Redox state of the convective mantle from CO₂-trace element systematics of oceanic basalts

J. Eguchi¹*, R. Dasgupta¹

Abstract

The redox state of mantle lithologies, based on xenoliths from continental lithospheric mantle, has been shown to decrease with depth and reach oxygen fugacities (fO₂) at which graphite/diamond will be the stable form of carbon at pressures greater than about 3–4 GPa (e.g., Frost and McCammon, 2008). On the other hand, the depth-fO₂ profile of the convecting mantle remains poorly known. We compare the CO₂-Ba and CO₂-Nb systematics of natural oceanic basalts to the CO₂-trace element concentrations that can be generated via contributions from depleted peridotite partial melts and graphite-saturated partial melts of subducted lithologies. Results suggest that to produce the CO₂ enrichments relative to the depleted end member observed in natural oceanic basalts, subducted lithologies cannot be graphite-saturated at the onset of melting or must undergo oxidative transformation below the respective volatile-free solidi. Therefore, the oxygen fugacity profile of the continental lithospheric mantle may not be applicable to the deep convecting upper mantle, with the convecting upper mantle to at least 150 km depth being more oxidised than the carbonate vs. graphite/diamond buffer.

Introduction

The oxidation state of the mantle plays a critical role in dictating the geochemical and geodynamic evolution of Earth and its atmosphere (e.g., Frost and McCammon, 2008). Current understandings of mantle redox are largely based on measurements of Fe³⁺ and Fe²⁺ in mantle-derived basalts, which suggest that the oxygen fugacity of Earth’s shallow mantle to about 1.5 GPa is close to the FMQ buffer (e.g., Cottrell and Kelley, 2011; Hartley et al., 2017). The fO₂ of the deeper portions of Earth’s mantle is chiefly known from mantle xenoliths recovered from continental lithospheric mantle (CLM), which suggest fO₂ decreases with increasing depth (e.g., Woodland and Koch, 2003). This trend has been attributed to the increasing stability of the Fe⁴⁺-bearing skiagite component of garnet with increasing depth (Gudmundsson and Wood, 1995). The fO₂ decrease with increasing depth observed in CLM has been proposed to apply to the convecting mantle (e.g., Frost and McCammon, 2008). However, several observations offer up the possibility that the fO₂ trend estimated for CLM may not be applicable to the convecting mantle. (1) Kimberlites (oxidised, CO₂-rich magmas) are generated deep in the mantle, then migrate through overlying cratons, often picking up diamonds, a reduced form of carbon, implying there are regions in the mantle deeper than CLM depths where diamond resides that are more oxidised (Yaxley et al., 2017, Dasgupta, 2018). (2) Carbonate inclusions have been found in diamonds from depths in the mantle that should be in the graphite/diamond stability field if the CLM fO₂ profile is applied to the convecting upper mantle (Brenker et al., 2007). (3) Kiseeva et al. (2018) argue that fO₂ measurements of garnet inclusions in diamonds from the mantle transition zone become more oxidised with depth, and are more oxidised than predicted by the Fe-controlled fO₂ profile inferred from CLMs. (4) Komatiites, which are generated deeper in the mantle than basalts have similar redox states to MORB (Gaillard et al., 2015). While these natural observations may be due to special circumstances, they raise the possibility that the CLM fO₂ profile may not be applicable to the convecting mantle.

CO₂ Enrichment of Oceanic Basalt – Graphite/Diamond or Carbonate-present Melting?

