

## Review of melting experiments on carbonated eclogite and peridotite: insights into mantle metasomatism

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Experimental studies on the partial melting of eclogite and peridotite provide important clues on mantle metasomatism. Here, we review results from some of the recent experiments and show that melting of carbonated eclogite and peridotite can produce carbonatitic to carbonated silicate melt, in which carbonates melt preferentially before Ti oxides and silicates. Low-degree melting results in carbonatitic melt coexisting with Ti oxides and silicates. This process also leads to the fractionation between some high-field strength elements (Nb, Ta, Zr, Hf, and HREE) and highly incompatible elements (U and Th) in the melt. When Ti oxides are nearly exhausted in eclogite, extremely high TiO<sub>2</sub> contents (e.g. 19 wt.%) are present in the melt with marked concentration of Nb and Ta. These results help to explain the features of carbonatitic metasomatism and the Nb–Ta spike in oceanic island basalts as identified in experimental studies. These studies also explain the reducing conditions that stabilize diamond in the deep mantle (>150 km) as well as the occurrence of diamond at different depths reported in various studies. Melting in such a reduced mantle can happen through redox reaction between diamond, pyroxene, and olivine, in which the initial liquid is a carbonated silicate melt. However, the theoretical oxygen fugacity (fO<sub>2</sub>) in the asthenosphere is much lower than that predicted by the reaction and requires elevated fO<sub>2</sub>, which can be caused by the addition of relatively oxidized materials from the lower mantle, deep asthenospheric material, and various recycled components. A combination of these processes generates locally oxidized domains in the deep mantle.

**Keywords:** melting experiments; carbonated eclogite; peridotite; carbonatitic and silicate melts; mantle metasomatism; redox state

### Introduction

Oceanic basalts can be modified by hydrothermal alteration on their way to trenches with carbonates, such as calcite and dolomite that are deposited on the ocean floor (Staudigel *et al.* 1981a; McDuff and Edmond 1982; Staudigel and Hart 1983; Von Damm 1990; Elderfield and Schultz 1996; Alt and Teagle 1999, 2003). It is estimated that each year subduction transports into the mantle 20 km<sup>3</sup> of oceanic crust with 2.3–3.7 × 10<sup>12</sup> mol carbon, most of which can survive the dehydration process and are carried into the deep mantle (Reymer and Schubert 1984; Hofmann 1997; Dasgupta *et al.* 2004). These recycled components are preserved as eclogite, garnetite, perovskite minerals, and post-perovskite phases in the asthenosphere, transition zone, lower mantle, and along the core–mantle boundary, respectively (Oganov and Ono 1990; Ringwood 1994; Irifune *et al.* 1996; Serghiou *et al.* 1998; Murakami *et al.* 2004; Maruyama *et al.* 2007; Ernst 2010). Controlled by its diverse redox state, carbon can occur as carbonate in an oxidized environment and elemental carbon or carbide

under reducing conditions. The return of subducted slabs can be realized with the help of mantle plumes (Hart *et al.* 1992), entraining various types of recycled materials (Zindler and Hart 1986; Chauvel *et al.* 1992).

Recent high *P–T* experiments have shown that the solidus of carbonated eclogite intersects the mantle geotherm at pressures of 10 GPa or higher, which is about 200 km shallower than that of CO<sub>2</sub>-free peridotite (Figures 1 and 4; Hammouda 2003; Dasgupta *et al.* 2004; Dasgupta and Hirschmann 2010). Carbonatitic and carbonated silicate melts produced from carbonated eclogites would thus become an efficient metasomatic agent for the surrounding peridotites and impose similar geochemical features on them. The existence of diamond from both lithosphere and asthenosphere suggests an adequately reduced environment to stabilize elemental carbon at depths > 150 km (Boyd *et al.* 1985; Simakov 1998; Stachel 2001; Boyd 2002; Shirey *et al.*, 2002; Tappert *et al.* 2005; Harte 2010; Harte and Richardson 2011; Dobrzhinetskaya 2012). However, asthenosphere-derived

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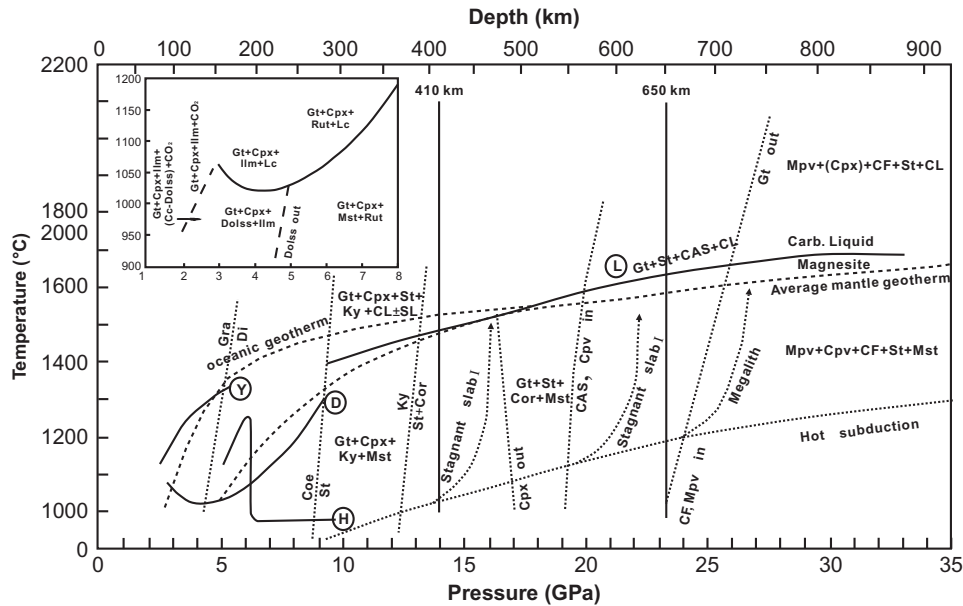


