The Behavior and Concentration of CO₂ in the Suboceanic Mantle: Inferences from Undegassed Ocean Ridge and Ocean Island Basalts

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Abstract (458 words)

In order to better determine the behavior of CO₂ relative to incompatible elements, and improve the accuracy of mantle CO₂ concentration and flux estimates, we determined CO₂ glass and vesicle concentrations, plus trace element contents for fifty-one ultradepleted mid-ocean ridge basalt (MORB) glasses from the global mid-ocean ridge system. Sixteen contained no vesicles and were volatile undersaturated for their depth of eruption. Thirty-five contained vesicles and were slightly oversaturated, and so may not have retained all of their CO₂. If this latter group lost some bubbles during emplacement, then CO₂/Ba calculated for the undersaturated group alone is the most reliable and uniform ratio at 98 ± 10 , and CO₂/Nb is 283 ± 32 . If the oversaturated MORBs did *not* lose bubbles, then CO₂/Nb is the most uniform ratio within the entire suite of ultradepleted MORBs at 291 ± 132 , while CO₂/Ba decreases with increasing incompatible element enrichment.

Additional constraints on CO₂/Ba and CO₂/Nb ratios are provided by published estimates of CO₂ contents in highly vesicular enriched basalts that may have retained their vesicles e.g., the Mid-Atlantic Ridge “popping rocks”, and from olivine-hosted melt inclusions in normal MORBs. As incompatible element enrichment increases, CO₂/Nb increases progressively from 283 ± 32 in ultradepleted MORBs to 603 ± 69 in depleted melt inclusions to 936 ± 132 in enriched, vesicular basalts. In contrast, CO₂/Ba is nearly uniform in these sample suites at 98 ± 10 , 106 ± 24 and 111 ± 11 respectively. This suggests that Ba is the best proxy for estimating CO₂ contents of MORBs, with an overall average CO₂/Ba = 105 ± 9 . Atlantic, Pacific and Indian basalts have similar values. Gakkel Ridge has lower CO₂/Ba because of anomalously high Ba, and is not included in our global averages.

Using the CO₂/Ba ratio and published compilations of trace elements in average MORBs, the CO₂ concentration of a primary, average MORB is 2085^{+473}_{-427} ppm, while primary NMORB magmas (>500 km from ocean island hotspots) have 1840 ppm CO₂. The annual flux of CO₂ from mid-ocean ridges is $1.25 \pm 0.16 \times 10^{14}$ g/yr, with possible values as low as 0.93 and as high as 1.61×10^{14} g/yr. This amount is equivalent to approximately 0.3% of the anthropogenic addition of CO₂ to Earth’s atmosphere. NMORB mantle has 183 ppm CO₂ (50 ppm C) based on simple melting models and 13% melting. More realistic estimates of incompatible element concentrations in the depleted mantle that are consistent with complex melting models yield much lower estimates for CO₂ in the depleted mantle: around 60 - 130 ppm CO₂, with large uncertainties that are more related to melting models than to CO₂/Ba. CO₂/Ba is not correlated with isotopic or trace element ratios, but there may be systematic regional mantle variations. Iceland melt inclusions and Gakkel Ridge MORBs have lower CO₂/Ba ratios, showing that these regional high Ba anomalies are not accompanied by correspondingly high CO₂ concentrations.

1. Introduction

The most direct means for estimating the flux of volatiles from Earth's interior is by determining the concentration of that volatile in basaltic magma as it is transported from the mantle to Earth's surface (Dasgupta and Hirschmann, 2010). This determination can also be used to estimate the concentration of volatiles in the mantle, after correction for fractional crystallization and modeling for partial melting (e.g., Dixon et al., 1988; Saal et al., 2002; Michael, 1988). Moreover, volatile behavior in the mantle can be compared to the behavior of elements that are incompatible during melting by determining the ratio of mantle-derived volatiles to incompatible trace elements for a range of depleted through enriched magmas, for example the $\text{H}_2\text{O}/\text{Ce}$ ratio (Michael, 1988; Dixon et al., 1988; Saal et al. 2002). However, CO_2 presents a greater challenge. Although CO_2 concentrations can be accurately measured in natural quenched glasses of mid-ocean ridge basalts (MORBs) or ocean island basalts (OIBs) there are very few instances where these measurements can be used to estimate the mantle-derived CO_2 content of magmas, because CO_2 is efficiently degassed from almost all magmas during ascent and eruption due to its low, pressure-dependent solubility (Gerlach, 1989; Stolper and Holloway, 1988; Dixon et al., 1995a). However, rare mid-ocean ridge basalts that are ultradepleted in incompatible elements provide an important opportunity. By virtue of their low initial CO_2 content and deep eruption depths, they never reached CO_2 saturation, and therefore have preserved their CO_2 inventory since formation in the mantle (Saal et al., 2002).

There are some questions concerning the representative nature of the rare undegassed MORBs that have been studied to date. For example, the ultradepleted basalts from the Siqueiros Transform Fault studied by Saal et al., (2002) could represent a local anomaly and not be representative of the MORB mantle source or even an ultradepleted source (Scaillet and Pichavant, 2004; Cartigny et al., 2008). There are also rare enriched MORBs that have been taken to represent undegassed magma, such as the highly vesicular "popping rock" from the Mid-Atlantic Ridge at 14°N . This magma ascended quickly, apparently as a closed system that never lost bubbles even though its CO_2 is extensively exsolved (Sarda and Graham, 1990; Graham and Sarda, 1991; Pineau et al., 2004). These basalts are commonly taken to have preserved their primary CO_2 content, but there are some questions as to whether they are representative of enriched MORB mantle, as well as the extent to which they may have lost or accumulated bubbles (Chavrit et al., 2013).

Saal et al. (2002) combined data from the ultradepleted Siqueiros basalt glasses and their olivine-hosted melt inclusions with data from popping rocks to examine a wide range of depleted to enriched magma compositions. They proposed that the CO_2/Nb ratio of the upper mantle was constant at 239 ± 50 , a proxy relationship that is widely used in estimating the original CO_2 concentration in degassed lavas. Cartigny et al. (2008) recalculated the CO_2/Nb in popping rocks and proposed estimated CO_2 contents in other depleted and enriched lavas by computing their degassing history. They suggested that upper mantle CO_2/Nb was closer to 576, and that the low CO_2/Nb values computed for ultradepleted magma from Siqueiros were atypical of Earth's mantle. Their CO_2/Nb estimate leads to a significant increase in estimates of mantle CO_2 output at mid-ocean

ridges, and helps to reconcile CO₂ flux estimates with those derived from comparison to noble gases, especially helium (Marty and Tolstikhin, 1998).

Here we present new CO₂ and trace element data from additional ultradepleted mid-ocean ridge basalts (UD-MORBs) to determine how variable the CO₂/trace element ratios are regionally and locally. In addition, we also consider highly vesicular rocks from the North Arch region of the Hawaiian swell (Dixon et al., 1997; Yang et al., 2003), and petit spot volcanoes near Japan (Okumura and Hirano, 2013; Hirano et al., 2006) in order to determine if there are consistent relationships between incompatible elements and CO₂ for enriched rocks. We discuss the question of bubble accumulation and loss in such rocks, and in MORBs in general. Recent studies of CO₂ and trace elements in olivine-hosted melt inclusions from ocean ridges (Shaw et al., 2010; Wanless and Shaw, 2012; Wanless et al., 2014) and from Iceland (Hartley et al., 2014; Neave et al., 2014; Hauri et al., 2002) provide additional data that we evaluate as proxy elements for CO₂. With the development of more accurate proxies for CO₂, we then calculate revised values for CO₂ flux from the mantle, consider mantle CO₂ concentration, and discuss some implications.

2. Analytical techniques

2.1. Major elements

Published major elements analyses were used in most cases. For the SM samples from the southern Mid-Atlantic Ridge, natural basalt glasses were analyzed for major elements using the automated four-spectrometer Cameca microprobe at the University of Tulsa. Details are in Supplementary Material S1a. Reported analyses are the average of four individual spots. Long counting times and high beam currents were used for K₂O. Two-sigma precision, based on multiple three-spot analyses of the same basalt glass, was $\pm 0.004\%$ K₂O.

2.2 – CO₃²⁻ and H₂O_{total}

Concentrations of H₂O and CO₃²⁻ dissolved in glasses were analyzed by Fourier Transform Infrared Spectroscopy at the University of Tulsa using published methods and calibrations (Dixon et al., 1988; 1995) with slight modifications (Michael, 1995). In most cases, reproducibility of H₂O from year to year, starting with different chips from the same rock, is better than 0.01 weight % (1-std. dev.).

All CO₂ is present as dissolved CO₃²⁻, which appears as an absorbance doublet at 1435 cm⁻¹ and 1515 cm⁻¹ (Fine and Stolper, 1986). Reproducibility from year to year, starting with different chips from the same rock, is generally better than ± 10 ppm (1-std. dev.). There is good correlation between our FTIR measurements and other labs except at low values, where our determinations are lower by as much as 30 ppm (Fig. S1.1). Additional details are provided in Supplemental Materials S1b.