Many oceanic basalts are argued to contain partial melt contributions of subducted lithologies such as sediments, MORB-eclogite, and pyroxenite (Hofmann and White, 1982), which begin to melt deeper than peridotite due to their lower solidi (e.g., Spandler et al., 2008). If there are redox sensitive geochemical proxies that track deep melting processes, they may provide constraints on the redox state of deeper portions of the convecting upper mantle, where the recycled lithologies undergo melting. Many of these basalts have elevated CO₂ concentrations relative to normal mid-ocean ridge basalts (Aubaud et al., 2006), which may be due to a CO₂ contribution

¹ Department of Earth, Environmental and Planetary Sciences, Rice University, 6100 Main Street, MS 126, Houston, TX 77005
* Corresponding author (email: james.eguchi@rice.edu)

Received 20 April 2018 | Accepted 1 August 2018 | Published 18 September 2018
CO₂-Nb and CO₂-Ba Systematics of Oceanic Basalts

Here we use CO₂-Nb and CO₂-Ba systematics of oceanic basalts argued to be receiving contributions from recycled lithologies (see Table S-2) to investigate the redox state of the deeper portions of the convective upper mantle. We use a new, compositionally dependent CO₂ solubility model for silicate melts (Eguchi and Dasgupta, 2018) applicable to graphite/diamond-saturated conditions to investigate a wide range of lithologies. We compiled partial melting experiments conducted on lithologies which may contribute to the generation of oceanic basalts. We only consider partial melting studies conducted at pressure-temperature conditions below the peridotite solidus to investigate processes which occur deeper than the onset of peridotite partial melting, as previous studies have already demonstrated that at shallow depths where major peridotite melting occurs, fO₂ is around the FMQ buffer (e.g., Cottrell and Kelley, 2011).

In Figure 2 we show CO₂ concentrations calculated for experimental partial melts at the CCO buffer (maximum amount of CO₂ dissolved with graphite present in the source) compared to the highest CO₂ concentrations measured in enriched oceanic basalts from several locations. CO₂ concentrations from basalts at Siqueiros are measured in undegassed melt inclusions and may be widely representative of CO₂ concentrations for basalts from partial melts of normal primitive mantle (Saal et al., 2002). Therefore, if the elevated CO₂ levels observed in enriched, natural oceanic basalts are due to contributions from subducted lithologies at graphite-saturation, then the CO₂ concentrations of the natural oceanic basalts must lie between CO₂ concentrations of Siqueiros and those calculated for the graphite-saturated experimental partial melts of subducted lithologies. Figure 2 shows that it is unlikely that a graphite/diamond-saturated melt derived from any recycled lithology can dissolve enough CO₂ to generate the high CO₂ concentrations observed at the North Arch of Hawaii and popping rocks from the North Atlantic (Dixon et al., 1997; Cartigny et al., 2008). For locations with lower CO₂ concentrations in basalts, such as those from Laki and Loihi, even many of the silica-rich melts may dissolve sufficient CO₂ under graphite/diamond-saturated conditions. The question, however, is whether realistic proportions of subducted lithology-derived melt can yield the CO₂-trace element systematics of these basalts.

In the following, we test whether CO₂ and other trace element enrichments observed in natural basalts can be produced by graphite-saturated melting of recycled lithologies. If CO₂ concentrations of natural samples are too high to be explained by recycled lithology contributions via graphite-saturated melting, it would suggest that the fO₂ of the subducted lithologies at or below their nominally volatile-free solidi must be high enough for carbon to exist as carbonate.

Figure 1 Pressure-temperature conditions for generation of partial melts from crustal/mafic lithologies in the mantle with colour map for wt. % SiO₂ in the melt. Also plotted for reference are mantle adiabats for mantle potential temperatures of 1350 and 1650 °C (dashed lines), solidi of various volatile-free lithologies (1-metapelite, 2-MORB-eclogite, 3-silica-deficient garnet pyroxenite, 4-peridotite, references given in footnote of Table S-3 – the table of compiled experiments), and graphite-diamond transition (dotted line).

