribute significantly to the ongoing chemical differentiation of the mantle (Dasgupta and Hirschmann, 2006; Dasgupta et al., 2009b). It has also been argued that the presence of carbonatite or carbonated silicate melts may be associated with the seismic low velocity in the Earth's upper mantle (Eggler, 1976; Presnall et al., 2002). Carbonated silicate melting (Wendlandt and Mysen, 1980; Hirose, 1997; Dasgupta et al., 2007a), may also be a catalyst to formation of oceanic lithosphere (Dasgupta et al., 2007a). Carbon may also induce incipient melting at depths approaching the mantle transition zone or deeper. At transition zone or lower mantle depths, carbonate-rich partial melts may be generated by partial melting of carbonated subducted oceanic crust and ocean-floor sediments (Dasgupta et al., 2004; Thomsen and Schmidt, 2008a) or if the conditions are oxidized enough, perhaps through partial melting of peridotite (Ghosh et al., 2009; Litasov and Ohtani, 2009b). Melting atop the transition zone or deeper may also occur by the combined effects of carbon dioxide and water (Karato et al., 2006) or carbon dioxide and halogens (Litasov and Ohtani, 2009a).

The impact of carbon on deep mantle melting could be more complex, as carbon may be stored in the solid mantle in various forms, depending on the oxygen fugacity and relative oxidizing power of carbon and iron species (Luth, 1999). Hence, at great depths, carbon may be stored as mineral carbonate (Dasgupta and Hirschmann, 2006; Brenker et al., 2007), as diamond (Walter et al., 2008), as metal carbide (Frost and McCammon, 2008; Dasgupta et al., 2009a), or dissolved in metals (Frost et al., 2004; Frost and McCammon, 2008; Lord et al., 2009). Thus depending on the form of carbon storage in the solid mantle, the petrology of initial carbonated melt generation in the upwelling mantle may take place either by direct melting of carbonated mantle lithologies or by redox melting in the presence of graphite, or diamond, or metal/metal carbide. Deep carbonate melts thus may be associated with diamond formation (Pal'yanov et al., 1999; Pal'yanov et al., 2002; Walter et al., 2008). We also note that while the stable form of carbon in the mantle depends on oxygen fugacity, oxygen fugacity itself can also be set by the redox reactions between oxidized and reduced forms of carbon (Luth, 1999) and in turn influence the speciation of iron between ferric, ferrous, and metallic forms.

There have been a number of reviews of Earth's carbon cycle that recognize the importance of mantle fluxes (e.g., Kerrick, 2001; Sleep and Zahnle, 2001; Hayes and Waldbauer, 2006). However, these reviews focused primarily on the surficial aspects of Earth's carbon cycle and did not consider in detail the petrology of carbon storage

and the influence of specific solid Earth processes in carbon fluxes. Here we discuss Earth's carbon cycle with an emphasis on Earth's interior and specifically with a focus on mantle melting and chemical differentiation. Further, we also discuss how the Earth's deep carbon cycle may have evolved through time and how some of the present-day deep Earth fluxes may have been quite different in the past.

## 2. Carbon budget in the Earth's interior – constraints from basalt geochemistry

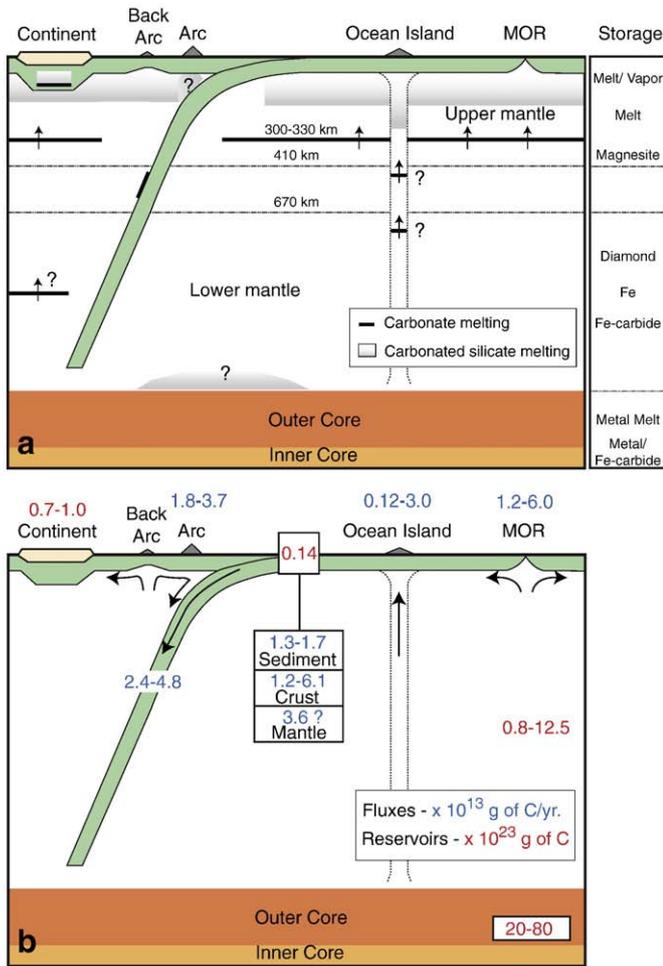
An obvious parameter that is critical to the deep Earth carbon cycle is the abundance of carbon in the interior. The most direct estimates of the modern mantle carbon come from concentrations in erupted basalts and associated fluids. Estimates come from measurements of dissolved CO<sub>2</sub> in basaltic glasses and melt inclusions (e.g., Dixon, 1997; Bureau et al., 1998), from measurements of mantle-derived fluids, including trapped gas bubbles in basalts (e.g., Aubaud et al., 2005), hydrothermal vent fluids, and by combining measurements of CO<sub>2</sub>/incompatible element ratios [CO<sub>2</sub>/He: (Trull et al., 1993; Zhang and Zindler, 1993; Marty and Tolstikhin, 1998; Shaw et al., 2003); CO<sub>2</sub>/Nb: (Saal et al., 2002; Cartigny et al., 2008; Shaw et al., 2010); CO<sub>2</sub>/Ar: (Tingle, 1998; Cartigny et al., 2001); CO<sub>2</sub>/Cl: (Saal et al., 2002)]. But owing to very efficient degassing of CO<sub>2</sub> during volcanic eruption and magma ascent, many estimates, particularly the ones based on dissolved CO<sub>2</sub> in basalts and even the melt inclusions likely provide a lower bound of the original CO<sub>2</sub> concentration in the primary magma (Wallace, 2005).

Extrapolations of magmatic CO<sub>2</sub> to mantle concentrations are performed by taking into account the effect of partial melting, crystal fractionation, and degassing or by assuming that the partitioning of CO<sub>2</sub> during mantle melting is similar to He (Marty and Jambon, 1987; Trull et al., 1993) or Nb (Saal et al., 2002) and these yield concentration for the MORB-source mantle between 20 and 300 ppm C. Though estimates of depleted MORB mantle source are as low as 20–30 ppm (Saal et al., 2002; Hirschmann and Dasgupta, 2009), those derived from oceanic island basalts (Dixon et al., 1997; Bureau et al., 1998; Aubaud et al., 2005, 2006) or enriched-MORBs (Pineau et al., 2004) extend to values as high as 300 to 1300 ppm C. Recent estimates based on H/C ratio of the mantle and independent estimates of the H content in the MORB-source mantle predict a depleted mantle C content as low as 16 ± 9 ppm (59 ± 33 ppm CO<sub>2</sub>) (Hirschmann and Dasgupta, 2009). An analogous exercise for the sources of oceanic island basalts yields 33–500 ppm C (120–1830 ppm CO<sub>2</sub>) (Hirschmann and Dasgupta, 2009).

If the MORB-source mantle carbon concentration (10–30 ppm C) applies to the entire mantle, the total carbon budget of the mantle amounts to (0.8–1.2) × 10<sup>23</sup> g of C (Fig. 1). Alternatively if the whole mantle is a mixture of depleted (40% by mass) and enriched mantle source (50–500 ppm C), then the whole mantle carbon budget amounts to (2.7–12.5) × 10<sup>23</sup> g of C. Given significant variations in the estimated carbon content of basalt source regions and the lack of constraints on the proportion of enriched and depleted source in the mantle, estimates of the total budget of mantle carbon vary by an order of magnitude. This owes in part to lack of constraints on the hosts of carbon and on the redox state of the mantle. We also note that this inventory may have varied over the geologic history of the planet. The following sections will touch on each of these topics.