Figure 1. Composite phase diagram of carbonated eclogite in the deep Earth from Dasgupta *et al.* (2004) and Litasov and Ohtani (2010). Solids labelled with D, H, L, and Y are from Dasgupta *et al.* (2004), Hammouda (2003), Litasov and Ohtani (2010), and Yaxley and Brey (2004). Coe – coesite, St – stishovite, Gra – graphite, Di – diamond, Gt – garnet, Cpx – clinopyroxene, Ky – kyanite, Mst – magnesite, Dol – dolomite, Ilm – ilmenite, Rut – rutile, Cc – calcite, Cpv – Ca perovskite, Mpv – Mg perovskite, CL – carbonatitic melt, SL – silicate melt. CAS and CF are phases that exist only in high-pressure experiments but have not been found in natural rocks.

rocks such as oceanic island basalt (OIB) and I-type kimberlite are much more oxidized than the theoretical oxygen fugacity ( $fO_2$ ) in the mantle (Green 1990; Ballhaus 1993; Ballhaus and Ronald Frost 1994; Kadik 1997; Holloway 1998; Stagno and Frost 2010; Rohrbach and Schmidt 2011). This paradox indicates either  $fO_2$  heterogeneity in the mantle or a changing redox state of the melts during upwelling.

High  $P$ – $T$  experiments can help constrain the various deep mantle processes such as mantle magmatism and metasomatism. In this article, we provide a brief review of some recent melting experiments on eclogite and peridotite with their near solidus phases and relate them to carbonatitic metasomatism, Nb–Ta spike in OIBs, and  $fO_2$  anomaly in the mantle.

## Melting behaviour of carbonated eclogite

### *Bulk composition and solidus of carbonated eclogite*

Carbonated eclogite is a carbonate-bearing (<2–3 wt.%) metabasite that forms under ultrahigh-pressure metamorphism (Kushiro and Yoder 1966; Ringwood and Green 1966; Green and Ringwood 1967; Dal Piaz and Lombardo 1986; Wang *et al.* 1989; Dasgupta *et al.* 2005). Starting materials in the melting experiments for carbonated eclogite are prepared from either natural rocks, such as basalt and eclogite, with addition of carbonate or artificial mixtures chemically equivalent to the former (Hammouda

2003; Pertermann and Hirschmann 2003; Dasgupta *et al.* 2004; Yaxley and Brey 2004; Litasov and Ohtani 2010). Apart from the major oxides such as  $SiO_2$ ,  $MgO$ ,  $FeO_T$ ,  $Al_2O_3$ ,  $Na_2O$ , and  $CaO$ ,  $TiO_2$  is an important component in the system because of the common presence of ilmenite and rutile in eclogites (Rudnick *et al.* 2000; Heaman *et al.* 2002; Pertermann and Hirschmann 2003; Dasgupta *et al.* 2005; Enami *et al.* 2011).

The solidus of carbonated eclogite can be influenced by factors like  $Ca\#$  ( $Ca/(Ca + Mg + Fe_T)$ ), contents of alkalis and Fe, and the presence of  $CO_2$  gas and  $H_2O$  (Kogiso *et al.* 2004; Dasgupta *et al.* 2005; Dasgupta and Hirschmann 2007). High solidus temperature can be observed in high  $Ca\#$  system because the initial carbonatitic melt is mainly derived from Ca–Mg carbonate, and the eutectic temperature in the  $CaCO_3$ – $MgCO_3$  binary system is at intermediate  $Ca\#$  (Irving and Wyllie 1975; Byrnes and Wyllie 1981; Buob *et al.* 2006). On the contrary, high alkali content would decrease the solidus temperature due to its fluxing effect as an active component in the melt (Wang and Takahashi 1999; Dasgupta *et al.* 2004; Kogiso *et al.* 2004; Dasgupta *et al.* 2005; Litasov and Ohtani 2010). The initial melting temperature can be significantly decreased by high contents of the fusible component Fe,  $CO_2$  gas, and  $H_2O$  (Kushiro *et al.* 1968; Kushiro 1972; Huang and Wyllie 1976; Gaetani and Grove 1998; Asimow and Langmuir 2003; Dasgupta *et al.* 2005; Litasov and Ohtani 2010).