2.3 Vesicle CO₂

Vesicle CO₂ contents were determined by capacitance manometry after *in vacuo* crushing of basalt glass chips. Samples typically consisted of 1-4 glass chips weighing a

total of 200-350 mg. The CO₂ extraction was followed by helium separation and He isotope analyses from the same gas aliquots as described in Graham et al. (2014). Briefly, CO₂ was trapped at 77°K and distilled from any minor amount of H₂O using a combination of liquid N₂ and frozen isopropanol traps. The calibrated volume of the ultra-high vacuum extraction system is 73 cm³, and employs an MKS® Baratron 1-torr capacitance manometer capable of measuring into the sub-millitorr range. Temperature drift is negligible through a strict control of laboratory T ($\pm 1^\circ\text{C}$). The pressure detection limit is below 1 mtorr, corresponding to $<0.001 \mu\text{mol CO}_2$ for this system ($\sim 0.2 \text{ ppm CO}_2$ for a 200 mg basalt glass sample).

2.4 Vesicle presence or absence

Presence of vesicles was determined by examining polished sections (1 x 1 cm) in reflected light on a petrographic microscope with 4X, 10X and 16X objectives. We also examined transparent, 150 μm thick sections with transmitted plane polarized light. We are able to see all vesicles $\geq 2\mu\text{m}$ in diameter. We can detect vesicularity down to 0.01% or less, except when vesicles are extremely sparse. It is impossible to say with 100% certainty that vesicles are absent.

2.5 Trace element analyses

New basalt glass analyses reported in this study were carried out by laser ablation ICP-MS at Oregon State University. Analytical precision determined from multiple analyses of the same glass sample was typically on the order of 5% or better for all elements, except for U which was typically $\sim 10\%$. This reproducibility is valid even for replicate analyses that were run several months apart in separate analytical campaigns. The accuracy for trace elements in measurements of secondary standards BHVO-2G, BIR-1G and GOR128G-1 glasses (Table S1.1) is typically better than 5%. Further details are presented in Supplemental Materials S1c, and in Loewen and Kent (2012).

3. Samples - Ultradepleted MORBs

The MORB database PetDB (<http://www.earthchem.org/petdb>) and recent publications with many analyses (Kelley et al., 2013; Gale et al., 2013) were surveyed for glasses having very low concentrations of incompatible elements, especially K₂O, Nb, La and Ba. The glasses selected for further study are typically primitive (almost all have Mg# >62) and have $<1.5 \text{ ppm Nb}$, $<300 \text{ ppm K}$ and $<1 \text{ ppm La}$. Many samples are olivine-phyric without plagioclase, but more evolved samples contain phenocrysts or microphenocrysts of plagioclase.

Ultradepleted basalts have been recovered from many parts of the mid-ocean ridge system (Fig. 1; Figs. S2.1 to S2.22), and appear to be clustered in some cases. For example at least two different, ultradepleted compositions were analyzed from dredge SM D13 (Fig S2.6). Ultradepleted basalts erupt most commonly but not exclusively in “leaky” transform faults (Perfit et al., 1996) and at near-ridge seamounts (Niu and Batiza, 1997). At least one sample is from a propagating ridge segment (EN112 from the Juan Fernandez Microplate), and several are from normal spreading segments. Most lavas

were collected from locations where they could not have flowed far downslope to greater water depths. Therefore, their depth of recovery cannot be much deeper than their depth of eruption. Dredge depths (Fig. 2) include a start and end depth wherever that information was preserved, and were obtained from the SESAR catalog (System for Earth Sample Registration: <http://www.geosamples.org/>) if possible. In some cases, dredge depths were obtained from cruise reports (e.g., EN113 from the Easter Microplate; SM from the southern Mid-Atlantic Ridge; and Gakkel Ridge samples, HLY and PS59 prefixes) or PetDB (single depth only). A single accurate depth is presented for samples collected by submersible (Siqueiros Transform Fault) or rock core (KM0417).

Samples used in this study are described further in Supplementary Materials S2.

4. Results

4.1. Major elements

Ultradepleted glasses are mostly primitive, with an average Mg# (i.e., $100 \times \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$) of 65.5, and a range from 56-70.5. Almost all glasses have thus experienced less than 25% crystallization from primitive MORB liquids with Mg#=68, based on least squares mixing calculations (e.g., Michael and Chase, 1987). There are no consistent, distinctive characteristics compared to N-MORBs (normal MORBs) in terms of Na₂O, FeO, TiO₂ or Al₂O₃, although the samples from Cox FZ have higher Na_{8.0} than basalts from the adjacent segments on the Mid-Atlantic Ridge at 32°-34°S, consistent with lower extents of partial melting. New major element results, along with data compiled from the literature, are reported in Table S3.1.

4.2. CO₂ in glass and vesicles

For all of the UD-MORB glasses studied here, dissolved CO₂ contents range from 69 to 330 ppm, and total CO₂ (dissolved + vesicles) ranges from 77-510 ppm. We separate the glasses of this study into two groups. The first group are clearly volatile-undersaturated for their depth of eruption, based on comparison of measured dissolved CO₂ + H₂O, with CO₂+H₂O solubility at the depth of recovery (Dixon et al., 1995) computed using VolatileCalc (Newman and Lowenstern, 2002). No vesicles were observed in these glasses during their examination using polished sections, and < 3 ppm CO₂ was released upon their crushing (Table S3.2). These glasses are typically the most depleted in terms of trace elements (see below). The undersaturated nature of this small group of samples (15 individual glass samples from 12 distinct localities) makes their measured CO₂ contents the most reliable in terms of estimating CO₂ flux and mantle chemistry. In contrast, there is a second group of samples that are oversaturated or just at the point of saturation for their depth of eruption. These basalts usually contain a small number of vesicles, and yield from 3-300 ppm CO₂ upon crushing (Table 3.2). In most cases, these glasses erupted at shallower depth compared to the undersaturated MORBs and/or they are slightly less depleted in terms of incompatible elements, although they are still much more depleted than typical N-MORBs. There is a very good correspondence between the glasses that were found to have bubbles during polished section examination and those that yield higher amounts of CO₂ upon crushing. These samples are

oversaturated based on a comparison of their dissolved $\text{CO}_2 + \text{H}_2\text{O}$ with computations from VolatileCalc (Newman and Lowenstern, 2002) (Fig. 2). Our observations can be considered as an independent test that confirms the accuracy of that model. In contrast, the correspondence is not very good when the saturation model of Papale et al. (2010) is used, suggesting that it is not accurate for these compositions and pressures.

The volatile oversaturated glasses (second group) have been included in this study to increase the data density and to help reveal possible chemical trends with increasing enrichment. Our rationale for inclusion is that unlike N-MORBs, this particular group would have attained CO_2 saturation at shallow depths in the crust (<1000 mbsf), only a short time before eruption, and therefore they probably still have remained largely undegassed because they probably have not lost their bubbles. However, they are plotted as separate groups from the volatile-undersaturated, UD-basalts to reveal any systematic differences between the groups that might arise if they did *not* remain a closed system to volatile loss.

4.3. CO_2 and incompatible elements in ultradepleted basalts

The new trace element analyses of ultradepleted natural basalt glasses (Table S3.3) show that most samples have concentrations of highly incompatible trace elements that are only 0.2 to 0.5 times those of average N-MORBs and D-MORBs respectively (Gale et al., 2013). In this section, we explore co-variations of incompatible elements and CO_2 , and we compare the order of incompatibility in UD-MORBs with the accepted order for N-MORB to E-MORB. If UD-MORBs show the same order of incompatibility as other basalts, it would suggest that they are anomalous only in the degree of their depletion. This would permit inferences for incompatible elements and CO_2 that are drawn from UD-MORBs to be applied to basalts in general, and would help establish which element is the best proxy for CO_2 .

For the suite of UD-MORBs analyzed here, incompatible elements are correlated with each other (Fig. 3), but there is a significant amount of scatter as well. In the figures, trace elements are all normalized to $\text{Mg}\# = 68$ to correct for different amounts of fractional crystallization that can create or improve correlations. Some of this scatter is due to analytical imprecision that is more influential for ultradepleted glasses having the lowest concentrations, and this becomes even more evident when comparing data from different labs. But significant scatter is apparent even when considering only the new analyses presented here, for which replicate analyses show high precision. The scatter for Ba *versus* other elements appears to be the greatest. There is much less scatter when plotting elements that have similar geochemical properties: (e.g., Ba vs. Rb or Nb vs. Th). Moreover, there is less scatter for samples *within* individual regions than for our overall data set. For example, in Nb vs. Th, Atlantic, Indian and Pacific seem distinct, and Gakkel samples have high Ba relative to other elements (Michael et al., 2003). These factors suggest that analytical imprecision plays a small role in the scatter. Samples from the Pacific show the least scattered correlations in Fig. 3, while those from the Indian Ocean and Gakkel Ridge exhibit the poorest correlations. This suggests that both local and regional variations in the trace element characteristics of UD-MORBs are significant, as they are with N-MORBs (Michael, 1995).