## 3. Carbon-bearing phases in the mantle

Carbon in the mantle is stored chiefly in accessory phases (e.g., Luth, 1999). This is owing to extremely low solubility of carbon in mantle silicates (Keppler et al., 2003; Shcheka et al., 2006; Panero and Kabbes, 2008), which makes the mantle, even with tens to hundreds of ppm by weight of carbon, saturated in a carbon-rich phase. The stable crystalline carbon-bearing phase, under the shallow oceanic upper mantle, is carbonate (e.g., Luth, 1999), which can be aragonite/calcite, or dolomite–ankerite<sub>ss</sub>, or magnesite<sub>ss</sub> (Fig. 1) depending on the pressure,

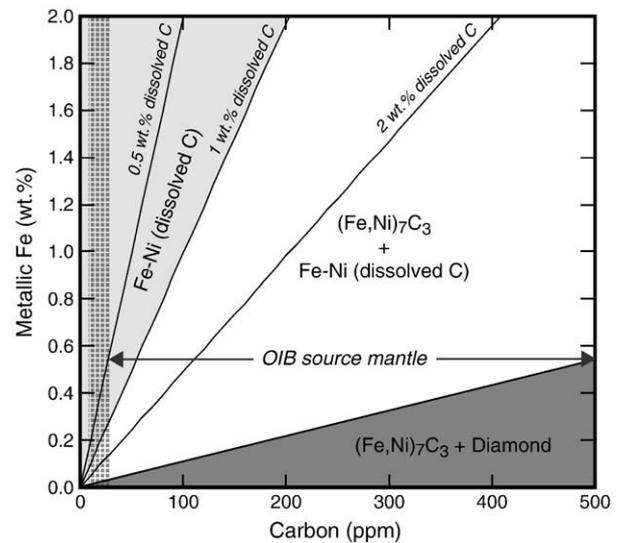


**Fig. 1.** (a) Plausible loci of carbonated melting in the Earth's mantle and (b) estimated flux (numbers in blue) and budget (numbers in red) associated with deep Earth carbon cycles. Also shown as a separate panel in (a), are the dominant carbon carrying phases in the Earth's mantle with increasing depth. We note that the accessory carbon-bearing phase assemblage at any given depth may vary, especially depending on the carbon concentration and oxygen fugacity. Thus a part of mantle carbon at shallow depths may be in metal alloy or metal melt and deep carbon could be in carbonate minerals or carbonated melts. Although the loci of carbonatite generation (black lines) and that of carbonated silicate melt generation (grey shades) are shown as discrete melting domains in (a), the two are connected, if melting occurs in a carbonated (oxidized) mantle. The carbon fluxes and inventories are given in the unit of g of C/yr and g of C respectively. For estimates in g of CO<sub>2</sub>, multiply the numbers by 3.67 and for estimates in moles of C, multiply the numbers by 0.0833. The sources of flux and reservoir estimates are given in the text. The carbon reservoir in continents are after Sleep and Zahnle (2001) and Hayes and Waldbauer (2006).

temperature and lithology of interest. At shallow depths, and especially for eclogitic assemblages (typically  $\leq 3\text{--}4$  GPa or  $\leq 90\text{--}120$  km deep), the stable crystalline carbonate is generally Ca-rich (Dalton and Wood, 1993; Hammouda, 2003; Yaxley and Brey, 2004; Dasgupta et al., 2005; Thomsen and Schmidt, 2008a), at intermediate depths (2 to  $\leq 4$  GPa; 60–120 km deep) it is dolomite-rich (Wallace and Green, 1988; Falloon and Green, 1989, 1990; Dasgupta et al., 2004; Dasgupta et al., 2005; Dasgupta and Hirschmann, 2006), and at greater depths ( $>4\text{--}5$  GPa;  $>120\text{--}150$  km deep) it is magnesite-rich (Dasgupta et al., 2004; Dasgupta and Hirschmann, 2006, 2007a,b; Brey et al., 2008; Ghosh et al., 2009; Litasov and Ohtani, 2009b). The presence of carbonate in mantle lithologies has a tremendous influence in partial melting in the mantle, as will be discussed in the following sections. However, not all the mantle domains may be conducive to storage of carbon in the form of carbonates. The very shallow part of the oceanic mantle is too hot to allow stability of crystalline

carbonate and carbon is generally dissolved in melts or fluids (e.g., Canil, 1990; Luth, 1999). The deeper part of the mantle can be too reduced to favor stable carbonates. If this occurs, a key question is the depth at which carbonate stability is replaced by a reduced carbon phase.

The most obvious host of reduced carbon is graphite or diamond. Indeed, many deep Earth diamonds are thought to come from transition zone or lower mantle depths (Stachel et al., 2005), validating the idea that diamond is likely the most common host of deep carbon. However, the recent suggestions that the Earth's lower mantle is saturated with metallic iron (Frost et al., 2004) and the Fe–Ni metal saturation may occur as shallow as the shallow upper mantle (150–250 km: Rohrbach et al., 2007; Frost and McCammon, 2008), raise a new question on the mutual stability of metal and reduced carbon in the Earth's mantle. Recent high pressure experimental works on Fe( $\pm$ Ni)–C( $\pm$ S) systems suggest that in the presence of Fe-rich metals, carbon can be stored as graphite/diamond, as carbides, or as a light, alloying element in metals (Hirayama et al., 1993; Wood, 1993; Dasgupta et al., 2009a; Lord et al., 2009; Nakajima et al., 2009). Stability of any of these phases in the mantle must depend on the ratio of the metallic iron and elemental carbon. In Fig. 2 we show the expected carbon-bearing assemblage at deep mantle (including the lower mantle and transition zone) conditions. Owing to lack of high pressure experimental constraints on the solubility of carbon in solid Fe–Ni metal, the boundary between metal and metal + carbide assemblage remains somewhat uncertain. But it is unavoidable that depleted mantle domains with 10–30 ppm C and saturated with  $\sim 1$  wt.% metallic Fe(–Ni) would store all of their carbon dissolved in a free metal alloy phase (Fig. 2). On the other hand, if deep mantle that contains  $\sim 1$  wt.% Fe<sup>0</sup>, is more enriched and has carbon content similar to those estimated for OIB source regions (up to 500 ppm C), the carbon must be stored in iron-carbide (Fe,Ni)<sub>7</sub>C<sub>3</sub> + Fe–Ni metal. An interesting observation from Fig. 2 is that in order for diamond to be stable in the deep mantle, the metallic Fe<sup>0</sup>



**Fig. 2.** Fraction of iron metal in the lower mantle (in weight percent) versus carbon content (ppm) of the mantle. Experimental and thermodynamic data on the Fe–C system (Tsuzuki et al., 1984; Hirayama et al., 1993; Wood, 1993; Lord et al., 2009) suggest that diamond and iron-rich alloy cannot be in equilibrium. If diamond is a major host of carbon in the lower mantle, then iron-saturation (Frost et al., 2004) is not possible; rather there must be a stable iron carbide, Fe<sub>7</sub>C<sub>3</sub>. If the lower mantle has as much as  $\sim 1$  wt.% Fe-rich metal as proposed by Frost et al. (2004), then for MORB-source composition mantle with 10–30 ppm C (stippled bar), all the carbon will be dissolved in metal alloys. Whereas for enriched mantle domains ( $>30$  to 500 ppm C; marked as 'OIB source mantle'), a reduced lower mantle likely hosts all its carbon in metal alloy plus (Fe,Ni)<sub>7</sub>C<sub>3</sub> metal carbides. The solubility limit of carbon in Fe–metal alloy is poorly constrained at present, hence, three different Fe–Ni alloys versus Fe–Ni alloy + carbide boundaries are shown, but recent estimates based on high pressure experiments suggest that C solubility in Fe metal is  $< 1$  wt.% at lower mantle conditions (Lord et al., 2009).

to carbon ratio must be less than  $\sim 10.9$ , which yields  $\text{Fe}^0$  content of the mantle of 0.05 wt.% and 0.54 wt.% respectively, for C content of 50 and 500 ppm. For  $\text{Fe}^0$ -poor, reduced mantle, which is modestly carbon-rich, the carbon is likely stored in diamond and  $(\text{Fe,Ni})_7\text{C}_3$ . Thus, if diamond is the sole deep mantle carbon host,  $\text{Fe}^0$  saturation is not thermodynamically feasible (Fig. 2). The only scenario that could prevent carbide formation in the Fe-metal saturated lower mantle is the isolation of metal nuggets and diamonds. However, recent experimental evidence of fast grain boundary diffusion of carbon in an olivine and periclase matrix suggests that carbide formation is unlikely to be kinetically limited as grain boundary mobility allows solid carbon to diffuse as far as  $\sim 10$  km over the age of the Earth (Hayden and Watson, 2008).