### Subsolidus phases in the melting of carbonated eclogite

Subsolidus phases of carbonated eclogite vary conspicuously at different pressures. The stability fields of garnet and clinopyroxene stretch into the transition zone (Hammouda 2003; Pertermann and Hirschmann 2003; Dasgupta *et al.* 2004; Yaxley and Brey 2004; Litasov and Ohtani 2010; Tsuno and Dasgupta 2011), where clinopyroxene dissolves into garnet and enriches it with a majoritic component (Ringwood and Major 1971; Moore *et al.* 1991; Ono and Yasuda 1996; Wang and Takahashi 1999; Litasov and Ohtani 2010). Ilmenite and calcite–dolomite solid solution (Cc–Dol<sub>ss</sub>)/aragonite occur as the host of titanium and carbon, respectively; they transform into rutile and magnesite ± aragonite at higher pressure (Hammouda 2003; Dasgupta *et al.* 2004; Isshiki *et al.* 2004; Yaxley and Brey 2004). Coesite and stishovite are common phases when the bulk composition is SiO<sub>2</sub> oversaturated with the latter more stable at depths greater than 300 km (Hammouda 2003; Thomsen and Schmidt 2008; Litasov and Ohtani 2010; Tsuno and Dasgupta 2011). Kyanite and corundum will appear when the system is extremely abundant in Al, and kyanite breaks down into stishovite and corundum at pressures above 10 GPa (Thomsen and Schmidt 2008; Zhai and Ito 2008; Litasov and Ohtani 2010). In a K-rich system, K can be stored in feldspar (<5 GPa), phengite (<10 GPa), and K-rich hollandite (>10 GPa); clinopyroxene is also an important reservoir of K at pressures above 5 GPa (Schmidt 1996; Schmidt and Poli 1998; Wang and Takahashi 1999; Hermann and Green 2001; Tsuno and Dasgupta 2011). As pressure increases in the transition zone, minerals will shift into a post-garnet assemblage, such as perovskite, CAS (CaAl<sub>4</sub>Si<sub>2</sub>O<sub>11</sub>), CF, and NAL (both CF and NAL are Na–Al-rich phases) (Wang and Takahashi 1999; Hirose and Fei 2002; Litasov and Ohtani 2004; Hirose *et al.* 2005; Maruyama *et al.* 2007; Zhai and Ito 2008; Litasov and Ohtani 2010). The various phases mentioned above are illustrated in Figure 1.

### Compositional variation and immiscibility of melts from carbonated eclogite

Dolomitic melt emerges as temperature increases across the solidus. Calcite–dolomite solid solution and magnesite melt into the liquid gradually with minor amounts of clinopyroxene and ilmenite/rutile, and they disappear after only tens of degrees (Hammouda 2003; Dasgupta *et al.* 2004, 2006; Litasov and Ohtani 2010; Tsuno and Dasgupta 2011). Those relative refractory Ti oxides and silicates can survive higher temperatures, making the first silicate drop generated subsequent to the carbonatitic melt. Figure 2 illustrates a typical melting process of formation of carbonated eclogite at 3 GPa (Dasgupta *et al.* 2006).

Immiscibility is liable to happen between the carbonatitic and silicate melt at low *P–T* conditions

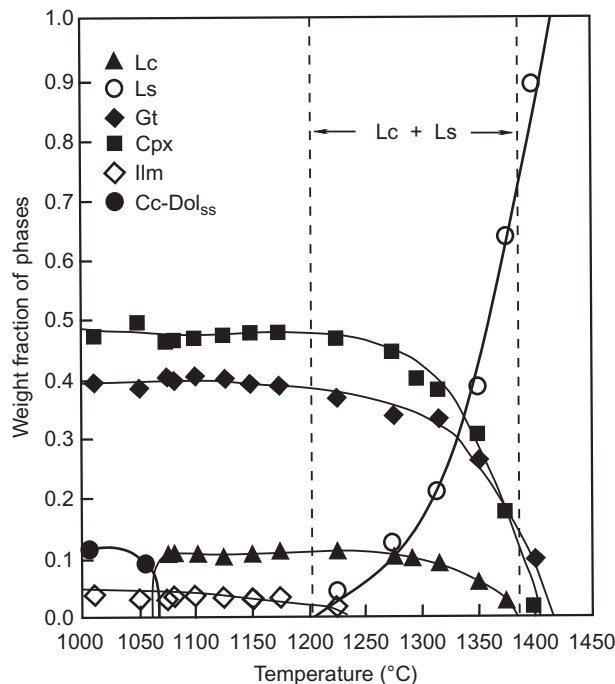


Figure 2. Weight fractions of garnet (Gt), clinopyroxene (Cpx), ilmenite (Ilm), Cc–Dol<sub>ss</sub> (calcite–dolomite solid solution), carbonatitic melt (Lc), and silicate melt (Ls) in melting of carbonated eclogite at 3 GPa (Dasgupta *et al.* 2006). Immiscibility between carbonatitic and silicate melts occurs in the temperature interval between the two dashed lines.

(Figure 3A and 3B). Immiscibility has been observed experimentally over the pressure ranges from 0.7 kbar to 6.5 GPa (Freestone and Hamilton 1980; Lee and Wyllie 1997; Hammouda 2003; Dasgupta *et al.* 2004; Thomsen and Schmidt 2008; Brooker and Kjarsgaard 2010; Tsuno and Dasgupta 2011). However, higher pressure promotes the mutual solubility of carbonatitic and silicate melts, and higher temperature activates the motion of ions and weakens the interfacial tension between two immiscible melts (Anastasiadis *et al.* 1988; Veksler *et al.* 2010). Thus, an increase in pressure and temperature can prevent the structural differentiation in melt and effectively hinder the immiscibility.

### Melting of mantle rocks in different redox conditions

Apart from pressure and temperature, the redox state is also a critical factor in controlling the melting process of peridotite. Magmas can be produced through melting of carbonated peridotite in oxidized conditions or through a redox reaction in relatively reduced mantle.