CO₂ exhibits moderate correlations with incompatible elements, and is best correlated with Nb and Th (Fig. 4). In these covariation diagrams, the saturated, ultradepleted samples form continuous trends with the undersaturated glasses, supporting the contention that most, if not all, of the saturated magmas did not lose bubbles. The poorest correlations are with Rb and especially with Ba; in the latter case, the saturated, ultradepleted basalt glasses lie away from any crude trends defined by the undersaturated glasses (Fig. 4) because their CO₂ is not as elevated as their Ba. This is true to a lesser degree for Rb than Ba. These characteristics resemble those seen in the covariation of Ba vs. Nb (Fig. 3).

The order of incompatibility of elements for the UD-MORBs can be compared to the widely accepted order for N-MORBs through E-MORBs, which is $Rb \approx Ba > Th \geq Nb > K \geq La > Ce$. The order for UD-MORB may be established by determining the intercepts on element vs. element diagrams (Fig. 3). (The correlation line intersects the axis of the element that is more compatible). For the UD-MORBs, the data are scattered (Fig. 3) but they result in intercepts that are very consistent with the order for N-MORBs-E-MORBs.

The incompatible ranking of CO₂ relative to the lithophile incompatible elements can be determined in a similar fashion (Fig. 4). The relatively tight correlation for CO₂ vs. Nb (Fig. 4c) provides the best-constrained intercept, which is close to the origin, thus providing the smallest range of CO₂/Nb ratios. CO₂ vs. Th has a similar intercept near the origin (Fig. 4d). The CO₂ vs. Ba and CO₂ vs. Rb diagrams (Fig. 4b and 4e) have a larger range of possible intercepts. Considering only the undersaturated glasses (minus Gakkel Ridge) there is less scatter and the intercept is near the origin on the CO₂ axis for both Ba and Rb. Considering both groups of UD-MORBs (saturated and undersaturated) together, the intercept is firmly on the CO₂ axis, suggesting CO₂ behaves more compatibly than Ba or Rb. Moreover, because the increase of CO₂ flattens out with increasing Ba, CO₂/Ba ratios decrease with increasing Ba concentration (not shown) and with increasing incompatible element enrichment. The intercept in CO₂ vs. La (Fig. 4a) is more clearly on the La axis.

The order of incompatibility can also be established from the slopes on ratio *versus* ratio diagrams, where one of the ratios reliably shows depletion/enrichment. We use the La/Nb ratio because they are both highly incompatible elements but Nb is more incompatible than La. We avoid using element vs. ratio plots (e.g. Ba vs. CO₂/Ba) because noisy or random data can produce spurious correlations in these diagrams (Jackson and Somers 1991). In ratio vs. ratio diagrams (Fig. 5) the slopes suggest that the order of incompatibility for ultradepleted basalts is consistent with the order for N-MORBs through E-MORBs.

Important for the present study, slopes of CO₂/La, (and CO₂/Ce or CO₂/Nd, not shown) are all negative when plotted *versus* La/Nb, while CO₂/Nb and CO₂/Th are flat and CO₂/Ba is positive (Fig. 5). This pattern of behavior suggests that CO₂ has a similar incompatibility to Nb within the entire group of UD-MORBs. Atlantic, Pacific and Indian Oceans have similar values. However, there are also regional differences in the ratios of incompatible elements that in some cases exceed the variations that are present through the range of more depleted to less depleted basalts. Most apparent is the previously documented high Ba contents and high Ba/La and Ba/Nb in MORBs from western

Gakkel Ridge (Michael et al., 2003; Goldstein et al., 2008). Gakkel Ridge has lower CO_2/Ba because of anomalously high Ba, and is not included in global averages.

If the saturated, ultradepleted glasses did *not* remain closed systems (as we suggested might be the case if they lost CO_2 bubbles), then their CO_2 contents must be considered as minima, and it would mean that the original (undegassed) CO_2/Nb might have been higher for the less depleted basalt glasses, but decreased during bubble loss. In this case, CO_2/Ba might be as uniform as CO_2/Nb for ultradepleted glasses, which is still generally consistent with the recent experimental evidence (Rosenthal et al., 2015). In summary, the most reliable data are from undersaturated MORBs, and suggest that CO_2/Ba is the most uniform ratio. If there has been no loss of bubbles in the oversaturated UD-MORBs, then CO_2/Nb is the most uniform ratio, and CO_2/Ba decreases with increasing enrichment within the ultradepleted magmas.

4.4 H_2O behavior in UD-MORBs

H_2O contents range from 0.059 to 0.37 weight %. When considering N-MORBs to E-MORBs, H_2O behaves as a moderately incompatible element, like Ce (Michael 1988; 1995; Dixon et al. 1988). We confirm the observation of Danyushevsky et al. (2000) that $\text{H}_2\text{O}/\text{La}$ is more uniform than $\text{H}_2\text{O}/\text{Ce}$ when considering only N-MORBs and UD-MORBs. There is larger range of $\text{H}_2\text{O}/\text{Ce}$ (or $\text{H}_2\text{O}/\text{La}$) for N-MORBs and UD-MORBs than more enriched basalts: from typical values of 150-200 up to values of >500. Regional variations observed in N-MORBs through E-MORBs (Michael, 1995) are also pronounced in UD-MORBs, with high $\text{H}_2\text{O}/\text{Ce}$ for Gakkel ridge (Michael et al., 2003) and some glasses from Gulf of Aden (Table 1). Possible causes of regional variations are: the presence of subcontinental lithospheric mantle containing amphibole or phlogopite; (Goldstein et al., 2008); wet subducted slabs (Michael, 1995; Rau et al., 2007); dry subducted slabs (Dixon et al., 2002); initial variations in the earth's mantle, or inhomogeneities from continental crust formation (Danyushevsky et al., 2000). Further consideration of H_2O is beyond the scope of this paper, except as it may be related to variations in CO_2 (see section 5.6).

5. Discussion

5.1 Source characteristics and petrogenesis of ultradepleted MORB.

In this section, we consider how ultradepleted MORB form. As a group, UD-MORBs have some of the lowest Sr and Pb isotope ratios and highest Nd and Hf isotope ratios measured for MORB, but also include samples with more moderate isotope ratios. They display similar correlations of isotopic ratios (e.g., Sr-Nd and Pb-Pb) with similar regional distinctions as do MORBs in general. For example, Indian Ocean UD-MORBs have higher $^{87}\text{Sr}/^{86}\text{Sr}$ at a given $^{143}\text{Nd}/^{144}\text{Nd}$, and higher $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ than Atlantic or Pacific samples. As a group, correlations between parent/daughter and isotopic ratios are poor or nonexistent. The scatter suggests that much, but not all, of the CO_2 and trace element depletion systematics represents an integrated history of melting and melt removal for incompatible elements, with one or more events that are too recent to yet be recorded in the isotope signatures everywhere. For example, UD-MORB

sources that are not strongly depleted isotopically may have experienced more recent depletion events.

Their tendency to erupt in intra-transform spreading centers and overlapping spreading centers (OSCs) suggests that UD-MORBs form preferentially (but not exclusively) in places where melt aggregation is incomplete, especially in places where deeply derived, enriched melts are not incorporated. One possibility is that deep melts from ascending mantle are channeled toward normal segments that are adjacent to transform faults (or OSCs or near-ridge seamounts), so that the only melts that reach the transform fault are from shallow melting of recently depleted material which has lost an enriched component. But we note that UD-MORBs (or their sources) *cannot* be the depleted mixing end member for the N-MORB to E-MORB array (Fig 7). Their source has higher La/Nb, suggesting it has undergone about 2% greater depletion than the typical N-MORB source. This suggests that additional processes may be important. Ultradepleted melts may reflect two-stage melting of a mantle source where initial, deep melting takes place beneath an adjacent normal ridge segment ridge, and depleted mantle later melts again after it is laterally transported beneath the transform fault (e.g., Wendt et al., 1999; Natland, 1989). In either case, the fact that the isotopic ratios of many of the UDMORBs tend to be the least enriched (i.e., low $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{143}\text{Nd}/^{144}\text{Nd}$) in their region suggests that the initial mantle source starts with enriched and depleted components: e.g., a veined mantle, in which the enriched veins melt deep.

It is also clear from Fig. 7 that the smallest amounts of melting lead to enriched (high-Ba/Nb) melts and depleted (low-Ba/Nb) residues, so are capable of fractionating ratios of incompatible elements, such as Ba/Nb or $\text{CO}_2/\text{H}_2\text{O}$. The extent of melting is probably not low enough to fractionate ratios of the *most* incompatible elements: e.g., those with Ba or CO_2 in the denominator. This is especially true for the residual sources of UD-MORBs that experienced 2% additional melting.