If saturation of Fe metal or Fe–Ni alloy occurs as shallow as 150–250 km depth in the mantle (Frost et al., 2004; Rohrbach et al., 2007), then the upper mantle pressure Fe–C phase diagram applies and the behavior of compositions along the  $\text{Fe}_3\text{C}$ –Fe join should be relevant. Comparison of ridge or plume adiabats with the melting curves of  $\text{Fe}_3\text{C}$  and the  $\text{Fe}_3\text{C}$ –Fe eutectic indicates that Fe–Ni metal saturation at a modest depth could stabilize a carbon-bearing metallic melt at moderate to deep upper mantle conditions, depending on whether carbide is present (Fig. 3) or if the carbon content of the alloy affects significant melting temperature depression.

Although diamond, Fe-carbide, or Fe–Ni metal are probably the most likely hosts of carbon in the lower mantle, thermodynamic stability of carbonate cannot totally be ruled out. Both magnesite and calcite are known to be thermally stable at lower mantle depths (Biellmann et al., 1993; Isshiki et al., 2004; Ono et al., 2005; Ono et al., 2007; Oganov et al., 2008), however, the most critical parameter controlling the stability of carbonate is the oxygen fugacity. If oxygen fugacity is controlled by reaction between oxidized and reduced species of iron, then the progressive reduction of the constant bulk composition mantle silicate

assemblage with depth (Wood et al., 1996) likely restricts carbonate only to locally oxidized domains of the lower mantle. On the other hand, if the lower mantle is sufficiently carbon rich, the carbon species would be responsible for controlling the intrinsic oxygen fugacity and magnesite can become the stable host of carbonate. Recent discovery of deep carbonates, associated with diamonds (Brenker et al., 2007) confirms the possible stability of deep carbonates in mantle transition zones or lower mantle. But if carbonate is stable in the lower mantle, it remains unclear whether it is a local or a global feature.

#### 4. Modern fluxes of carbon in and out of the mantle

The principal mechanism of ingassing of carbon to the Earth's interior is subduction or an equivalent process that may have operated during the early history of the Earth. On the other hand magmatic and volcanic processes are responsible for liberating carbon from the interior to the exosphere. In this section, we review the information available for modern cycling of deep carbon.

All the three subducting lithologies, i.e., basaltic crust, overlying sediments, and mantle lithosphere carry carbon into the mantle. The dominant source of carbon entering the present-day trenches globally is the carbonate-bearing altered oceanic basalt (Alt and Teagle, 1999; Jarrard, 2003). About two-thirds of all the carbon that enters the trenches is composed of low-temperature carbonate precipitated as veins and present in vesicles in the upper volcanics of ocean-floor basalt. Most of the crystalline carbonates that precipitates in the crust are calcite-rich (Alt, 1995; Alt and Teagle, 1999; Alt, 2004), although siderite- or ankerite-rich carbonates are also found (Laverne, 1993). The mean concentration of this secondary carbon is age-dependent and is  $\sim 5$  wt.%  $\text{CO}_2$  in the top 200–500 m of  $>100$  Ma old basalts (Alt, 2004; Kelley et al., 2005). Using this average  $\text{CO}_2$  content for the topmost basaltic portion of mature oceanic crust, combined with older estimates of deeper pillow basalts, transitional basalts, sheeted dikes, and gabbro (Alt and Teagle, 1999), we estimate the average  $\text{CO}_2$  content of typical 7 km thick basaltic crust to be  $\sim 0.3$  wt.%. For a subduction rate of  $3 \text{ km}^2/\text{yr}$  (Reymer and Schubert, 1984), this amounts to subduction of  $6.1 \times 10^{13} \text{ g of C/yr}$  via basaltic crust subduction (Fig. 1). The sedimentary contribution to the subducted carbon flux varies significantly from one subduction zone to the other, but the global sum is about one-third of that of basaltic crust (Fig. 1) and likely accounts for a flux of  $(1.3\text{--}1.7) \times 10^{13} \text{ g of C/yr}$  (Plank and Langmuir, 1998). There are no well-constrained estimates for the mass of carbon stored in subducting mantle lithosphere, but this may contribute significantly to the overall ingassing flux of carbon. Ophicarbonates (hydrated and carbonated mantle peridotite), on average, contains  $\sim 11$  wt.%  $\text{CO}_2$  (Sciuto and Ottonello, 1995; Poli and Schmidt, 2002). If we assume ophicarbonate is restricted to only the top 100 m of the subducting lithosphere, for subduction rate of  $3 \text{ km}^2/\text{yr}$ , the carbon flux through subduction of mantle lithosphere can be as much as  $3.6 \times 10^{13} \text{ g of C/yr}$ . This would imply a total flux of carbon via subduction is  $(6.1\text{--}11.4) \times 10^{13} \text{ g of C/yr}$ . However, there are considerable uncertainties with this estimate. On the one hand, it is surely not realistic to assume that there is a pervasive world-wide ophicarbonate layer just below the Moho, as secondary carbonates are generally not pervasive features in terrestrial peridotite outcrops; they are generally markers of tectonized regions of enhanced fluid flow. On the other hand, carbonate mineralization could extend to much greater depths if faulting at the outer rise outboard of trenches introduces fluids to several kms below the Moho (Ranero et al., 2003).

Compared to carbon ingassing through subduction, outgassing through arc volcanism appears smaller. Estimates range from  $1.8 \times 10^{13} \text{ g of C/yr}$  to  $3.7 \times 10^{13} \text{ g of C/yr}$  (Sano and Williams, 1996; Marty and Tolstikhin, 1998; Hilton et al., 2002), which is  $\sim 40\text{--}70\%$  of the initial budget entering the trench; the balance could be introduced to the deep mantle. However, fluxes associated with metamorphic and hydrothermal fluids not associated with volcanos may also lead to

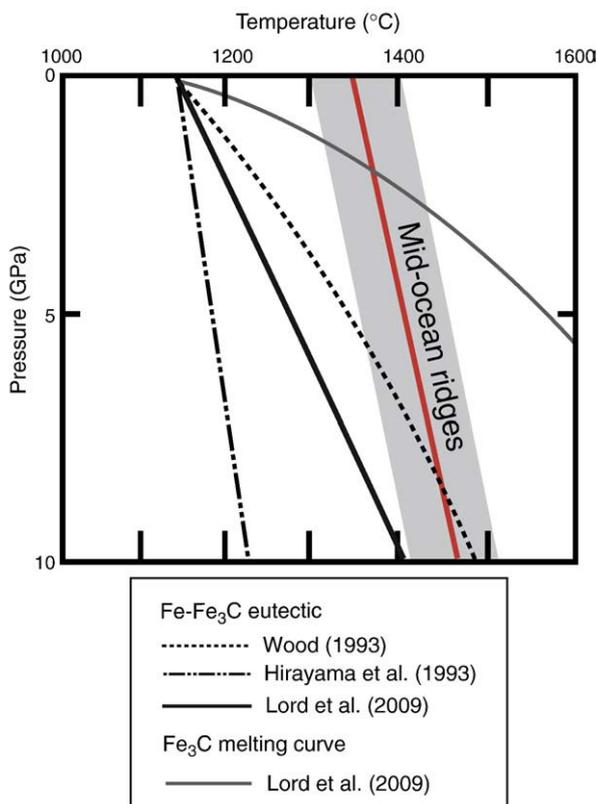


Fig. 3. Comparison of melting temperatures in the Fe–C system as a function of pressure with average mantle adiabat beneath mid-oceanic ridges (potential temperature,  $T_p = 1350 \pm 50$  °C). The plot suggests that if shallow mantle of the Earth is both metal and carbide saturated, then the metal carbide must be partially or completely molten.