### Melting of carbonated peridotite

The starting materials for carbonated peridotite are prepared with CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Na<sub>2</sub>O, FeO<sub>T</sub>, and carbonate in proportion to natural peridotite. Several

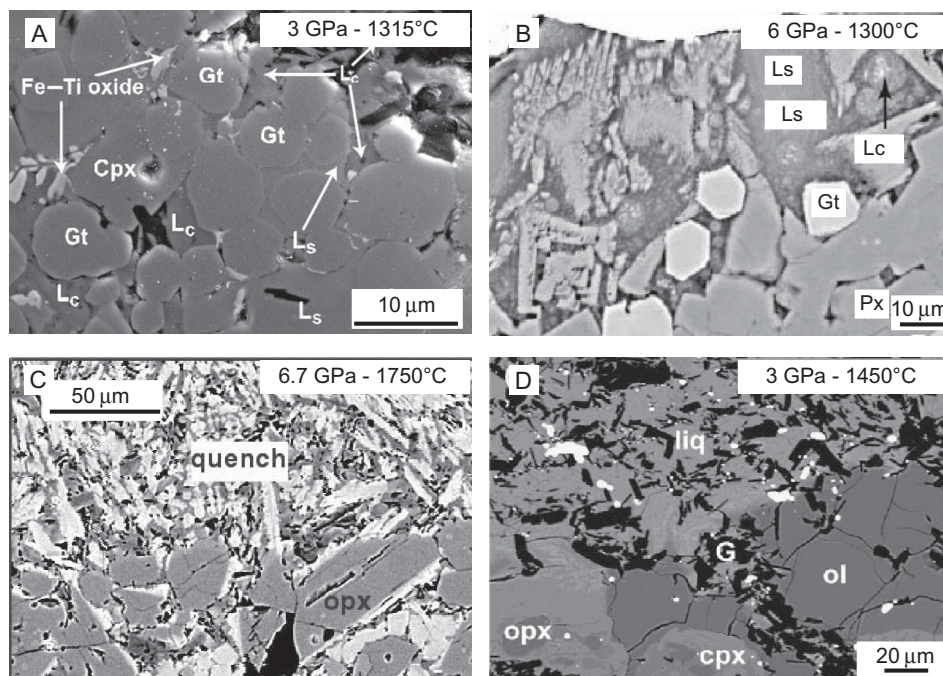


Figure 3. Quenched melt pictures for the melting of carbonated eclogite and peridotite. Pictures (A) and (B) show the immiscibility between carbonatitic liquid (Lc) and silicate liquid (Ls) in melting of carbonated eclogite (Hammouda 2003; Dasgupta *et al.* 2006). Picture (C) is the quenched product of carbonated silicate melts from carbonated peridotite (Dasgupta *et al.* 2007); no obvious immiscible texture was observed. Picture (D) shows carbonated silicate melt coexisting with graphite-containing peridotite (Stagno and Frost 2010).

studies have constrained the solidus of carbonated peridotite, but the results show an obvious scatter in the  $P$ - $T$  diagram, because the solidus location of carbonated peridotite is substantially influenced by  $\text{Na}_2\text{O}/\text{CO}_2$  (Pickering-Witter and Johnston 2000; Dasgupta and Hirschmann 2007). Dasgupta and Hirschmann (2010) adjusted these published data based on the effect of  $\text{Na}_2\text{O}/\text{CO}_2$  (Falloon and Green 1989; Dasgupta and Hirschmann 2006; Ghosh *et al.* 2009; Litasov and Ohtani 2009) and gave a revised solidus function (from 2 to 35 GPa) as follows (Figure 4):

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

No immiscibility has been reported in the melting of carbonated peridotite so far (Figure 3C). At pressures <5 GPa, dolomitic melt is produced first, mainly at the expense of carbonates. Subsequently, a sharp change can be observed, after a small temperature interval, from carbonatitic to carbonated silicate melt as a consequence of the reaction among carbonatitic melt, clinopyroxene, and garnet (Canil and Scarfe 1990; Moore and Wood 1998; Lee *et al.* 2000b; Gudfinnsson and Presnall 2005; Dasgupta *et al.* 2007; Foley *et al.* 2009). This is similar to the paragenesis of carbonatite and nephelinite-melilitite with rarity of intermediate composition. However, the melting behaviour of carbonated peridotite changes at pressures >5 GPa.

Early carbonatitic melt experiences a gradual transition to carbonated silicate melts. The contents of MgO and  $\text{SiO}_2$  in the melt increase with temperature;  $\text{Al}_2\text{O}_3$  is initially elevated and then diminishes, whereas there is a decrease in CaO, alkalis, FeO, and  $\text{CO}_2$  (Ryabchikov *et al.* 1993; Dalton and Presnall 1998; Gudfinnsson and Presnall 2005; Brey *et al.* 2008).