Figure 2 CO₂ concentrations calculated at the CCO buffer for each experiment in Figure 1. Vertical blue lines are highest CO₂ concentrations measured in natural oceanic basalts from different locations (Table S-2) that are thought to receive contributions from subducted lithologies. Red band is for CO₂ content expected in depleted peridotite-derived partial melts based on undegassed melt inclusions from Siqueiros (Saal et al., 2002) and calculations using an experimental bulk partition coefficient for CO₂ and source CO₂ estimate of −75 ppm at F = 10 % (Rosenthal et al., 2015).
Figure 3  CO₂-Nb and CO₂-Ba mixing lines between depleted peridotite melts and graphite-saturated melts of subducted lithologies. Mixing lines are calculated at different log fO₂s relative to FMQ up to the CCO buffer as denoted by numbers above mixing line (the average fO₂ of eclogites based on CLM xenoliths at this pressure is marked with bold text). Each marker along a mixing line represents 10 wt. % incremental contribution from subducted lithology partial melt. Data points are the CO₂-Nb/CO₂-Ba concentrations recorded in the least degassed natural basalts at each location. Data point and mixings lines coloured for melt SiO₂ (wt. %) contents. Pink shaded region shows CO₂-Nb-Ba contents at graphite-saturation from CCO to FMQ-2.5 for all relevant experimental partial melts for a particular lithology from Figure 1. Gray band shows CO₂-Nb-Ba calculations for a depleted peridotite from 1-10 % melting degree (see also Fig. S-1). Data for generation of Figure 3 given in Supplementary Information.
Figure 3 shows CO$_2$-Nb and CO$_2$-Ba mixing lines between basalts from Siqueiros (see Fig. S-1 for mixing with variable melting degrees of a depleted peridotite) and partial melts of various graphite-saturated recycled lithologies, compared with the highest CO$_2$-Nb-Ba concentrations of oceanic basalts. The enriched endmember melts are generated by calculating graphite-saturated CO$_2$ concentrations at different fO$_2$ (Eguchi and Dasgupta, 2018) and trace element concentrations using the batch melting equation (more details in Supplementary Information). Data points and mixing lines are coloured for wt. % SiO$_2$ measured in natural basalts and wt. % SiO$_2$ resulting from mixing depleted peridotite partial melt and partial melts of recycled lithologies.

Figure 3 demonstrates that mixing between (graphite-absent) peridotite melts and partials of graphite-saturated subducted lithologies are unlikely to explain CO$_2$-trace element concentration measurements in minimally degassed basalts. While some natural basalts compositions lie along the mixing lines, the required extent of contributions from subducted lithologies would result in reacted (Mallick and Dasgupta, 2012) or mixed melt major element compositions that do not match the natural data, particularly for metapelite and MORB-eclogite (Fig. 3a,b,d,e). In the case of mixing with partial melts of garnet pyroxenite, results demonstrate that CO$_2$-Nb concentrations measured at Laki, Loihi, and Galapagos may be reproduced by mixing of basalts from depleted peridotite and graphite-saturated melts of pyroxenite at ~FMQ -2.5, while also producing major element composition consistent with natural data (Fig. 3c,f). The required mass fractions of melt derived from a pyroxenitic source would be about 50% at Laki to 80% at Loihi, which lie at the extreme upper end for estimates made for plume-fed basalts (Shorttle et al., 2014). Therefore, it is possible that for some CO$_2$-enriched plume-fed basalts, melting of pyroxenites under graphite-saturated conditions can deliver enough CO$_2$ to match the observed enrichment.