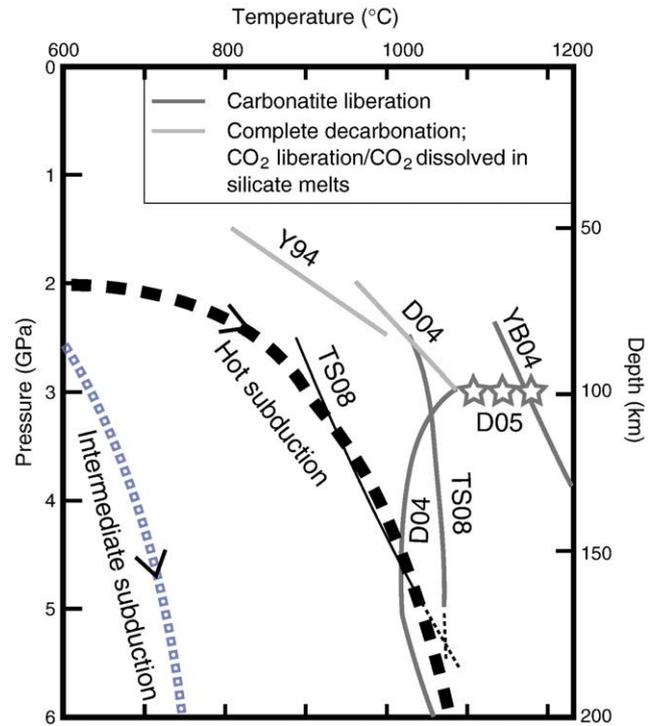
significant volatile transport from the slab to the surface (Ingebritsen and Manning, 2002). In addition, the CO<sub>2</sub> outflux related to magmatic intrusion is unconstrained. Further, recent discovery of liquid CO<sub>2</sub> emissions from a submarine arc volcano in the Marianas (Lupton et al., 2006) and the recent proposition that primary arc magmas might be more CO<sub>2</sub>-rich than previously thought (Blundy et al., 2010), suggest that arc flux of CO<sub>2</sub> may be larger than previously estimated.

A number of studies over the last two decades have estimated the mid-oceanic ridge flux of CO<sub>2</sub> (e.g., Marty and Tolstikhin, 1998; Dasgupta and Hirschmann, 2006; Cartigny et al., 2008; Shaw et al., 2010). If extremely enriched popping-rock data (Javoy and Pineau, 1991) are excluded, most of the recent data agree on estimates within a factor of five, ranging from 1.2 to 6.0 × 10<sup>13</sup> g of C/yr. The flux of carbon through ocean island volcanism is highly uncertain. This is partly owing to degassing-induced loss of CO<sub>2</sub> in sub-aerial intraplate eruptions and partly to variable degrees of enrichment of ocean island basalt source regions. For the purpose of this review, we assume that the OIB flux is ~10–50% of the MORB C-flux. Comparison of the total volcanic outflux with the subduction influx of carbon indicates that at the present-day rate, the net flux of surficial carbon to the mantle may be positive or negative. The uncertainties in the modern fluxes are too great to equivocally evaluate the balance. However, we estimate an upper bound for the present-day net flux of carbon into the mantle of 3.1 × 10<sup>13</sup> g of C/yr.

Comparison of the present-day carbon outgassing rate and the estimate of the total carbon budget of the mantle (Fig. 1) suggests that the residence time of carbon in the mantle is > 1 Ga and perhaps as long as 4.6 Ga. This suggests that deep carbon inventories are in large part a consequence of processes that occurred in the early Earth. We will return to the topic of early Earth carbon cycle in a later section.

## 5. Ingassing of carbon – petrology of carbonate subduction

Because most of the carbon that enters subduction zones is in the form of carbonate minerals, the ingassing of carbon into the mantle depends heavily on the stability of carbonates during subduction. The fate of carbonates in basaltic crust is most well constrained among all the different subducting packages. Phase equilibria experiments (Yaxley and Green, 1994; Molina and Poli, 2000; Poli et al., 2009) and thermodynamic calculations (Kerrick and Connolly, 2001b; Connolly, 2005) suggest that carbon remains stable in residual crust as calcite during shallow dehydration and possible hydrous melting. The fate of residual carbonates in subducting crust then hinges on the location of the solidus of carbonated eclogite relative to the thermal structure of the subduction zone. Recent experimental observations (Hammouda, 2003; Dasgupta et al., 2004; Yaxley and Brey, 2004; Dasgupta et al., 2005) reveal that the near-solidus phase equilibria of carbonated, basaltic eclogite can be quite complex, as the solidus temperature is influenced by a number of key bulk compositional parameters that vary substantially in subducting basaltic crust. Similar to the observations made for carbonate-free basaltic eclogite (Kogiso et al., 2004), the presence or absence of a free-silica phase (quartz or coesite) has no obvious effect on the solidus temperature of carbonated eclogite (Yaxley and Brey, 2004). The solidus temperature increases with increasing bulk Ca# (molar Ca/(Ca + Mg + Fe) × 100) and decreases with increasing bulk Na<sub>2</sub>O, Na<sub>2</sub>O/CO<sub>2</sub> (Dasgupta et al., 2005). Higher Ca# lithologies have higher Ca# in their equilibrium crystalline carbonate, making them more refractory (Irving and Wyllie, 1975; Dasgupta et al., 2005; Buob et al., 2006). Higher bulk alkalis, on the other hand, allow more alkali-rich near-solidus melt compositions, which achieve its thermodynamic stability at lower temperatures (Dasgupta et al., 2005). For plausible ranges of bulk Ca# (~30–55; PetDB database) and Na<sub>2</sub>O (~1.5–3.2 wt.%; PetDB database; Staudigel et al., 1996) of altered oceanic crust, the solidi of carbonated eclogite remain hotter than the slab-top conditions of most modern subduction zones (Fig. 4). Hence present-day subduction of oceanic crust likely introduces carbon deep into the mantle in the form of carbonated eclogite. The only exceptions are Cascadia and Mexican



**Fig. 4.** Experimental melting and devolatilization relations of carbonated subducting lithologies compared to the slab-top depth-temperature path, which is the temperature along the slab-mantle interface. Basaltic eclogite data are from Yaxley and Green (1994) – Y94, Dasgupta et al. (2004) – D04, Yaxley and Brey (2004) – YB04, and Dasgupta et al. (2005) – D05 and pelitic eclogite experiments are after Thomsen and Schmidt (2008a) – TS08. The stars correspond to the isobaric solidi of three different carbonated basaltic eclogite bulk compositions explored by Dasgupta et al. (2005), with the hottest solidus T corresponding to eclogite with highest bulk Ca# and lowest Na<sub>2</sub>O. The ‘Hot subduction’ and the ‘Intermediate subduction’ curves represent depth-temperature trajectories for hottest and average slab-top conditions after Syracuse et al. (2010). The figure indicates that liberation of carbonatitic melt and/or CO<sub>2</sub> from subducting lithologies is unlikely in modern subduction zones, with such possibility restricted only for estimated conditions in Cascadia and Mexico subduction zones (Hot subduction).

subduction zones (van Keken et al., 2002; Syracuse et al., 2010), where slab-mantle interface temperatures may exceed the solidi of carbonate melting.

The behavior of ocean-floor carbonated sediments may be even more variable. The composition and carbonate fraction of subducting sediments of ocean-floor sediments vary significantly from one subduction zone to the other (Plank and Langmuir, 1998; Jarrard, 2003). Computed phase equilibria of a selected set of sediment bulk compositions (Kerrick and Connolly, 2001a) suggest that carbonate remains stable in dehydrated sedimentary assemblages and enters the deeper parts of subduction zones, beyond sub-arc depths. Data on the partial melting behavior of carbon-bearing sedimentary eclogite assemblages remains limited (Thomsen and Schmidt, 2008a; Thomsen and Schmidt, 2008b). Experimental work on a calcareous clay composition similar to that entering the Lesser Antilles trench (Thomsen and Schmidt, 2008a) showed that melting induced breakdown of carbonates is unlikely along any plausible subduction paths and magnesian-calcite survives melting induced release in subduction zones. Although a large compositional parameter space needs to be explored to constrain the behavior of different carbonated sediment packages, it is possible that, like basaltic crust, carbonated sediments also retain much of their carbon inventory at the slab-top conditions occurring in modern subduction zones. Decarbonation induced by flushing of hydrous fluids derived from subjacent mantle lithosphere has been suggested as a possible mechanism of carbon extraction from crustal assemblages during subduction (e.g., Kerrick and Connolly, 2001b; Molina and Poli, 2000; Gorman et al., 2006), however, phase equilibria or dynamics of such a process are largely unconstrained.

## 6. Petrology of carbon outgassing – partial melting of the carbon-bearing mantle

Oxidized carbon behaves as an incompatible element in magmatic systems and hence generation and extraction of magmas in the Earth's mantle is a key step in carbon outgassing from the planetary interior. While partial melting in the Earth's interior is responsible for releasing carbon to the atmosphere, carbon also controls the loci and extent of magma generation in the Earth's mantle. In this section we review the possible loci of mantle melting in the presence of carbon.