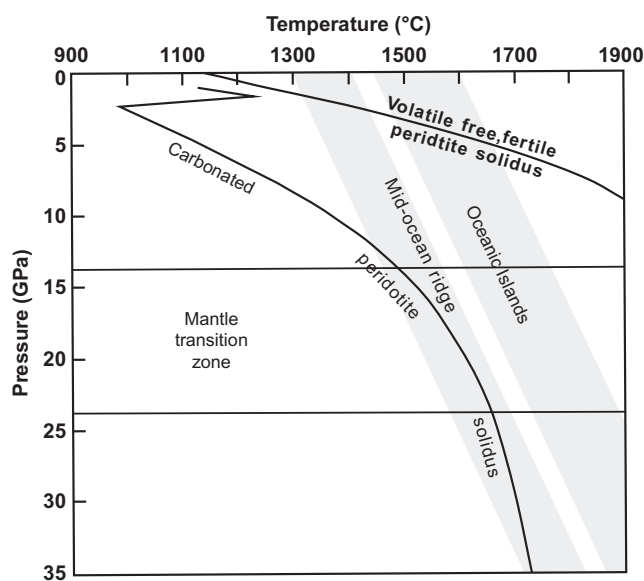
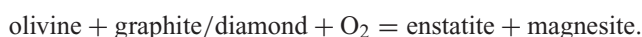


Figure 4. Phase diagram of carbonated peridotite solidus (Dasgupta and Hirschmann 2010) and the grey areas show the geotherms under oceanic ridges and islands.

### Melting of peridotite under reduced condition

Carbon can exist as graphite, diamond, or carbide in the deep mantle if it is too reduced to stabilize magnesite (Ballhaus 1995; Rohrbach *et al.* 2007; Rouquette *et al.* 2008; Dasgupta and Hirschmann 2010; Stagno and Frost 2010). Peridotite in such circumstances melts through a redox reaction, during which carbon transfers into the oxidized form (Green 1990; Ballhaus 1993; Ballhaus and Ronald Frost 1994; Kadik 1997; Holloway 1998; Dasgupta and Hirschmann 2010; Rohrbach and Schmidt 2011). Experimental studies have demonstrated that the initial liquid is a carbonated silicate melt (Figure 3D; Stagno and Frost 2010). This is consistent with silicate minerals taking part in the oxidation process of carbon, for example EMOG/D:



The redox reaction of carbon can occur in different ways. For instance, Stagno and Frost (2010) suggested that diamond can be oxidized into either magnesite or carbonatitic melt at 270 km and  $f\text{O}_2$  around FMQ-2 along the adiabat (Figure 5A). However, the  $f\text{O}_2$  condition in the asthenosphere can delay the occurrence of melting upward to 150 km or shallower. Thus, an elevated  $f\text{O}_2$  is

needed at depths greater than 150 km, from where some carbonatitic melts are derived. The  $f\text{O}_2$  of melt will be buffered by C–CO<sub>2</sub> before its separation from the carbon-bearing residue (Figure 5B; Ballhaus 1993; Holloway 1998; Ryabchikov and Kogarko 2010; Stagno and Frost 2010; Rohrbach and Schmidt 2011). Once the melt leaves, the  $f\text{O}_2$  is buffered by its own property (Ballhaus 1993; Holloway 1998; Bézou and Humler 2005; Rohrbach and Schmidt 2011). The variations of ferric/ferrous content in spinel indicate that there is a decrease of  $0.5 \log(f\text{O}_2)/\text{GPa}$  in the ascending melt. The fractionations of olivine and pyroxene with abundant  $\text{Fe}^{2+}$  will also promote an elevated  $f\text{O}_2$  (Ballhaus *et al.* 1991). Consequently, the melt becomes more and more oxidized.

### Melting in the lower mantle

Perovskite-structured minerals are dominant in the lower mantle and  $\text{Fe}^{3+}$  is strongly stabilized if the minerals are rich in Al. Excessive  $\text{Fe}^{3+}$  can be generated through disproportionation reaction of ferrous iron (Irfune *et al.* 1996; McCammon *et al.* 2004; Frost and McCammon 2008; Frost *et al.* 2008; Irfune *et al.* 2010; Ryabchikov and Kogarko 2010; Rohrbach and Schmidt 2011):