5.2 CO_2 in melt inclusions and “popping rocks”

In order to describe how CO_2 varies relative to incompatible elements, and to estimate the mantle concentration and flux of CO_2 to the surface, it is also necessary to determine CO_2 concentrations in normal mid-ocean ridge basalts (N-MORBs) and in enriched basalts. Although the UD-MORB glass data presented here are sufficiently precise, by themselves they do not provide much “leverage” when determining enrichment trends compared to more enriched basalts. Moreover, N-MORBs and enriched basalts transport by far the bulk of the CO_2 from the mantle to Earth’s surface. But almost all of these more enriched lavas have lost much of their CO_2 during magma ascent, and consequently they no longer preserve accurate CO_2 -trace element co-variations (Gerlach, 1989; Aubaud et al., 2005). We discuss below two types of sample suites that have been used to extend the discussion to more enriched compositions: melt inclusions in N-MORBs and Icelandic lavas, and highly vesicular E-MORBs and OIBs that appear to have ascended and erupted so quickly that no bubble loss occurred. A less direct method involves reconstruction of initial CO_2 abundances by calculation of a degassing history using carbon isotopes and an assumed initial magmatic ^{13}C (Cartigny et al., 2008; Aubaud et al., 2005)

5.2.1 Highly vesicular enriched submarine basalts

Here we briefly discuss key occurrences of enriched submarine basalts that appear to have remained quasi-closed systems with respect to CO₂ loss. There are only four of these well-studied, highly vesicular deep submarine lavas. These include popping rocks from the Mid-Atlantic Ridge (MAR) at 14°N and E-MORBs from the MAR near 35°N. Because MORB examples are so rare, we also include non-MORB occurrences: “petit spot” volcanoes in the Pacific. And, we discuss alkaline lavas from the North Arch volcanic field of the Hawaiian Swell, which are probably associated with the Hawaiian mantle plume. In the last part of this section, we discuss whether vesicular basalts have remained closed systems, or have gained or lost bubbles.

The highly vesicular popping rock: sample 2PiD43 recovered from 3700 m water depth at 14°N on the MAR was proposed to have remained a closed system from the point of initial bubble formation in the mantle through emplacement on the seafloor (Sarda and Graham, 1990; Javoy and Pineau 1991; Pineau and Javoy 1994). Thus, their vesicle CO₂ + dissolved CO₂ might preserve the initial magmatic CO₂ content. However, the breaking of vesicles (popping) has resulted in the loss of much CO₂, so most estimates of initial CO₂ content (Graham and Sarda, 1991; Javoy and Pineau, 1991) have been based on the volume fraction of vesicles rather than CO₂ measurements, and the assumption of near-ideal gas behavior at the depth of eruption. Initial CO₂ contents of ~0.8% (Sarda and Graham, 1990) to ~1.4% (Javoy and Pineau, 1991) have been calculated, but refined estimates are 1.1 – 1.4% CO₂ (Cartigny et al, 2008). Together with our new trace element analyses (Table S3.3) this provides values of 336-615 for CO₂/Nb, and CO₂/Ba is 45-82. We favor the higher estimates, which are slightly higher than those of Cartigny et al. (2008), and more than 2 times higher than the estimate for the popping rock in Saal et al. (2002).

N-MORBs, E-MORBs and alkali basalts collected by submersible around 34°55'N on the MAR included samples that contain <5% up to 65% vesicles (Hekinian et al., 2000). From the vesicle amounts and the concentrations of dissolved volatiles, these authors calculated magma concentrations of 0.1 - 5.76 wt.% CO₂, assuming ideal gas behavior. Their CO₂ amounts are roughly correlated with incompatible element contents. Cartigny et al. (2008) calculated a wide range of CO₂/Nb (190-1947) for these same samples. CO₂/Ba ranges from 31-296 (Fig. 6).

The North Arch volcanic field is a 200 m high flexural arch north of Oahu that formed in response to loading of the Hawaiian Islands (Moore, 1970; Clague *et al.*, 1990). It consists of highly enriched alkali basalts and nephelinites erupted at 3900-4380 m depth. The most vesicular lavas from this area were proposed to represent closed systems, with magmatic CO₂ contents ranging up to 5.4 wt.% (Dixon et al., 1997). Using the calculated CO₂ amounts of Dixon et al (1997) and the trace element analyses of Yang et al. (2003) we calculate CO₂/Nb of 779-1116 and CO₂/Ba of 80-115 for the most vesicular samples (Fig. 6).

“Petit spot” volcanism at the Japan and Tonga trenches consists of small alkali basalt volcanoes that are proposed to form by low extents of decompression melting in the asthenosphere as a response to downgoing plate flexure (Hirano et al., 2006; 2008). Okumura et al. (2013) estimated a wide range of CO₂ contents from 5-10% based on 22-

43% vesicles at eruption depths of 5900 meters. The corresponding range of CO₂/Nb is 717-1505 and CO₂/Ba is 66-155. (Fig. 6).

Whether or not these examples of highly vesicular lavas remained closed systems prior to emplacement is crucial to the validity of their calculated CO₂ contents, and therefore, to their applicability to studies of CO₂ behavior in the mantle. The closed system proposal for the popping rocks (MAR, 14°N) has been questioned but is supported by various lines of evidence. The lava's high vesicularity and primitive nature are consistent with rapid transit from mantle to surface, which would limit bubble segregation. Furthermore, the vesicle size distribution is consistent with continuous bubble nucleation and growth during magma ascent, with minimal bubble loss or accumulation (Sarda and Graham 1990). A notable and distinguishing feature of the popping rocks (MAR, 14°N) is that their ⁴He/⁴⁰Ar* ratio is close to the production ratio for the mantle (~2 to 4) based on its known K/U (~10⁴) and an age range of 0 to 10⁹ years (Graham 2002). Gas loss leads to increased ⁴He/⁴⁰Ar* ratios in MORB magmas, with some cases of ⁴He/⁴⁰Ar* reaching above 100, due to the higher solubility of He with respect to Ar (e.g., Moreira and Sarda 2000). The closed system proposal for the popping rocks (14°N) was also favored by Javoy and Pineau (1994), but they also did not rule out bubble accumulation at the top of a magma column. However, the He/Ar systematics in the MAR popping rock make it difficult to explain its high CO₂ content by bubble accumulation from any typical MORB magma, since low ⁴He/⁴⁰Ar* is only preserved in primitive and relatively undegassed melts. The high $\delta^{13}\text{C}$ (-3.7‰) compared to many other MORBs is also consistent with little or no gas loss (Javoy and Pineau 1991). Dixon et al. (1997) presented additional evidence supporting a closed system assumption for highly vesicular submarine lavas from North Arch, Hawaii. Using calculated bulk H₂O/P₂O₅ contents, they showed that the most vesicular glasses (56% vesicles) were unlikely to have lost or gained bubbles before emplacement. They computed bulk CO₂ contents of up to 5.4±0.4 wt.%.

On the other hand, certain other observations cast doubt on highly vesicular glasses being closed systems, and suggest that bubbles may have been lost or accumulated. The large range of vesicle contents and computed CO₂/incompatible element ratios in lavas of the same composition at 34°N on the MAR (Hekinian et al., 2000) and other areas is consistent with bubble loss or accumulation. Otherwise, extensive mantle heterogeneity in CO₂/incompatible elements is required. Sample 79-6-32-1V (Tables S3.1, S3.2, S3.3), a primitive glassy MORB from Explorer Deep in the NE Pacific has >50% vesicles, and is only moderately enriched in incompatible elements (Michael, 2009), so it has extremely high CO₂/Nb or CO₂/Ba (>600) ratios, possibly reflecting bubble accumulation. Its noble gas composition and vesicle size distribution have not yet been studied. The eruption of deep submarine hyaloclastites (including *limu o Pele*) (Clague et al. 2009) shows that bubble accumulation and segregation certainly occurs in some eruptions or settings. Chavrit et al. (2013) showed that the MAR popping rocks from 14°N deviated from their global correlations of vesicles with spreading rate, mantle enrichment and depth, and proposed that they had accumulated vesicles. In contrast to the view that most MORBs have lost a significant fraction of their bubbles (Gerlach, 1989; Aubaud et al., 2005) while popping rocks have retained them (Graham and Sarda, 1991), Chavrit et al. (2013) argued that the existence of the global correlations shows that most MORBs have not lost many bubbles at all (especially those from slow-spreading ridges);

otherwise no correlations between vesicles and composition or eruption depth should be observed. We feel that these correlations would still be observed even if a large percentage of the bubbles had been lost in most lavas. Essentially, the race between magma ascent and bubble migration means that magmas that produce more bubbles should retain more bubbles, unless the magma stalls at some depth for a significant time period; for example in an axial magma lens such as often observed beneath fast-spreading ridges.

