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

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doi: 10.7185/geochemlet.1823

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 (fO_2) 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- fO_2 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.

Received 20 April 2018 | Accepted 1 August 2018 | Published 18 September 2018

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 fO_2 of the deeper portions of Earth's mantle is chiefly known from mantle xenoliths recovered from continental lithospheric mantle (CLM), which suggest fO_2 decreases with increasing depth (e.g., Woodland and Koch, 2003). This trend has been attributed to the increasing stability of the Fe³⁺-bearing skiaegite component of garnet with increasing depth (Gudmundsson and Wood, 1995). The fO_2 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 fO_2 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 fO_2 profile is applied to the convecting upper mantle (Brenker *et al.*, 2007). (3) Kiseeva *et al.* (2018) argue that fO_2 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 fO_2 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 fO_2 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

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from subducted lithologies, which have higher CO₂ concentrations relative to primitive mantle (Anderson and Poland, 2017; Hauri *et al.*, 2017). At sub-solidus conditions, the stable form of carbon depends on f_{O_2} ; at low f_{O_2} C exists as graphite/diamond, at high f_{O_2} C exists as carbonate. Graphite-bearing lithologies melt at the lithology's nominally volatile-free solidus and generate a silicate melt with f_{O_2} -dependent CO₂ concentrations (*e.g.*, Eguchi and Dasgupta, 2017, 2018). In addition, the presence of graphite during partial melting has negligible effect on the composition of generated melts due to the refractory nature of graphite. On the other hand, carbonate-bearing lithologies melt at the lithology's carbonated solidus and generate a carbonated melt with up to ~45 wt. % CO₂ (*e.g.*, Dasgupta and Hirschmann, 2006). Therefore, oceanic basalts receiving contributions from crustal/mafic lithologies will have different CO₂ concentrations depending on whether partial melting of these easily fusible lithologies occurred under graphite/diamond-saturated *versus* carbonated conditions.

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 f_{O_2} of the subducted lithologies at or below their nominally volatile-free solidi must be high enough for carbon to exist as carbonate.

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, f_{O_2} is around the FMQ buffer (*e.g.*, Cottrell and Kelley, 2011). Figure 1 shows compiled experiments in P - T space with colours corresponding to wt. % SiO₂ in the melt, which is a major controller of CO₂ solubility, with more silica-depleted melts dissolving more CO₂.

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.

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 contents 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 CO_2 -Nb and CO_2 -Ba mixing lines between depleted peridotite melts and graphite-saturated melts of subducted lithologies. Mixing lines are calculated at different $\log f\text{O}_2$ s relative to FMQ up to the CCO buffer as denoted by numbers above mixing line (the average $f\text{O}_2$ 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 CO_2 -Nb/ CO_2 -Ba concentrations recorded in the least degassed natural basalts at each location. Data point and mixings lines coloured for melt SiO_2 (wt. %) contents. Pink shaded region shows CO_2 -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 CO_2 -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 CO₂-Nb and CO₂-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 CO₂-Nb-Ba concentrations of oceanic basalts. The enriched end member melts are generated by calculating graphite-saturated CO₂ concentrations at different fO_2 s (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. % SiO₂ measured in natural basalts and wt. % SiO₂ resulting from mixing depleted peridotite partial melt and partial melts of recycled lithologies.

Figure 3 demonstrates that mixing between (graphite-absent) peridotite melts and partial melts of graphite-saturated subducted lithologies are unlikely to explain CO₂-trace element concentrations measured in minimally degassed basalts. While some natural basalt compositions lie along the mixing lines, the required extent of contributions from subducted lithologies would result in reacted (Mallik 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 CO₂-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 CO₂-enriched plume-fed basalts, melting of pyroxenites under graphite-saturated conditions can deliver enough CO₂ 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 CO₂-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 CO₂-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 CO₂ 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 CO₂-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 CO₂-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 solidus. 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 DCDD/G 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 ($\geq$ 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 Pressure vs. fO_2 computed for continental lithospheric mantle xenoliths versus those that have been estimated here for oceanic mantle sources (gray region). DCDD/G is the graphite/diamond transition in eclogite/pyroxenite (Luth, 1993). Graphite/diamond transition in peridotite is shown for reference (EMOG/D). References for xenolith data are in Table S-4.

Conclusions

Our results suggest the CLM fO_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 fO_2 of subducted lithologies. However, if the subducted lithologies and ambient mantle are in redox-equilibrium, then the fO_2 of the ambient mantle should also be in the carbonate stability field because the carbonate to graphite/diamond transition occurs at higher fO_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>.

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Cite this letter as: Eguchi, J., Dasgupta, R. (2018) Redox state of the convective mantle from CO_2 -trace element systematics of oceanic basalts. *Geochem. Persp. Let.* 8, 17–21.

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