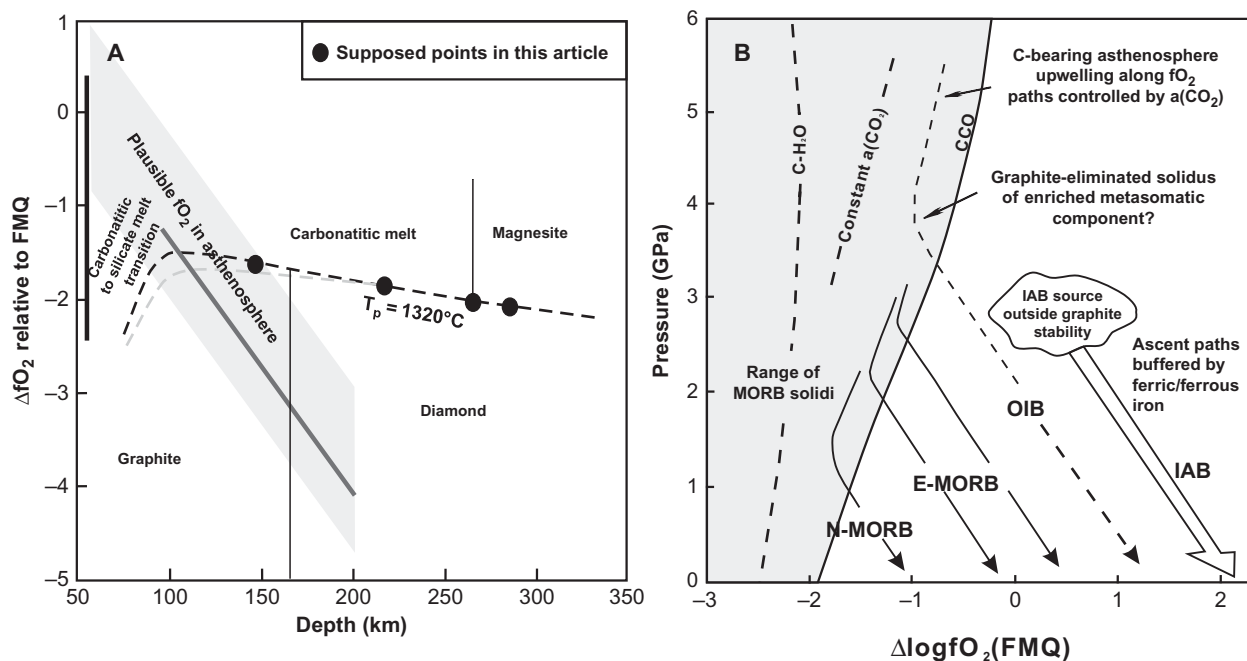


Figure 5. Diagram (A) (modified from Stagno and Frost 2010) shows the stability areas of graphite, diamond, magnesite, and carbonatitic melt in asthenosphere. The plausible oxygen fugacity is placed in the oblique grey area (Gudmundsson and Wood 1995). The two dashed curves are calculated along an adiabat with a potential temperature of  $1320^\circ\text{C}$ ;  $f\text{O}_2$  on them are buffered by C–CO<sub>2</sub>. The black curve is established by assuming that the content of CO<sub>2</sub> in melt is determined as a function of temperature from Stagno and Frost (2010); melt composition for the grey curve is based on the experiment of Dasgupta and Hirschmann (2006). Diagram (B) shows how  $f\text{O}_2$  varies in the ascending process of basaltic melts (Ballhaus 1993).

The eutectic temperature in a Fe–S system is much lower than the estimated temperature of the lower mantle and therefore the metallic iron produced as above can be easily dissolved in the Fe–S system (Chudinovskikh and Boehler 2007; Morard *et al.* 2008; Zhang and Fei 2008; Kamada *et al.* 2010). As a result, it is rational to predict that these dense Fe<sup>0</sup> will stay still or descend as soon as plumes stem from the lower mantle, making these ascending components more oxidized than their source region.

## Discussions on mantle metasomatism

### Carbonatitic metasomatism in mantle

Carbonatitic melt is one of the most powerful metasomatic agents in the mantle, and it can also occasionally generate metasomatic dolomite and magnesite (Kushiro 1975; Ionov *et al.* 1993; Yang *et al.* 1993; Lee *et al.* 2000a; Yang and Jahn 2000). Some carbonatitic metasomatized peridotites show a contrasting fractionation between some high-field strength elements (HFSE; e.g. Nb, Ta, Zr, Hf, and HREE) and highly incompatible elements (e.g. U, Th, and LILE) in their normalized trace element diagrams (Yaxley *et al.* 1991, 1998; Rudnick *et al.* 1993; Gorrying and Kay 2000; Zheng *et al.* 2006; Xu *et al.* 2008; Su *et al.* 2010). This can be well explained by the melting of carbonated eclogite and peridotite.

Carbonate takes priority over other phases to melt in both the aforementioned carbonated rocks. Melting at low degree (depending on the content of carbonate) induces liquefaction of carbonate, simultaneously with alkaline earth (e.g. Ca, Sr, and Ba), alkaline (if there is

no phlogopite), and highly incompatible elements (e.g. U and Th) concentrated into the melt (Brenan and Watson 1991; Adam and Green 2001; Hammouda *et al.* 2009), while most Ti-rich phases and silicate remain as a solid (Moore and Wood 1998; Hammouda 2003; Dasgupta *et al.* 2004, 2006, 2007; Gudfinnsson and Presnall 2005; Foley *et al.* 2009; Litasov and Ohtani 2010; Tsuno and Dasgupta 2011). Some HFSE, e.g. Nb, Ta, Zr, Hf, and HREE, would be strongly retained in Ti oxides, clinopyroxene, and garnet for their high  $D_{\text{min/melt}}$  (ranging from  $10^{-2}$  to  $10^2$  for different minerals) (Klemme *et al.* 1995; Sweeney *et al.* 1995; Foley *et al.* 1999; Adam and Green 2001; Klemme *et al.* 2002; Xiong *et al.* 2005; Giris *et al.* 2006; Bromiley and Redfern 2008; Gaetani *et al.* 2008; Tang *et al.* 2008; Dasgupta *et al.* 2009). Consequently, fractionation among trace elements occurs at low-degree melting of carbonated rocks.

### Metasomatism of Nb–Ta-rich melts in asthenosphere

OIBs provide one of the most robust geochemical probes into the asthenosphere (White 1985; Sun and McDonough 1989; Weaver 1991; Hofmann 1997). All of the typical OIB rocks share a common characteristic of a Nb–Ta spike in the spider diagram (Figure 6; Hofmann 1997), and this spike is particularly remarkable for HIMU-type basalts and those with high <sup>3</sup>He/<sup>4</sup>He (Sun and McDonough 1989; Chauvel *et al.* 1992; Hilton *et al.* 1999, 2000; Jackson *et al.* 2008). OIBs show relatively higher radiogenic Pb and Os contents and more enriched components than N-MORB, a feature that has been explained as the consequence of