Basalts at Pitcairn, North Arch of Hawaii, and the popping rocks cannot be explained by mixing with a graphite-saturated partial melt of any lithology, and require mixing with carbonated silicate melts, which have been demonstrated to reproduce CO$_2$-trace element systematics of even the popping rocks (e.g., Dasgupta et al., 2009). Although Figure 3 only shows results at 5 GPa, the findings in Figure 3 are consistent with all experimental partial melts in Figure 1 which lie between adiabats for mantle potential temperatures of 1350 and 1650 °C and below the peridotite solidus. The CO$_2$-Ba-Nb concentrations for all of these experiments are shown as a pink shaded region in Figure 3 (see also Fig. S-1), which demonstrates that even when partial melts generated over a wide pressure range are considered, graphite-saturated partial melts fail to deliver enough CO$_2$ and trace elements to explain natural, enriched basalts. We acknowledge that the simple binary mixing model presented here is unlikely to represent melt-mixing in nature, however we do not seek to explain the entire array of basalts for a particular location (e.g., Matthews et al., 2017). Rather, we only test whether the least degassed basalt CO$_2$-trace element systematics for a given location can be explained by melt contribution from a graphite-saturated crustal lithology, and the simple mixing model used here is appropriate for that test. In addition to melt-melt mixing, we also test another scenario where the graphite-saturated partial melt of the subducted lithology is reactively frozen in upon interaction with ambient peridotite, and this new fertilised lithology melts at shallower oxidised conditions (see Fig. S-2). We find these calculations do not change the main conclusions, especially when the limit of eclogite melt addition through complete reactive crystallisation is considered.

**Oxygen Fugacity of the Mid- to Deep Oceanic Upper Mantle**

We show that if CO$_2$-trace element enrichment observed in minimally degassed oceanic basalts is due to contribution from recycled crusts, then the onset of melting must occur at carbonate-saturated conditions, which along mantle adiabats occur at pressures >10 GPa (Dasgupta et al., 2004); or oxidative transformation of diamond-bearing lithologies must occur deeper than their respective volatile-free solids. If the lithologic heterogeneity is silica-deficient pyroxenite, then our results do not preclude the possibility that basalts such as those at Laki and Galapagos may derive contributions from graphite-saturated melting. However, more enriched basalts such as those at Pitcairn, North Arch of Hawaii, and the North Atlantic popping rocks require generation of a carbonated silicate melt and therefore relatively oxidised conditions. In addition, previous studies on Iceland have shown a positive correlation between melt enrichment and oxidation state of erupted basalts (Shorttle et al., 2015), lending support for the oxidised nature of source regions for enriched oceanic basalts proposed here.

Based on our analyses that graphite-present melting of deeply embedded crustal rocks is mostly inconsistent with geochemistry of oceanic basalts, we show in Figure 4 the plausible fO$_2$ range of oceanic mantle. The DCDG/D buffer, which is the fO$_2$ at which graphite/diamond will coexist with carbonate in eclogite, and may also be applicable to pyroxenite (Luth, 1993), marks the lower fO$_2$ limit (≥FMQ) of mafic/crustal lithologies in the convecting upper mantle up to ~5 GPa. fO$_2$s calculated for CLM peridotite and eclogite xenoliths at similar depths suggest that C will be hosted in graphite/diamond.

![Figure 4](image-url)
Conclusions

Our results suggest the CLM $\text{O}_2$-depth profile may not be applicable to the convecting upper mantle, with the convecting upper mantle being more oxidised than the continental lithospheric mantle (Fig. 4). We note that our calculations only make predictions on the $\text{O}_2$ of subducted lithologies. However, if the subducted lithologies and ambient mantle are in redox-equilibrium, then the $\text{O}_2$ of the ambient mantle should also be in the carbonate stability field because the carbonate to graphite/diamond transition occurs at higher $\text{O}_2$s in eclogite/pyroxenite (DCDD/G) compared to mantle peridotite (EMOG/D) (Fig. 4) (Luth, 1993).

Acknowledgements

The authors thank Dr. Oliver Shorttle and an anonymous reviewer for their thoughtful comments which helped improve the manuscript. The authors also thank Dr. Helen Williams for handling the manuscript. The research received support from NSF grants EAR-1255391, OCE-1338842, EAR-1763226, and the Sloan Foundation through Deep Carbon Observatory.

Editor: Helen Williams

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1823.

This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at http://www.geochemicalperspectivesletters.org/copyright-and-permissions.


References