In summary, we suggest that most evidence supports a quasi-closed system assumption for some highly vesicular submarine lavas, especially for those from the MAR 14°N and from North Arch, Hawaii. Evidence for such behavior in the other vesicular examples is weaker and questionable. We feel that most mid-ocean ridge magmas rise more slowly and have lost a majority of their bubbles during ascent.

5.2.2 Melt inclusions in N-MORBs

Typical MORBs have incompatible element enrichment that is intermediate between UD-MORBs and the enriched, highly vesicular popping rocks. Although they rarely preserve their original magmatic CO₂ contents because of degassing (Gerlach, 1989), they sometimes contain olivine-hosted melt inclusions (OHMIs) that preserve evidence of earlier magma compositions that were subsequently overprinted by processes such as magma degassing or mixing (Sobolev and Shimizu, 1993; Saal et al., 2002). CO₂ concentrations in OHMIs in MORBs are often much higher than in their host lavas (Wanless and Shaw, 2012; Shaw et al., 2010). The few sites that have been studied typically have inclusions with a very wide range of CO₂ concentrations, which would be in equilibrium from seafloor depths to several km below the seafloor. Most authors propose that the highest CO₂ contents (and highest CO₂/Nb or CO₂/Ba ratios) in OHMIs most closely approach mantle values, but that even these inclusions may have lost some CO₂ by degassing (Rosenthal et al., 2015). We agree with this assessment and for the sake of clarity, we include only the highest CO₂ inclusions from each studied site in Fig. 6. Even with this filtering, there are still trends *within* each suite of OHMIs, where the most depleted inclusions (higher La/Nb) tend to have the highest CO₂/Nb or CO₂/Ba, suggesting some loss of CO₂ before inclusion entrapment. This would affect the most enriched inclusions the most, and would mean that the low CO₂/Nb or CO₂/Ba values of each OHMI suite plotted in Fig. 6 may be low compared to mantle values.

Additionally, Esposito et al. (2014) demonstrated considerable variation of CO₂ contents within individual melt inclusions and melt inclusion assemblages (groups of inclusions that were trapped simultaneously during crystal growth). They questioned whether melt inclusion analyses by secondary ion mass spectrometry (SIMS) accurately represented CO₂ contents of the melt at the time of entrapment, and suggested that the CO₂ concentration of melt inclusions determined by SIMS has a large uncertainty of about 60%. Consequently, we consider the results of melt inclusion studies that are discussed below with some caution.

In the Pacific, CO₂-rich OHMIs have been studied from the 2005-6 flow at 9°53'N on the EPR and from a site on Juan de Fuca Ridge; these have CO₂ contents approaching 1600 ppm (Wanless and Shaw, 2012). Their CO₂/Nb varies between 700-955 while CO₂/Ba varies from 137-167 (Fig. 6). On Axial Seamount, which straddles Juan de Fuca

Ridge, the CO₂-richest inclusions range up to 3900 ppm CO₂ and have CO₂/Nb=700-800 and CO₂/Ba=100-180 (Helo et al., 2011). One OHMI contained a remarkable 9159 ppm CO₂ with much higher CO₂/incompatible element ratios. In the Atlantic, the recent study of Lucky Strike (Wanless et al., 2015) includes several melt inclusions with >900 ppm CO₂. Atlantic OHMIs with the highest Ce/La have the highest CO₂, and have high CO₂/Nb (476-615) and CO₂/Ba (79-104). Thus the highest CO₂/Nb ratios in OHMIs from Atlantic and Pacific MORBs are intermediate between UD-MORBs and enriched, vesicular basalts from those basins. The average CO₂/Ba for UD-MORBs, OHMIs and enriched basalts is nearly constant, by comparison.

OHMIs in MORBs from the Gakkel Ridge have generally lower CO₂/Nb and CO₂/Ba than OHMIs from the Pacific (Wanless et al., 2014; Shaw et al., 2010), consistent with the lower CO₂/Nb and CO₂/Ba of Gakkel host glasses (Fig. 5). At four sites (85°E, 72°E, 57°E and 31.5°E), inclusions with the highest CO₂ (600-1600 ppm) have CO₂/Nb from 232-440, which is slightly higher than in Gakkel basalts. CO₂/Ba varies from 31-89, and is lower than Atlantic and Pacific OHMIs, similar to Gakkel basalts. This range of ratios for bulk samples and OHMIs partly reflects the anomalously high Ba and wide range of Ba/Nb values along Gakkel ridge (Michael et al., 2003; Goldstein et al., 2007). There are no enriched vesicular rocks from Gakkel Ridge for comparison.

Although a mantle plume has influenced Icelandic basalts, they are examined here because they are related to the Mid-Atlantic Ridge. The three important studies of CO₂ in OHMI from Iceland show consistent CO₂/Nb and CO₂/Ba values for the CO₂-richest inclusions (Fig. 6). OHMIs of the Laki flow of the Eastern Volcanic Zone (EVZ) of Iceland have CO₂-rich vapor bubbles, possibly due to slow cooling. Their total CO₂ ranges up to almost 5000 ppm, with CO₂/Nb values up to 364 and CO₂/Ba up to 89 (Hartley et al., 2014) (Fig. 6). For the subglacial Skuggafjöll eruption, also in the EVZ, the highest CO₂ contents (1200 ppm) are found in depleted inclusions, which have CO₂/Nb up to 417 and CO₂/Ba up to 79 (Neave et al., 2014). Meanwhile, CO₂/Nb values of undegassed melt inclusions from Borgarhraun in the Northern Volcanic Zone of Iceland are reported as 314±125 (Hauri et al., 2002). Thus OHMIs from Iceland have similar CO₂/trace element ratios as those from Gakkel Ridge.

5.3 CO₂ behavior relative to incompatible elements

When the full range of compositions from UD-MORBs → OHMIs → highly vesicular enriched basalts is considered together, CO₂/Nb (and CO₂/Th) increase with increasing enrichment (Fig. 6), while CO₂/Ba is constant, at 105±9 (Table 1). This observation is consistent with a recent experimental study (Rosenthal et al., 2015), which showed that partition coefficients of CO₂ between melt and olivine, orthopyroxene, clinopyroxene and garnet at 0.8-3.0 GPa and 1250-1500°C are lower than those of Nb and slightly higher than those of Ba. It is also consistent with Rosenthal et al.'s conclusions that were based on basalt compositions. Moreover, it is consistent with the trends that are observed when undersaturated, UD-MORBs are considered alone (Fig 5).

We also showed that when *all* of the UD-MORBs (undersaturated and saturated) are considered together, CO₂/Nb or CO₂/Th are constant and CO₂/Ba decreases with increasing enrichment (Fig. 5). If this trend is valid and is not due to CO₂ loss from the

saturated UD-MORBs, then we must consider why it contrasts with the overall trend. One possible explanation is that the highly vesicular samples from the Pacific and from 34°55' on the MAR, which largely account for the increase in CO₂/Nb with increasing enrichment, have accumulated bubbles, leading to an incorrectly high estimate of CO₂/Nb in enriched basalts. This possibility is discounted by the fact that the most reliable OHMIs have CO₂/Nb that is intermediate between UD-MORBs and enriched, vesicular basalts. In other words, the increasing trend of CO₂/Nb is still apparent when considering only UD-MORBs and OHMIs. A second alternative is that the partition coefficients for CO₂ and incompatible elements were different during the formation of the UD-MORB sources, as compared to the formation of the E-MORB sources. The depletion-enrichment events that formed these different sources may have occurred at different pressures, or by different extents of melting. The UD-MORB source can be modeled by about 2% depletion (Fig. 7) of N-MORB mantle source or 1% depletion of DMM. In contrast the E-MORB source might form by enrichment from low-extent melts that formed by 0.1% melting of a N-MORB mantle source, or even less melting of DMM (Fig. 7; see also Donnelly et al., 2004). Partition coefficients might change over this interval of melting.

The enrichment and depletion of CO₂ relative to other elements may also be subject to regional variations. Gakkel Ridge and the northernmost Atlantic (e.g., Iceland) appear to have low CO₂/Ba and CO₂/Nb compared to other regions. It is already known that H₂O/Ce, Ba/Nb and Ba/La are elevated in MORBs from the northernmost MAR northward to Gakkel Ridge (Michael, 1995; Goldstein et al., 2008; Michael et al. 2003, 2009). The difference in CO₂/Ba between the MAR 34°55'N and Laki melt inclusions could also be a result of regional variation. Essentially, it means that CO₂/Ba in the enriched mixing component is regionally variable, and that the anomalous Ba enrichment in that region is not accompanied by a similar enrichment in CO₂.