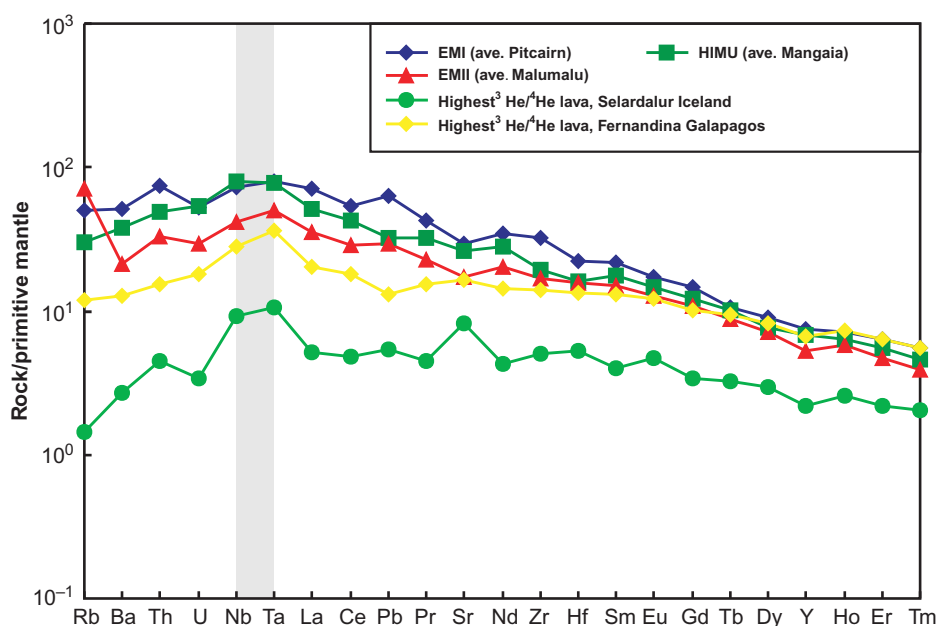


Figure 6. Nb–Ta spike in the trace element diagrams of OIBs. Data source: EMI-type basalt from Pitcairn Island (Eisele *et al.* 2002), EMII-type basalt from Malumalu (Workman *et al.* 2004), and HIMU-type basalt from Mangaia (Woodhead 1996). Basalts with high <sup>3</sup>He/<sup>4</sup>He from Iceland and The Galapagos Islands are from Jackson *et al.* (2008).

recycled materials in their source (Chauvel *et al.* 1992; Reisberg *et al.* 1993; Marcantonio *et al.* 1995; Roy-Barman and Allegre 1995; Hofmann 1997). Hence, the OIBs with a marked Nb–Ta spike cannot be considered as the products of melting of depleted asthenosphere alone.

Geochemists have argued that rutile-bearing eclogites contribute the Ti–Nb–Ta-rich metasomatic agent in the mantle. This prevalent idea can be supported effectively by melting experiments of eclogite in which Ti-rich melts have been observed (Klemme *et al.* 2002; Pertermann and Hirschmann 2003; Dasgupta *et al.* 2006; Gaetani *et al.* 2008; Bromiley and Redfern 2008). For example, Dasgupta *et al.* (2006) reported a value of 19% TiO<sub>2</sub> in silicate melt at 1225°C (3 GPa). Bromiley and Redfern (2008) recorded 13.24% of Ti, 0.013% of Nb, and 0.005% of Ta in melt at 1600°C (6 GPa) and 12.78% of Ti, 0.086% of Nb, and 0.037% of Ta at 1900°C (10 GPa). The content of Ti climaxes at the temperature where TiO<sub>2</sub> phases nearly run out. Such kinds of melt are able to resist chemical dilution at low melt/rock ratios and considerably elevate the contents of Ti–Nb–Ta in peridotite or transform a large proportion of the peridotite completely into pyroxenite. These elements can be preserved in minerals like amphibole, phlogopite, ilmenite, rutile, and clinopyroxene (Forbes and Flower, 1994; Ionov and Hofmann 1995; Konzett 1997; Grégoire *et al.* 1999; Pearson *et al.*, 2003). Thus, the extraordinary contributions of recycled oceanic crusts can be well reflected in OIBs by the Nb–Ta spike.

### Oxygen fugacity anomaly in the mantle

Existence of diamond at the bottom of the lithosphere (at least > 150 km) suggests that the deep lithosphere is reduced enough to stabilize elemental carbon (Boyd *et al.* 1985; Simakov 1998; Boyd 2002; Shirey *et al.*, 2002). Low  $f_{O_2}$  in the asthenosphere and deeper mantle can be evidenced from the various reports worldwide on diamonds of deep origin (Stachel 2001; Tappert *et al.* 2005; Harte, 2010). These findings indicate that carbonate cannot be the dominant host of carbon in the deep part of the mantle and that melting of carbon-bearing peridotite can happen only through redox reaction. However, experiments demonstrate that the thermodynamic conditions in the asthenosphere are not suitable for the redox melting of peridotite (Stagno and Frost 2010). Thus, an elevated  $f_{O_2}$  is required to explain those asthenosphere-derived carbonated silicate melt (e.g. I-type kimberlite) and melt at 200–300 km beneath ridges (Dunn *et al.* 2001; Gu *et al.* 2005; Baba *et al.* 2006), and this requires some connection with metasomatism in the deep mantle.