### 6.1. First melting of carbonated mantle in oceanic provinces

Fig. 5 shows the solidus of carbonated, natural mantle peridotite. The onset of dolomite stability marks the lowest point on the solidus of carbonated mantle lithologies. For carbonated peridotite, this occurs at a depth of ~60–70 km and the solidus temperature drops to ~1000 °C (Falloon and Green, 1989; Dasgupta and Hirschmann, 2006) (Fig. 5). At greater depths the solidus temperature gradually increases. In Fig. 5, we fit all the available experimental constraints on carbonated peridotite solidus (in CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Na<sub>2</sub>O–CO<sub>2</sub> ± FeO\* ± other oxide systems; Falloon and Green, 1989; Dasgupta and Hirschmann, 2006, 2007a; Ghosh et al., 2009; Litasov and Ohtani, 2009b) between 2 and 35 GPa by a third order polynomial. The preferred solidus corrects for the effect of variable bulk Na<sub>2</sub>O/CO<sub>2</sub> ratio on experimental solidus (Dasgupta and Hirschmann, 2007a) in the study of Falloon and Green (1989), Dasgupta and Hirschmann (2006) and Ghosh et al. (2009) and also corrects for the absence of FeO\* in the experiments of Litasov and Ohtani (2009b). The solidus, over the pressure range of 2 to 35 GPa, is given by

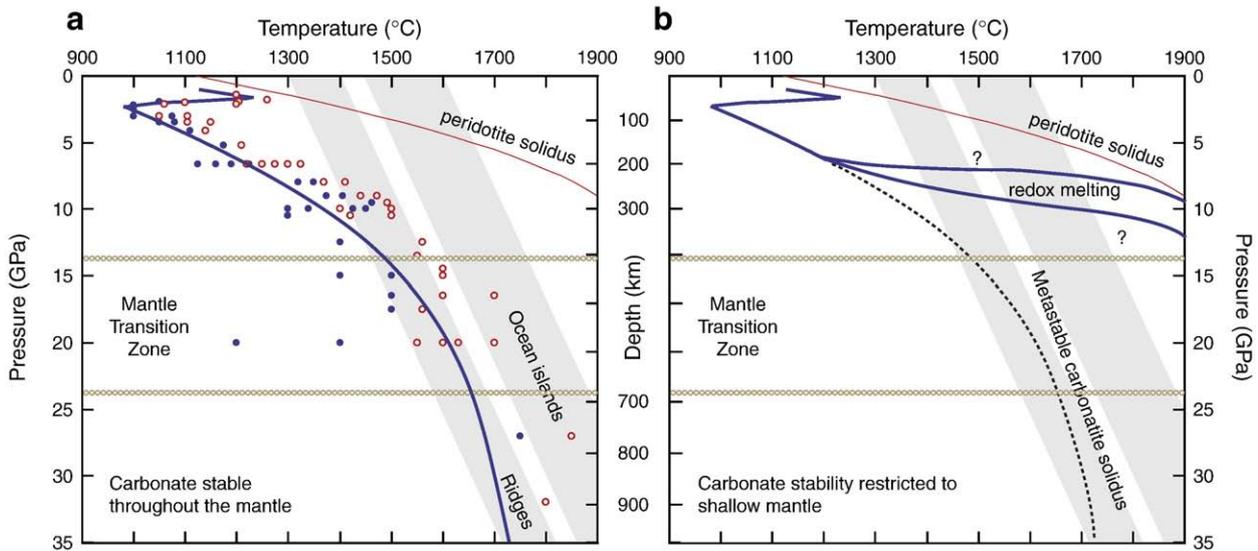
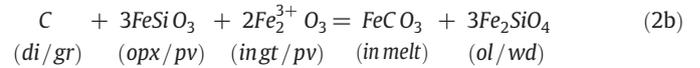
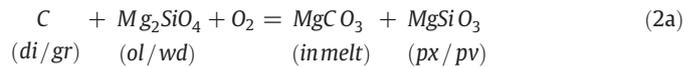
$$T(^{\circ}\text{C}) = 0.0238 \times [P(\text{GPa})]^3 - 2.2084 \times [P(\text{GPa})]^2 + 73.7991 \times [P(\text{GPa})] + 830.3808. \quad (1)$$

We note that the solidus equation given above should be applicable to any nominally anhydrous Earth's fertile mantle composition, with CO<sub>2</sub> concentration >10 ppm that lie in carbonate stability field. The

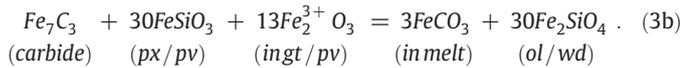
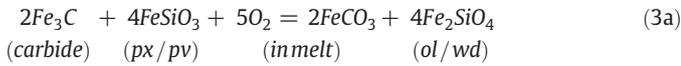
solidus fit is observed to converge to the average mantle geotherm at the top of the mantle transition zone (Fig. 5). If the convective mantle continues to remain oxidized, this leads to initial melting of upwelling mantle at a depth of ~300–330 km or deeper beneath oceanic ridges. Experiments at transition zone to lower mantle conditions (Ghosh et al., 2009; Litasov and Ohtani, 2009b) suggest that the solidus of carbonated peridotite may become parallel to the average mantle adiabat; the preferred fit to the solidus in Fig. 5 captures that and the solidus and the adiabat within error appear parallel to each other. It is unclear whether at depths exceeding the top of the transition zone, magnesite<sub>ss</sub> remains the dominant host of carbon, but if it does, carbonate-assisted melting might be ubiquitous throughout much of the Earth's mantle, including that of the Earth's lower mantle (Figs. 1 and 5).

Near-solidus partial melting of carbonated mantle rocks produces carbonatite melt Dasgupta and Hirschmann, 2007b. The fraction of melt produced by this deep melting is likely vanishingly small. For a MORB-source mantle with 25 to 95 ppm bulk CO<sub>2</sub> (Hirschmann and Dasgupta, 2009), the fraction of carbonatitic melt, with ~40 wt.% CO<sub>2</sub>, (Dasgupta and Hirschmann, 2006; Dasgupta and Hirschmann, 2007b) is ~0.01–0.02 wt.%. If estimates for OIB source mantle, with 120 to 1830 ppm CO<sub>2</sub> (Hirschmann and Dasgupta, 2009) are more appropriate, then the carbonatitic melt fraction of interest would be 0.03–0.46 wt.%.

The locus of onset of deep partial melting beneath ridges may be modified if the mantle at depths is too reduced to stabilize magnesite. If carbon is stored in diamond or metal/metal carbide, the path of mantle upwelling likely experiences a gradual oxidation such that the melting coincides with a change of carbon speciation from a reduced to an oxidized form, such as (di/gr – diamond/graphite; ol/wd – olivine/wadsleyite; px/pv – low-Ca pyroxene/perovskite):



**Fig. 5.** (a) Solidus of nominally anhydrous, carbonated peridotite constrained by laboratory partial melting experiments. The experiments include those from Falloon and Green (1989) at 1.4–3.5 GPa, Dasgupta and Hirschmann (2006) at 3.0–10.0 GPa, Dasgupta and Hirschmann (2007) at 6.6 GPa, Ghosh et al. (2009) at 10.0–20.0 GPa, and Litasov and Ohtani (2009b) at 16.5–32.0 GPa. The subsolidus and the supersolidus experiments are given by solid blue and open red circles, respectively. The preferred solidus from 2 to 35 GPa is fitted with a third order polynomial given in the text. The preferred solidus at >10 GPa is not a fit to the data as it corrects for the excess alkali in the study of Ghosh et al. (2009) and the absence of Fe in the study of Litasov and Ohtani (2009b). The intersection of sub-oceanic ridge geotherm with the experimental solidus suggests that generation of carbonatitic melt can occur as deep as 300–600 km. Close convergence of the carbonated peridotite solidus with the mantle adiabat at transition zone and lower mantle depths also suggests that a small volume carbonatitic melt may be stable in much of mantle, if remains sufficiently oxidized at depth. (b) Schematic phase diagram indicating the modified shape of the C-bearing mantle solidus, assuming that carbon is in reduced phases below a certain depth. The location and the shape of the redox melting solidus are not well constrained. However, if this form of the solidus applies, deep formation of carbonatite in oceanic provinces may not occur or may be restricted to a small depth range. The solidus of volatile-free, fertile peridotite (Hirschmann, 2000) is also included for comparison.