5.4 Concentration of CO₂ in MORBs and the mantle

Recent compilations of the mean composition of MORBs, especially that of Gale et al. (2013) which includes a large set of high-quality analyses and more realistic averaging than earlier studies, enable more accurate estimates of the average concentration of CO₂ in MORB magmas and in the mantle. The concentration of CO₂ in “mean undegassed MORBs” would be 3066⁺⁶⁹⁶/₋₆₂₈ ppm, using our highly averaged estimate for CO₂/Ba (105±9; Table 1), and Gale et al.’s. (2013) arithmetic mean of Ba concentration for “ALL MORBs” (29.2 ppm±3.8). Their values were calculated as the mean for all possible segments except back-arc basins, weighted by spreading rate and segment length. Using the same method with our average CO₂/Nb ratio results in a mean CO₂ concentration of ALL MORB of 3166 ppm, but it is less reliable because of the large range of CO₂/Nb ratios from depleted through enriched lavas. It would require weighting the different lava types by volume and by Nb concentration. By comparison, Cartigny et al.’s (2008) estimate of CO₂ in average MORB (1800 ppm) is lower, mostly because they used a lower concentration of Nb: 3.31 ppm vs. 5.24 ppm for ALL MORB in Gale et al. (2013).

The mean concentration of CO₂ estimated for mean undegassed MORBs (3066 ppm CO₂) must be corrected for fractional crystallization to be used for estimating CO₂

flux and mantle CO₂ concentration. The Mg# of “ALL MORB” (Gale et al., 2013) is 60.7 if Fe³⁺/Fe_{total} = 0.16 (Cottrell and Kelley, 2011). From least squares mixing calculations (see Supplemental Materials 4 and Michael and Chase, 1987), we estimate that 32% crystallization of plagioclase + clinopyroxene + olivine can account for the evolution from near primary liquids (Mg#=70) to liquids with Mg#=60.7. The mean CO₂ concentration in near-primary, undegassed MORBs would therefore be 2085⁺⁴⁷³/₋₄₂₇ ppm. By similar calculations, the mean “NORMAL MORB” of Gale et al. (2013), which includes only mid-ocean ridge segments located >500 km from hotspots would contain 2625 ppm CO₂ before degassing, which would be 1840 ppm CO₂ for the primary magma after correction for fractional crystallization.

Estimates of the mantle’s CO₂ and incompatible element concentrations depend strongly on how melting takes place. In the simplest model, the mantle concentration (C_S) would be calculated directly from the primary magma composition (C_L). Because Ba and CO₂ are nearly perfectly incompatible, and would enter the liquid completely, their concentration in the source (C_S) would be calculated as:

$$C_S = C_L * F, \text{ where } F = \text{extent of melting.}$$

We estimate F of ALL MORB from its Na_{8.0} and Na₉₀ contents: 2.69% and 2.20%, respectively. (These are the wt.% Na₂O corrected for fractionation to 8 wt.% MgO, or to a liquid in equilibrium with Fo₉₀ olivine, using typical slopes for MgO vs. Na₂O). Considering the ranges of Na_{8.0} (1.9-3.2%) and extent of melting (22%-8%; Klein and Langmuir, 1987; Langmuir et al., 1996; Gale et al., 2014; their Fig. 21) this corresponds to about 13% melting (12% melting for N-MORB). The mean concentration of CO₂ in the ALL MORB mantle would then be 271⁺⁶²/₋₅₆ ppm (74⁺¹⁷/₋₁₅ ppm C) and their N-MORB mantle has 183 ppm CO₂ (50 ppm C). (The estimated uncertainties do not account for uncertainties in the corrections for crystallization or melting). These estimates for N-MORB and ALL MORB are at the low end of the broad range (180-920 ppm) suggested by Trull et al. (1993) but are much higher than the estimates of Chavrit et al. (2013) (66-78 ppm CO₂) that were based on vesicle contents of MORB glasses, also using the simple melting model.

However, the simple melting model may yield inaccurate mantle concentrations for highly incompatible elements. MORB variability in highly incompatible element ratios such as Th/U, U/Pb and Rb/Sr, considered in the framework of isotope systems (²³⁰Th/²³⁸U, ²⁰⁶Pb/²⁰⁴Pb and ⁸⁷Sr/⁸⁶Sr, respectively), reveals that even highly incompatible elements may be fractionated during melting beneath ridges (Galer and O’Nions, 1986). This may be explained by the separation of a small fraction (F ~ 0.1%) of enriched melt at depths below the peridotite solidus. If so, then the volume of mantle contributing to the major elements in mid-ocean ridge basalts may be less than the volume supplying the incompatible trace elements. Workman and Hart (2005) and Salters and Stracke (2004) calculated concentrations of all elements in the depleted MORB mantle (DMM and DM, respectively) that would better account for their isotopic ratios. These more depleted compositions may be closer to the actual MORB source composition and are consistent with models in which the upwelling mantle melts by a more complex process that involves the initial formation of small-F, carbonated silicate melts at >200km depth (Dasgupta et al., 2007; 2013). In this model, highly incompatible elements are scavenged from a larger mantle volume than the volume that supplies most of the major elements

(Hirschmann and Dasgupta, 2009, and consequently a much more depleted mantle source would be able to produce the trace element characteristics of N-MORB or ALL MORB. Using our estimate of CO_2/Ba of 105 ± 9 and the Ba content of DM (Salters and Stracke, 2004; 1.2 ppm with 49% uncertainty), the mantle CO_2 would be 126^{+78}_{-68} , which is higher than their estimate of 50 ppm that relied on Saal et al.'s (2002) CO_2/Nb ratio. For Workman and Hart's (2005) DMM (0.56 ppm Ba), mantle CO_2 would be 59^{+43}_{-34} ppm. Rosenthal et al.'s estimate of mantle CO_2 using DMM (75 ± 25) is similar. In summary, the uncertainties in the CO_2/Ba of MORB contribute less to the uncertainty in mantle CO_2 content than do the uncertainties in incompatible element concentrations. The melting model that is used is at least as important as the proxy element ratios in calculating the mantle's CO_2 content.

5.5 CO_2 flux from mid-ocean ridges

The flux of CO_2 from mid-ocean ridge magmatic activity can be calculated as the product of the arithmetic mean of the concentration of CO_2 of primary basalts that are supplied to the ridge and the volume of basaltic magma that is produced.

There are several estimates of the volume of magma produced at mid-ocean ridges. Schilling et al. (1978) estimated a rate of $20 \text{ km}^3/\text{yr}$. Newer estimates for current crustal mid-ocean ridge flux range from $21 \text{ km}^3/\text{yr}$ (Crisp, 1984) to $22.4 \text{ km}^3/\text{yr}$ (Cogne and Humler, 2006), and are all based on the assumption of an average crustal thickness of 7 km. The areal estimate ($3.06 \text{ km}^2/\text{yr}$) of Gale et al. (2013) yields a similar estimate (21.4 km^3) for 7 km-thick crust. At this point, crustal thickness, widely assumed to be 7 km, is among the most poorly constrained variables for estimating MOR magma flux. Recently, much thinner crust and exposed peridotites have been discovered along ultraslow ridges (Michael et al., 2003; Jokat et al., 2003), at ocean core complexes (Dick et al. 2010) and some elevated ocean ridges (Zhou and Dick, 2013). Although these ultraslow and slow-spreading ridges are less influential in flux estimates, we speculate that actual magma flux may be lower than the above estimates. Using our estimate for average primary MORB of 2085^{+473}_{-427} ppm CO_2 , and the range of 20 - 22.4 km^3 of basalt, we estimate a mid-ocean ridge flux of $1.25 \pm 0.16 \times 10^{14} \text{ g/yr CO}_2$, with possible values as low as 0.93 and as high as $1.61 \times 10^{14} \text{ g/yr}$.

Our estimates using Ba are about half of the Rosenthal et al. (2015) estimate ($2.5\text{--}2.9 \times 10^{14} \text{ g/yr}$) that was also based on CO_2/Ba in basalts. Three factors account for the difference. First, we corrected for fractional crystallization (0.68x). Second, we estimate $\text{CO}_2/\text{Ba} = 105 \pm 9$ instead of 133 ± 44 (0.79x). Finally, we use only the Ba estimate ($29.2 \pm 3.8 \text{ ppm}$) of Gale et al. (2013) and do not consider the higher estimate of Arevalo and McDonough (2010) (0.85x). Compared to earlier estimates based on CO_2/Nb , our estimate is higher than that of Saal et al. (2002) ($4.0 \pm 1.2 \times 10^{13} \text{ g/yr}$) who used the low CO_2/Nb ratio of UD-MORBs. Our estimate overlaps with more recent estimates of $1.0^{+1.19}_{-0.57} \times 10^{14} \text{ g/yr}$ by Cartigny et al., (2008) and is slightly higher because the ALL MORB value we used is more enriched than their mean MORB value.

CO_2 flux estimates based on trace element proxies in basalts can be compared to flux estimates calculated by other means. Our estimate is slightly lower than the $1.6^{+0.6}_{-0.3} \times 10^{14} \text{ g/yr}$ of Aubaud et al. (2005), that was based on CO_2 abundances of basalts from Pito Deep that were reconstructed through modeling carbon isotopic changes during

degassing. As expected, our estimate is much higher than the $3.8 \pm 1.2 \times 10^{13}$ g/yr flux estimated by Chavrit et al., (2012) which was based on vesicle abundances (see section 5.2.1).