Magma sourced from the lower mantle and deep asthenosphere progressively oxidized during their ascent to shallower levels. These magmas are able to modify the composition of peridotite along their upward path and also remarkably change the  $f_{O_2}$  conditions; a similar result can also be brought about by fluids and melts released from recycled materials. The final combined influence of metasomatism would generate various different redox

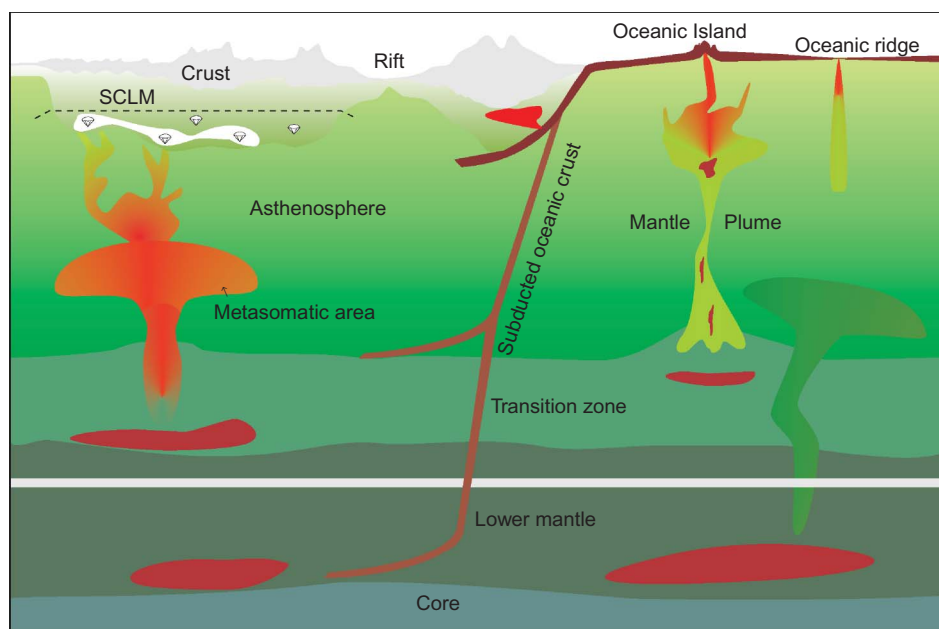


Figure 7. Distribution diagram of redox states in the mantle. The blank stripe stands for the compressed part in lower mantle. Reduced and oxidized regions are coloured with green and red, respectively. In the asthenosphere, the oxygen fugacity decrease with depth; this is expressed by a transition from light to dark green. A mantle wedge manifests a high  $f_{O_2}$  due to addition of slab-derived fluid. Melt from recycled crustal materials and the lower mantle would become more and more oxidized during their ascent. Metasomatism by such melts would change the original redox state in the deep mantle.

states in the mantle, leading to locally oxidized domains in the reduced deep mantle where diamond and carbide alloy are the dominant host of carbon (Figure 7).

### Summary

Carbonated eclogite consists of garnet, clinopyroxene, Ti oxide, carbonate, and other minor phases. Carbonated peridotite is mainly composed of olivine, clinopyroxene, orthopyroxene, garnet, and carbonate. These minerals transform into post-garnet phases such as perovskite, CAS, NF, and NAL in the mantle transition zone and lower mantle. Carbonates melt at lower temperatures than do Ti oxides and silicates. Low-degree melting of carbonated eclogite and peridotite can produce carbonatitic liquid mainly at the expense of carbonate, containing minor Ti oxide and silicate, leading to the coexistence of carbonatitic melt with solid and resultant fractionation between some HFSEs (Nb, Ta, Zr, Hf, and HREE) and highly incompatible elements (U and Th) in the melt due to their different  $D_{\text{min/melt}}$ .

Carbonated silicate liquid can be produced through an increase in the degree of melting. In the fusion of carbonated eclogite, immiscibility between carbonatitic and carbonated silicate melt occurs at pressure <6.5–7.0 GPa. At temperatures where Ti oxide is impoverished in the protolith, extremely high TiO<sub>2</sub> contents (e.g. 19 wt.%) can occur in the silicate melt. Nb and Ta are also remarkably concentrated due to their high partition coefficients for Ti oxide. In the melting of carbonated peridotite, immiscibility is not observed. Melt compositions change from carbonatite to melilitite-nephelinite at pressure < 5 GPa and from carbonatite through kimberlite to komatiite at higher pressure. These experimental results help to explain carbonatitic metasomatism and the Nb–Ta spike characteristic of OIB.

With increasing depth, the mantle becomes more and more reduced, and the  $f\text{O}_2$  is low enough at 150 km to stabilize diamond, as supported by the reports of diamond from both lithosphere and asthenosphere. Melting in such reduced mantle can take place through a redox reaction between diamond, pyroxene, and olivine, in which the initial liquid is carbonated silicate melt. In the lower mantle, perovskite would stabilize Fe<sup>3+</sup> through the reaction  $3\text{Fe}^{2+} = \text{Fe}^0 + 2\text{Fe}^{3+}$ . The metallic iron so produced is easily dissolved in the Fe–S system. The Fe<sup>0</sup> will remain, or descend as soon as plumes rise from the lower mantle, making these ascending components more oxidized than their source regions. Theoretically calculated  $f\text{O}_2$  in the asthenosphere is much lower than that predicted by redox reactions. This requires an elevated  $f\text{O}_2$  that can be caused by the addition of relative oxidized materials from the lower mantle, deep asthenosphere, and various recycled components; these processes make the presence of locally oxidized domains possible in the reduced deep mantle.

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