The reactions are shown with both oxygen and  $\text{Fe}^{3+}$  as the oxidant. It is unclear whether these reactions are applicable to any mantle domains or at what depths these redox reactions take place. But if they are applicable, then the mantle solidus may have a very different shape (Taylor and Green, 1988; Green and Falloon, 1998; Foley, 2008; Foley et al., 2009) than derived from carbonated lithologies (Fig. 5b). If the mantle continues to be carbonated at depths, the first melting will produce carbonatitic melt (Fig. 5a). However, if the mantle stores carbon in diamond or in carbide/metal at depth, deep formation of carbonatite melt beneath ridges may not occur and the first melt, formed via redox melting, may be carbonated silicate melt (Fig. 5b). Whether the first melt formed by a redox reaction is a carbonatite or a carbonated silicate melt depends on the relative depth of the redox reaction and the reaction describing the transition from carbonatite to carbonated silicate melt. The relative position of these two reactions relevant for the Earth's upper mantle is presently unknown.

Which of these two possibilities is appropriate for first melting in upwelling oceanic mantle influences the efficiency of carbon outgassing. If carbonatitic melt forms at depths exceeding 300 km, then magmatic release of carbon to the exosphere is likely very efficient, leading to residence times of carbon in the mantle near 1 Ga (Dasgupta and Hirschmann, 2006). However, if the deep formation of carbonatite is impeded owing to storage of carbon in diamond or metal carbide, carbon liberation is a less efficient process and the residence time of carbon in the mantle approaches the age of the planet. Interestingly, this span of residence times is similar to that derived independently from global flux estimates (see Section 4 above). Mantle carbon residence times derived solely from deep (~300–330 km) extraction of carbonate melt (Dasgupta and Hirschmann, 2006) fall towards the lower bound of times estimated from fluxes and reservoir sizes. This may indirectly suggest that some domains of the mantle lose carbon less efficiently than would be true by release of mobile carbonated melts at great depths, and hence some small fraction of shallow mantle carbon may indeed be stored in less easily fusible diamond or metal–metal carbide.

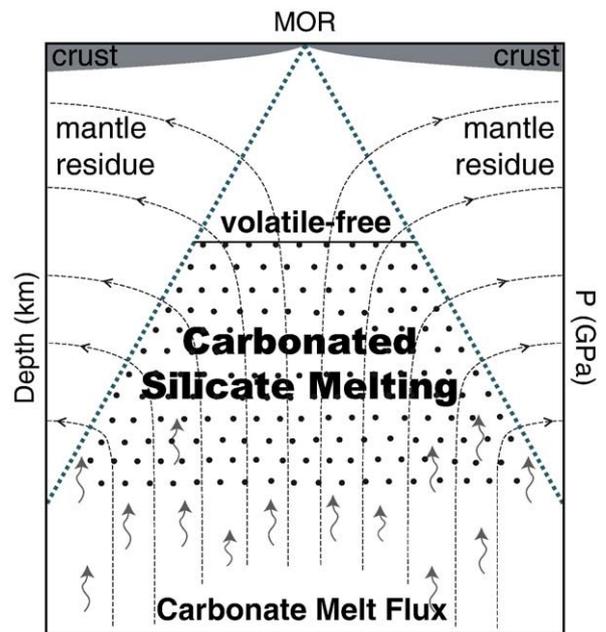
## 6.2. Carbonated silicate melts in the mantle

Irrespective of whether the first melting in the upwelling mantle is via decompression of a carbonated mantle or redox melting of a reduced mantle, the manifestation of such melts in the shallow mantle occurs through production of silicate melts with dissolved  $\text{CO}_2$  (hereafter referred to as carbonated silicate melt). Owing to diluted  $\text{CO}_2$  content and hence much greater volume, carbonated silicate melts play a more important role in the chemical differentiation of the planet than trace carbonatitic melt (Dasgupta et al., 2009b). In this section we review various petrologic and dynamic scenarios of carbonated silicate melt formation in the Earth's upper mantle. We arbitrarily define carbonated silicate melts as melts with dissolved  $\text{CO}_2$  content of 20–25 wt.% or less. Thus the onset of carbonated silicate melting is defined as the depth where a silicate melt with 20–25 wt.%  $\text{CO}_2$  is stabilized; in a carbonated mantle, this likely occurs at a finite melt fraction, through transition from carbonatite to carbonated silicate melts, and not at the solidus (melt fraction,  $F=0$ ). However, if the onset of melting occurs through a redox process (e.g., Eqs. (2a–b) and (3a–b)), then the carbonated silicate melt can be the first formed melt at the solidus ( $F=0$ ; Fig. 5b).

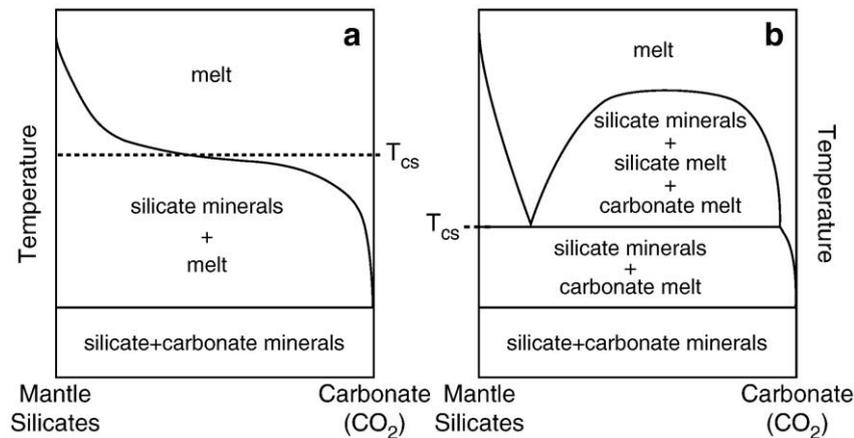
We envision that carbonated basalt generation in the mantle more likely occurs via transition from carbonatite to silicate melts (e.g., Hirose, 1997; Dasgupta et al., 2007a, b; Foley et al., 2009). In this case, unlike the production of basalt that occurs by depressurization of a mantle domain above its solidus, first basalt generation in a carbonated mantle can occur by a reactive or a metasomatic process. This is owing to the fact that decompression of carbonated peridotite or eclogite produces carbonatite melt near the solidus and the highly mobile melt must largely be expelled from the mantle matrix (Hunter and McKenzie, 1989; Minarik and Watson, 1995; Minarik, 1998; Hammouda and Laporte, 2000). However, the ascending carbonatite melt will act as a flux to the overlying mantle and will react with the mantle silicates to stabilize a carbonated silicate melt at depths below the volatile-free silicate solidus. Carbonated silicate melting is not actually a true solidus but a reaction front (Fig. 6). At any given pressure in the carbonate stability field, the onset of carbonated silicate melting marks either a temperature interval of 10–50 °C at which significant dissolution of silicate starts taking place in  $\text{CO}_2$ -rich carbonatitic fluid (Fig. 7a) (Hirose, 1997; Dalton and Presnall, 1998; Moore and Wood, 1998; Gudfinnsson and Presnall, 2005; Dasgupta et al., 2007a, b; Brey et al., 2008) or a temperature at which an immiscible silicate melt appears in the presence of carbonatitic melt (Fig. 7b) (Hammouda, 2003; Dasgupta et al., 2006). Which of these two scenarios is applicable depends on the phase equilibria of silicate melt formation, which in turn depends on pressure, temperature, and bulk composition of the mantle lithologies.

The depth of first generation of carbonated silicate melts in oceanic mantle remains poorly constrained, owing to lack of experimental constraints on the  $P$ - $T$  slope of carbonated silicate melting for natural peridotite. However, carbonated silicate melts have tremendous importance in geochemical and dynamical evolution of the planet as these are likely sources of primary, silica-undersaturated, alkali basalts (Hirose, 1997; Dasgupta et al., 2006; Dasgupta et al., 2007b) and melts in the asthenosphere/low-velocity zone (Eggler, 1976; Presnall et al. 2002; Hirschmann, 2010) and are to the ultimate source of  $\text{CO}_2$  dissolved in oceanic basalts.

We also note that reaction such as in Eq. (2a–b) and (3a–b) may also incite carbonated silicate melting the core–mantle boundary



**Fig. 6.** Cartoon depicting the concept of carbonated silicate melt production beneath oceanic ridges, where a flux of carbonatitic melt rising from greater depths incites silicate melting of the shallow mantle. The onset of carbonated silicate melting can be significantly deeper than the volatile-free peridotite solidus, but the exact depth of this melting remains unconstrained owing to uncertainties in the slope of the carbonated silicate melting of natural peridotite in  $P$ - $T$  space.