Our estimate is similar to the $1.0 \pm 0.4 \times 10^{14}$ g/yr that was estimated by Marty and Tolstikhin (1998) using the $\text{CO}_2/{}^3\text{He}$ ratio in basalts ($2.2 \pm 0.9 \times 10^9$) and measurements of ${}^3\text{He}$ flux into the abyssal oceans (1000 moles/year) (Craig et al., 1975; Farley et al., 1995). However, new global ocean circulation models (Bianchi et al., 2010) result in lower estimates of ${}^3\text{He}$ input into the ocean by about a factor of two from the original estimate of Craig et al., and therefore lead to lower estimates of the CO_2 flux from mid-ocean ridges that contrast with our estimates. These lower flux estimates are closer to those of Saal et al. (2002) and also Chavrit et al. (2014).

The reason why the CO_2 flux calculated using Bianchi et al.'s (2010) lower ${}^3\text{He}$ flux estimates is lower than our flux estimate may lie with the choice of a mantle $\text{CO}_2/{}^3\text{He}$ ratio, and the way that this ratio is calculated globally. Marty and Tolstikhin, (1998) tabulated $\text{CO}_2/{}^3\text{He}$ for 23 MORBs and calculated a mean of 2.2×10^9 . Resing et al. (2004) estimated a similar $\text{CO}_2/{}^3\text{He}$ based on CO_2 and He contents of hydrothermal plumes from Axial Seamount and the East Pacific Rise (9°N). But with increasing mantle enrichment, CO_2 and He are expected to increase substantially, while $\text{CO}_2/{}^3\text{He}$ appears to increase (e.g., Kingsley and Schilling, 1995). $\text{CO}_2/{}^3\text{He}$ in fluid inclusions of enriched mantle xenoliths is greater than 2×10^9 (Trull et al., 1993), as are fumarolic emanations from Kilauea (Marty and Jambon, 1987). The incompatible element enriched popping rock (MAR 15°N) has a considerably higher $\text{CO}_2/{}^3\text{He}$ ratio: 7.5×10^9 in the glass and perhaps 3×10^9 overall (calculated from data in Graham and Sarda, 1991).

We suggest that $\text{CO}_2/{}^3\text{He}$ ratio that is output by mid-ocean ridge magmatism globally should be weighted more toward enriched basalts that would be expected to have higher CO_2 and He concentrations and higher $\text{CO}_2/{}^3\text{He}$ ratios than the mean ratio in MORBs. Essentially, the ratio should be calculated from the mean concentrations of CO_2 and He in MORBs prior to any degassing, and not as the mean of the $\text{CO}_2/{}^3\text{He}$ ratios. However, this calculation is not straightforward because the original concentrations have all been changed drastically by volatile loss. The fact that Gale et al.'s (2013) ALL MORB is more enriched in incompatible elements than most estimates of N-MORB also supports use of a higher $\text{CO}_2/{}^3\text{He}$ ratio in flux calculations based on ${}^3\text{He}$. A second factor that could lead to underestimates of the true $\text{CO}_2/{}^3\text{He}$ ratio in primary magmas relates to the degassing path. For example, early equilibrium Rayleigh degassing (via the Henry's Law predicted solubilities of CO_2 and He) produces a volatile phase with elevated $\text{CO}_2/{}^3\text{He}$ compared to the initial magma. The loss of such a high- $\text{CO}_2/{}^3\text{He}$ gas phase consequently leads to lower $\text{CO}_2/{}^3\text{He}$ in the residual magma, and therefore in the basalt glasses or their vesicles that are subsequently analyzed (Marty and Zimmerman, 1999). This early (equilibrium) high- $\text{CO}_2/{}^3\text{He}$ gas phase is different from the commonly observed late-forming vesicles that form during eruption, which may have relatively low $\text{CO}_2/{}^3\text{He}$ because of kinetic fractionation during rapid magma ascent and emplacement on the seafloor (Gonnerman and Mukhopadhyay, 2007; Graham et al., 2014).

5.6 Relation of CO_2/Ba to other ratios in UD-MORBs

In this section, we briefly return to UD-MORBs to search for correlations between CO_2/Nb and isotopic and trace element ratios that would illuminate how CO_2 might be related to the evolution of the mantle source.

CO_2/Nb is also not correlated with other trace element ratios that are constant between depleted and enriched components. It is not correlated with $\text{H}_2\text{O}/\text{Ce}$ (Michael, 1995), suggesting that if variations in $\text{H}_2\text{O}/\text{Ce}$ are related to subduction components such as wet or dry slabs, that H_2O and CO_2 become decoupled during subduction. CO_2/Nb and CO_2/Ba are not correlated with Sr/Nd ratio, which might be expected if there was extra residual carbonate mineral during evolution of the depleted source. CO_2/Nb also seems unrelated to the interesting Ba enrichment observed along Arctic mid-ocean ridges (Michael et al., 2003). Whatever source material gives these MORBs their elevated Ba and Ba/La, it does not also have extra CO_2 . It could be continental lithospheric mantle (Goldstein et al., 2008). If so, it would suggest that continental lithospheric mantle has low CO_2/Ba , and that, unlike phlogopite, carbonates were not residual after the evolution of the proposed source by small extents of melting.

6. Summary

1. The most reliable measurements of CO_2 in ocean basalts are for ultradepleted MORBs that remained undersaturated in volatiles and never produced bubbles. Ultradepleted undersaturated MORBs from the Atlantic, Pacific and Indian have uniform CO_2/Nb ratios of 283 ± 32 (averaged by ocean) that confirm values of earlier studies from a single site in the Pacific (Saal et al., 2002) and show that they are globally applicable. Their CO_2/Ba ratio is uniform at 98 ± 10 .
2. Considering a wide range of ocean basalts, from ultradepleted MORBs to depleted melt inclusions to enriched vesicular basalts, CO_2/Nb increases with enrichment while CO_2/Ba is constant, showing that CO_2 behaves more like Ba. The result confirms experimental studies and additional analytical data for basalts (Rosenthal et al., 2015).
3. Based on our estimate of the CO_2/Ba ratio and a comprehensive compilation of the average compositions of ocean ridge basalts (Gale et al., 2013), an average primary MORB has 2086 ppm CO_2 and the average primary NMORB has 1840 ppm.
4. The calculated concentration of CO_2 in the NMORB mantle is 126 ppm for the estimated mantle composition of Salters and Stracke (2004), 59 ppm for the estimate of Workman and Hart (2005) and 183 ppm if MORB from as simple batch melts of the mantle. The melting model contributes greater uncertainty to estimates of CO_2 in the mantle than does the CO_2/Ba ratio.
5. The annual flux of CO_2 from mid-ocean ridges is $1.25 \pm 0.16 \times 10^{14}$ g/yr, with possible values as low as 0.93 and as high as 1.61×10^{14} g/yr. The value is approximately 0.3% of the anthropogenic addition of CO_2 to Earth's atmosphere (Friedlingstein et al., 2010).

Acknowledgements

The authors were supported by the U.S. National Science Foundation: Grants OCE0242902, PLR0425892, OCE1132038, OCE1259916 to PJM and Grant OCE1259964 to DWG. However, all inferences, suggestions and conclusions are the

authors'. PJM recognizes support from the endowment provided by the McMan Chair in Geosciences of the University of Tulsa. We thank Adam Kent for guidance and help in carrying out the laser ablation analyses in the ICP-MS facility at OSU. Samples were collected many different seagoing expeditions involving the authors and many other investigators. We thank the Smithsonian, URI and OSU repositories for providing sample materials. Figure 1 and maps in the Supplementary Information were produced using GeoMapApp (<http://www.marine-geo.org/geomapapp>), which is supported by the National Science Foundation and internal funding from Lamont-Doherty Earth Observatory. We thank Marc Hirschmann and Pierre Cartigny for their thoughtful and constructive reviews.

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Figure Captions

Figure 1. Locations of ultradepleted mid-ocean ridge basalts used in this study. Red=Atlantic Ocean; Green=Indian Ocean; Blue=Pacific Ocean; Black=Arctic Ocean. Circles denote volatile undersaturated glasses while triangles denote saturated glasses (see text). Square represents three saturated back-arc basin basalts from Lau basin. Inset: Gakkel ridge, Arctic Ocean. Details of each location are presented in Supplemental Materials.

Figure 2. Collection pressure versus volatile pressure for ultradepleted MORB glasses. Collection pressure is based on dredge or dive depth, and is calculated using the equations for seawater pressure and density that take into account the compression of seawater with depth and the variation of gravity (g) with latitude (Fofonoff and Millard, 1983). Volatile pressure is the pressure (MPa) at which the liquid would be volatile saturated with its dissolved ($\text{CO}_2 + \text{H}_2\text{O}$) content. It is calculated using VolatileCalc (Newman and Lowenstern, 2002) with measured dissolved CO_3^{2-} and $\text{H}_2\text{O} + \text{OH}^-$ in the glasses (Table S3.2). Pressure increases approximately 1MPa per 100 m water depth. Filled symbols (UndersatMORBs) are volatile undersaturated: they contain no vesicles and yielded extremely low (≈ 0 ppm) CO_2 when crushed. All of them were recovered at depths below their saturation depth based on their volatile pressure. Open symbols with crosses are oversaturated (SatMORBs) and contain vesicles, and yielded significant amounts of CO_2 when crushed. All of them were recovered at depths shallower than their saturation depth. Horizontal lines with some symbols show the minimum and maximum dredge depths, where available. Symbols without lines are based on submersible depths, or rock core depths or average dredge depths.

Figure 3. – Covariation of incompatible elements in ultradepleted MORB glasses. Concentrations are normalized to $\text{Mg\#} = 68$, where $\text{Mg\#} = 100 * \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$, and $\text{Fe}^{2+} = 0.9 * \text{Fe}_{(\text{total})}$. The normalization procedure is described in Supplemental Materials 4. Element_{68} is preferred over raw concentration data because fractional crystallization can improve poor correlations or create spurious ones. All symbols as in Fig.2. Linear regressions in each figure include all ultradepleted basalts except those for Gakkel Ridge. Regressions were calculated keeping both variables independent, and including errors for both x and y (York, 1966). The small black rectangle is the intercept, which lies on the axis of the element that is more compatible. The rectangle represents ± 1 std. dev. of the calculated intercept. Regression parameters (slope and intercepts) are given in Table S5.1. Data sources are described in Table S3.3. All data for undersaturated MORB are from this work except ALV2384-009. Data for saturated, ultradepleted MORB are mostly from this work and also include data from: Saal et al. (2002); Gale et al. (2013); Langmuir, (Pers. Comm.); Jenner & O'Neill (2012); Cartigny et al. (2008); Michael (unpub. Solution ICP-MS); Kelley et al. (2013); Christie et al. (2004); Escrig et al. (2009); Schilling et al. (1995).

Figure 4. Covariation of total CO_2 (dissolved + vesicle components, in ppm) with incompatible element concentrations (in ppm). Symbols, data and regressions as in Figs.

2 and 3. All concentrations are normalized to $Mg\#=68$ to account for different amounts of fractional crystallization.

Figure 5. La/Nb versus CO_2 /incompatible element ratios for ultradepleted MORB glasses. La/Nb is used as an (positive) indicator of source depletion. For the entire group of ultradepleted MORB, there is a rough positive correlation between La/Nb and CO_2/Ba and a negative correlation with CO_2/La , while CO_2/Nb and CO_2/Th are relatively flat. The smaller group of undersaturated glasses have either CO_2/Nb or CO_2/Ba as the most uniform ratios. Symbols and data as in Fig. 2.

Figure 6. La/Nb versus CO_2 /incompatible element ratios for ultradepleted MORB glasses, olivine hosted melt inclusions (OHMIs; small squares), EMORBs and OIBs (triangles or diamonds). Circle symbols and data as in Fig. 2. Data sources are: Wanless et al. (2014) and Shaw et al. (2010) for Gakkel OHMIs; Neave et al. (2014), Hartley et al. (2014) and Hauri et al. (2002) for Icelandic OHMIs; Wanless et al. (2015) for Atlantic OHMIs; Helo et al. (2011) and Wanless and Shaw (2012) for Pacific OHMIs. Dixon et al. (1997) and Yang et al. (2003) for North Arch, Hawaii; Javoy and Pineau (1991), Pineau et al. (2004), Graham and Sarda (1991), Cartigny et al. (2008) and Hekinian et al. (2000) for Atlantic E-MORBs; Hirano et al. (2006, 2008) and Okumura and Hirano (2013) for Pacific EMORBs and Petit Spot.

Figure 7. La/Nb vs. Ba/Nb of MORBs and intraplate vesicular glasses. Filled circles (volatile undersaturated) and circled crosses (volatile saturated) are ultradepleted MORBs (this study). The modeling shows an enrichment and depletion scenario similar to the two-stage process outlined by Donnelly et al. (2004). We start with a typical N-MORB (19.6 ppm Ba, 4.19 ppm La, 3.62 ppm Nb; Gale et al., 2013), that would have a source containing 1.6 ppm Ba, 0.34 ppm La, 0.30 ppm Nb (orange star; after correction for 32% crystallization and 12% batch (equilibrium) melting). A highly enriched liquid (low-F melt) formed by 0.1% melting of that source (red cross in upper left corner) has 1334 ppm Ba, 31.0 ppm La, and 120 ppm Nb. The metasomatized source for E-MORBs (open star) consists of the original N-MORB source (99.5%) plus 0.5% of this highly enriched liquid. Because MORBs form by large extents of melting, the MORB source and the MORB liquids are presumed to have the same ratios in this diagram. The fractionation of highly incompatible elements in that E-MORB source is a result of the 0.1% melting. For reference, red crosses are liquids that form at 0.1%, 0.2%, 0.5%, 1%, 2%, 3%, 4%, 5% etc. melting (left to right).

Orange crosses and thick black line show the solid residue for 0.1%, 0.2%, 0.5%, 1%, 2%, 3% and 4% melting (left to right). All model residues retain 0.05% melt in the source (otherwise their Ba content approaches 0). Note that about 0.5% - 4% melting is needed to produce the source of UD-MORBs, whereas the source of a less-depleted MORB might form by 0.1-0.2% melting, like the low-F melt. Melting for liquids and residues is non-modal. Bulk solid distribution coefficients (D) for Ba, La and Nb are 0.0002, 0.01 and 0.0015, respectively. Bulk distribution coefficients of phases contributing to the melt (P) for Ba, La and Nb are 0.0005, 0.045 and 0.0045, respectively. The model results on this diagram are very sensitive to the distribution coefficients used.

The entire modeling exercise could also be carried out with DM as the starting mantle (Salters and Stracke, 2004) instead of a N-MORB source. In that case, the low-F melt and the residue needed to account for the source of UD-MORB would both form by slightly less melting than the figure shows.

The negative trend displayed by most Mid-Atlantic Ridge and East Pacific MORBs and seamounts is consistent with variable amounts of enriched, low-F melt or E-MORB source mantle, mixing with either an N-MORB (*not* UD-MORB) source mantle, or with an N-MORB mantle residue produced during earlier extraction of a low degree partial melt (illustrated here as 0.1 %). In this diagram, UD-MORB liquids and their UD-MORB sources plot together.

Table 1. Average CO₂/Nb and CO₂/Ba for concentration and flux estimates.

	CO ₂ /Ba ±		CO ₂ /Nb ±		samples or sites
<u>Ultradepleted</u>					
<u>MORBs</u>					
Atlantic ¹	100	1	285	12	n = 2
Pacific ¹	107	29	250	44	n = 9
Indian ¹	87	7	314	103	n = 2
Gakkel ¹	27	2	212	86	n = 3
UDMORB²	98	10	283	32	average²
<u>E-MORBs/</u>					
<u>OIBs</u>					
Atlantic ³	119	53	843	322	14°N, 34°N
Pacific ³	103	6	1029	4	N. Arch, Petit Spot
EMORB/					
OIB	111	11	936	132	average⁴
<u>Olivine-Hosted</u>					
<u>Melt Inclusions</u>					
Atlantic ³	88	14	554	71	Lucky Strike
Pacific ³	126	26	652	162	Axial, 9.8°N, Juan de Fuca
Gakkel ³	46	23	288	112	32°E, 39°E, 57°E, 73°E, 85°E
OHMI	106	24	603	69	average⁴
Preferred					
<u>Global⁵</u>	105	9	607	327	
ppm	Ba	±	Nb	±	
Gale et al.	29.2	3.8	5.24	0.59	
Calculated	105xBa		607xNb		
Ppm CO ₂	3086		3181		

¹Average and standard deviation (1-sigma) of ratios for individual samples from that ocean. Includes only undersaturated, ultradepleted MORBs.

²Average and standard deviation (1-sigma) of Atlantic, Pacific and Indian Ocean averages. (No Gakkel).

³Average and standard deviation (1-sigma) of site averages from each ocean. Each site's average (not shown) is the average of individual samples for that location. For OHMIs, only samples with the highest CO₂/Ba or CO₂/Nb ratios were included (see Fig. 6).

⁴Average and standard deviation (1-sigma) of the Atlantic and Pacific Ocean averages.

⁵Average and standard deviation (1-sigma) of averages of: UD-MORBs; E-MORBs and OIBs; and OHMIs.

Gakkel Ridge is excluded from the averages because it has anomalously high Ba, and ultraslow spreading so it would overly influence flux estimates.

Outliers such as the OHMI from Axial seamount with 9159 ppm CO₂ (Helo et al., 2013) were also excluded.