**Fig. 7.** Schematic, isobaric,  $T$ - $X$  sections illustrating two different scenarios of carbonated silicate melt production. In (a) the initiation of carbonated silicate melting occurs through a miscible transition from a carbonatite ( $\text{CO}_2$ -rich) melt at low temperature to a carbonated silicate-rich melt at high temperature and in (b) silicate melt appears immiscibly, coexisting with a carbonatitic melt. The nature of transition, i.e., the phase relation of carbonated silicate melt formation depends on bulk composition, temperature, and pressure of transition.  $T_{cs}$  marks the onset of carbonated silicate melting of the lithology of interest. For most of the upper mantle, partial melting of peridotite displays the behavior in (a) (Dasgupta et al. 2007b) whereas shallow melting of carbonated mafic eclogite shows a melting behavior more akin to (b) (Dasgupta et al. 2006).

(Fig. 1a), where a strong redox gradient could exist. If such melting occurs, this may provide a mechanism of carbon exchange between the core and the mantle. Carbonated silicate melts at such great depths could be denser than the surrounding mantle, although density estimates of carbonated silicate melt are only available at upper mantle conditions (Ghosh et al., 2007). Formation of dense, carbonated silicate melts may contribute to ultra-low-velocity zone at the core–mantle boundary.

## 7. The early Earth carbon cycle

Because the residence time of carbon in the mantle, as derived from the present-day fluxes, is  $>1$  Ga and possibly greater than 4.6 Ga, the distribution of carbon on Earth must reflect events from a much younger planet, when fluxes of carbon between the mantle and the exosphere were undoubtedly different from those today. Constraints on these early processes are incomplete, but two key questions form the basis for any preliminary inquiry: (1) What was the distribution of carbon in the Earth following the violent Hadean events of accretion and magma ocean solidification? (2) How was C cycling into and out of the mantle different from the present on an earlier, hotter Earth?

### 7.1. Whole Earth carbon distribution in the Hadean

The processes of accretion, and magma ocean formation and solidification inevitably had a profound influence on the planetary distribution of carbon. A key constraint is that virtually all ( $\sim 95\%$ ) of the primordial (non-fissionogenic) Xe was stripped from the interior in the first 100 Ma, requiring a degassing event that affected nearly the whole mantle (Staudacher and Allègre, 1982). If carbon were highly volatile in this environment, then the early atmosphere should have contained virtually all of the Earth's carbon not in the core (Javoy et al., 1982), producing a partial pressure on the order of 10–300 MPa (Elkins-Tanton, 2008). If significant degassing preceded the giant Moon-forming impact, then much of this early atmosphere may have been lost to space (Genda and Abe, 2003). Thus, near the outset of Earth history, the mantle could have been nearly devoid of carbon. Retention of carbon would only have occurred if (a) the magma ocean was saturated in a C-rich refractory phase, such as graphite, diamond, carbide, or alloy (Hirschmann and Dasgupta, 2009) or (b) fractional crystallization were inefficient, leaving large amounts of trapped C-bearing silicate liquid in the cumulates solidifying from the crystallizing magma ocean.

Core formation removed some of the C from the primordial mantle, though the concentration of C in the core is subject to debate (Wood, 1993; Jana and Walker, 1997; Williams and Knittle, 1997; Dasgupta and Walker, 2008). The concentration of C in the core depends on the conditions at which metal-silicate equilibrium was established (Walter and Tronnes, 2004; Dasgupta and Walker, 2008) and on the amount of C present at the time of equilibration and segregation. If substantial amounts of metal segregation occurred at a time when much of the Earth's initial budget of carbon was degassed in a thick protoatmosphere or had already been lost to space, the core could be relatively carbon poor. If substantial metal segregation preceded massive C degassing, a more C-rich core may have formed. Mass balance arguments are consistent with a significant fraction of terrestrial carbon in the core (McDonough and Sun, 1995; McDonough, 2003; Dasgupta and Walker, 2008) (Fig. 1b). If these estimates are appropriate, this may be a clue to the relative timing of core segregation and degassing of the early massive atmosphere.

### 7.2. Ingassing and outgassing of carbon in the early Earth

If early in Earth history the majority of the carbon not in the core was in the early atmosphere, then there must have been large-scale ingassing of carbon at some later time, as the present inventory of mantle carbon exceeds that in the exosphere. Did this ingassing occur rapidly in the Hadean, or did it occur gradually over a much longer time? Sleep and Zahnle (2001) argued for catastrophic carbon ingassing soon after solidification of the magma ocean. They reasoned that the thick  $\text{CO}_2$  atmosphere would be drawn down rapidly by extensive carbonate weathering of impact ejecta and that this material would be efficiently returned to the mantle via subduction or a similar process.<sup>1</sup> This efficient carbonate ingassing could have stripped virtually all the carbon from the exosphere, depleting the greenhouse potential of the atmosphere and, owing to a faint young sun, possibly creating icehouse conditions (Sleep and Zahnle, 2001; Zahnle et al., 2007).

There is, however, an important problem with this catastrophic ingassing scenario, as it requires effective transport of carbonated mafic supracrustal rocks to the mantle via subduction. Thermobarometric investigations of Hadean and Archaean subduction temperature–depth

<sup>1</sup> In the rest of this section, we write simply “subduction” for a process that recycles lithosphere into the mantle, even though we acknowledge that the tectonic mechanism of lithospheric recycling in the early Earth may have been quite distinct from modern subduction.

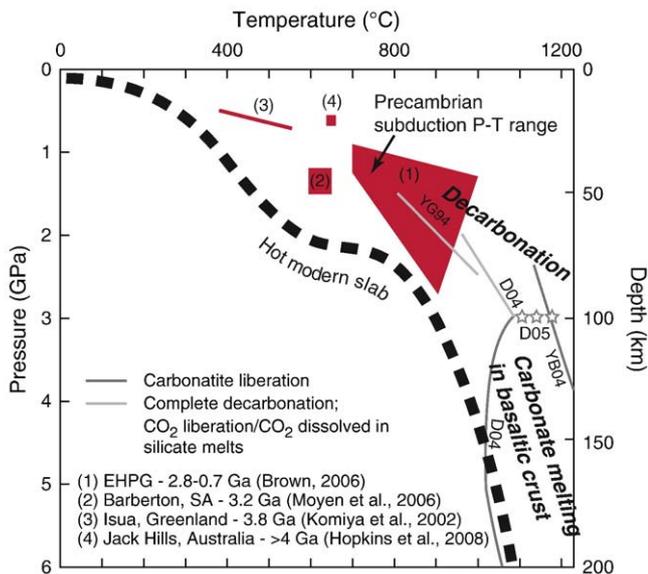
paths (Fig. 8) suggest that carbonate would not be retained in subducted lithosphere, as the temperature–depth trajectories are hotter than that required to avoid either decarbonation (Yaxley and Green, 1994; Dasgupta et al., 2004) or carbonate melting (Dasgupta et al., 2004; Yaxley and Brey, 2004; Dasgupta et al., 2005). Note that the subduction zone  $P$ – $T$  constraints in Fig. 8 come from observations of ancient rocks, rather than from models and the interpretation that the metamorphic conditions record subduction rather than metamorphism in some other tectonic environment is subject to debate. However, the temperature–depth trajectories are not too different from those expected from models of Archaean subduction (e.g., Foley et al., 2003; Sizova et al., 2010). The critical point is that these paths indicate that carbonate would be stripped from the top of subducting lithosphere by evolution of  $\text{CO}_2$  vapor or carbonatite partial melting and, largely returning to the surface by magmatism, leaving the majority of Earth's carbon near the surface and maintaining a carbon-poor mantle. This barrier to ingassing could have persisted until subduction temperature–depth paths become cooler than the carbonated eclogite solidus.

Despite the barriers to carbonate subduction in the early Earth, subduction of reduced carbon may have been a mechanism for carbon ingassing in the Hadean, as graphite has little effect on the solidus of dry mantle lithologies [in the presence of  $\text{H}_2\text{O}$ , solidi of graphite-bearing lithologies are greatly diminished (e.g., Jakobsson and Holloway, 2009), but this does not apply if subducting lithologies are effectively dehydrated before any solidi are approached]. On the early Earth, a significant fraction of near-surface carbon was likely graphite or other reduced phases (Catling et al., 2001). Even if the majority of near-surface carbon was carbonate, and therefore resistant to ingassing, a modest fraction of reduced, surface carbon could have partly replenished the mantle through vigorous litho-

sphere recycling. And although subduction of biogenically reduced carbon is too isotopically light to account for mantle  $\delta^{13}\text{C}$  (e.g., Hayes and Waldbauer, 2006), reduced carbon in the Hadean may have been chiefly inorganic and isotopically similar to meteoritic material, which spans mantle values (Kerridge, 1985).

Following the violent outgassing and possible ingassing events of the Hadean, significant ingassing of carbonate could not commence until temperature–depth trajectories became sufficiently cool to avoid decarbonation reactions during subduction. The oldest rocks clearly indicating temperature–depth conditions akin to modern subduction zones are Neoproterozoic blueschists, which date to ~800 Ma (Maruyama et al., 1996). Constraints on earlier subduction temperature–depth profiles are more open to interpretation. Brown (2006) argued that “eclogite high pressure granulite” (EHPG) terranes represent Proterozoic and Neoproterozoic (<2.7 Ga) subduction temperature–depth conditions. As shown in Fig. 8, these trajectories lead to decarbonation during subduction. If EHPG rocks truly reflect subduction conditions during Neoproterozoic–Proterozoic time, then carbonated supracrustal rocks (either sediments or altered basalts) were decarbonated during subduction (Fig. 8) until approximately 800 Ma. This leads to the rather startling inference that carbonate subduction, which is usually assumed to be a key element of the deep Earth carbon cycle, did not function for more than 80% of Earth history. However, it does not mean that carbon ingassing was negligible prior to the Neoproterozoic. First, carbonate sequestered deep in the subducting plate as hydrothermally altered peridotite (ophicarbonate) may have followed cooler  $P$ – $T$  paths than those represented by EHPG rocks. Second, carbon released from subducting slabs may be trapped in the lithosphere of the overriding plate in a mechanism similar to that recently envisioned for kimberlites in continental lithosphere by Sleep (2009). Third, subduction temperature–depth paths of any particular era show considerable dispersion owing to variations in plate age and subduction rate. The oldest and fastest subducting crust may well have a lower potential for continental accretion and preservation. Fourth, there were presumably no barriers to subduction of reduced carbon. Black shales are common throughout the Archaean and Proterozoic (Condie, 2001). Of course, isotope ratios of mantle C ( $\delta^{13}\text{C} \sim -5\text{‰}$ ) (Deines, 2002) are substantially heavier than the low  $\delta^{13}\text{C}$  characteristic of reduced sedimentary carbon ( $\delta^{13}\text{C} \sim -30 \pm 10\text{‰}$ ) (Strauss and Moore, 1992) and so subducted black shales could only account for a portion of ingassed carbon. It seems inevitable that carbon ingassing did occur prior to the predominance of modern subduction conditions at ~800 Ma, but perhaps at a markedly lower flux than at present and perhaps dominantly through mantle subduction rather than crustal subduction.

Given the apparent impediments to carbonate subduction through much of Earth history, one might imagine that exosphere maintained comparatively large inventories of carbon until carbon ingassing became efficient in Phanerozoic. Presumably this would be reflected in extensive carbonate sediments on the continents, which are the chief repository of exosphere carbon storage, as they provide protection from recycling. However, the evidence from the sedimentary record does not suggest so. Carbonates are an insignificant fraction of continental sediments prior to ~2 Ga, and then grow with time until recent times (Veizer et al., 2003; Hayes and Waldbauer, 2006). Even allowing for the relatively low preservation potential of carbonates as compared to siliclastic sediments, this suggests that the exosphere carbon reservoir was small through the first 2.5 Ga of Earth history. This would mean that carbon ingassing at least kept pace with volcanogenic outgassing even through times when the petrology suggests that carbonate ingassing was greatly restricted. Further, the exosphere carbon inventory has not been reduced significantly since the advent of modern subduction, which would have seemed to have allowed much more efficient ingassing. Thus, the sedimentary record and petrologic constraints yield conflicting views of the history of the deep Earth carbon cycle.



**Fig. 8.** Comparison of ancient subduction (or subduction-like) temperature–depth ( $T$ – $d$ ) trajectories with decarbonation reactions of subducting carbonated, mafic eclogite (Yaxley and Green, 1994; Dasgupta et al., 2004; Yaxley and Brey, 2004; Dasgupta et al., 2005). Individual Hadean and Archaean metamorphic  $T$ – $d$  data come from Isua (Komiya et al., 2002), Barberton (Moyen et al., 2006) and from >4 Ga mineral inclusions in Jack Hills zircons (Hopkins et al., 2008). EHPG = “eclogite high pressure granulite” facies metamorphic conditions inferred to be subduction  $T$ – $d$  conditions from 2.7 to 0.8 Ga (Brown, 2006). The near-intersection of this trajectory with the experimentally-determined solidus of carbonated eclogite indicates that decarbonation melting will only possibly occur in the hottest modern subduction zones. The fact that the EHPG and older subduction conditions are hotter than the ‘Hot modern slab’ trajectory suggests that subduction decarbonation was the norm prior to 800 Ma.

The efficiency of outgassing of carbon from the post-magma ocean, ancient Earth's mantle was also likely very different than that observed in the present day. On one hand, mantle potential temperature in the Archean, as derived from komatiites (Lee et al., 2009; Lee et al., 2010), was in excess of 1700 °C. This suggests that the first melting of carbonated mantle and carbonatitic melt release may have occurred much deeper than the present day, leading to very efficient release of primordial carbon to the exosphere. However, if the Archean mantle was more reduced than the storage of carbon in metal alloy/metal carbide or in graphite/diamond may have resulted in preferential retention of primordial carbon in the interior. There have been a number of suggestions that at least some domains of the Archean mantle likely had oxidation states similar to the modern mantle (Canil, 1997; Delano, 2001; Li and Lee, 2004; Dauphas et al., 2009). If this is correct, then even in the Archean shallow mantle may have stored carbon in the form of carbonates and outgassing fluxes in the early Earth may have been higher. This could exacerbate the challenge in accounting for how the mantle now holds a large fraction of the early Earth surface carbon inventory.

### 8. The deep Earth C and H<sub>2</sub>O geodynamic cycles: a brief comparison

Finally, it is of interest to compare the deep Earth carbon cycle with the analogous water cycle. The latter has been the focus of significantly more attention (e.g., Williams and Hemley, 2001; Ohtani, 2005; Hirschmann, 2006) and might have fewer uncertainties. Quantitative comparisons between the two cycles thus place constraints on the deep Earth C cycle (e.g., Hirschmann and Dasgupta, 2009). Both cycles, of course, are controlled chiefly by volcanic degassing and by subduction, and are characterized by ~Ga residence times. Also, long-term balances between ingassing and outgassing of both species are required to maintain an equable terrestrial climate and to sustain the biosphere. But there are also important differences. Whereas carbon subduction is thought to be very efficient on the modern Earth and strongly linked to the inventory of carbon on the subducting crust, H<sub>2</sub>O subduction is much less efficient, with nearly complete dehydration of subducting crust expected for all but the coldest modern subduction temperature–depth paths (Kerrick and Connolly, 2001b; Luth, 2003; Hacker, 2008). The principal modern flux of subducted H<sub>2</sub>O may be dominated by the inventory of serpentine in the subducting mantle (Rüpke et al., 2004) and so subduction of H<sub>2</sub>O in the modern Earth may be more akin to subduction of C in the ancient Earth, in which subducted mantle may have been the only viable mechanisms of ingassing. Finally, the deep Earth H<sub>2</sub>O cycle has direct feedbacks with solid Earth geodynamics, because H<sub>2</sub>O is hosted chiefly in the principal mineral constituents of the mantle and has a profound effect on mantle viscosity (Mei and Kohlstedt, 2000). Mantle carbon is hosted in accessory minerals, and therefore does not have direct effects on the bulk physical properties of the mantle. Rather, the impact of carbon is likely indirect, stemming from control on partial melting. Carbon-induced partial melting of the asthenosphere may contribute to the oceanic low-velocity zone (e.g., Egger, 1976; Presnall et al., 2002; Dasgupta et al., 2007a; Hirschmann, 2010) and hence contribute to the stabilization of plate tectonics (e.g., Höink and Lenardic, 2008). On the other hand, extraction of partial melts induced by carbon may be the essential mechanism by which H<sub>2</sub>O is extracted from the growing oceanic lithosphere (Dasgupta et al., 2007a), and consequently an important contributor to the mechanical stiffening of Earth's upper boundary layer.

The possibility of widespread traces of carbonated melt through a large part of the Earth's mantle (Fig. 5a) also opens up questions regarding the impact of such melt on geophysical properties of the 'solid' Earth. Although compaction of mantle matrix likely extracts most of the mobile carbonate melt, aided by surface tension, a trace amount may reside as grain boundary films or at triple grain junctions. Whether such small fractions of melt have measurable influence on the creep behavior

of the mantle or affects seismic attenuation remain open questions. Hydrous melts may have similar effects on geophysical properties, but traces of carbon-rich melts might be more pervasive in the Earth's mantle compared to that of hydrous partial melt.

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