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Invited review article

The behavior and concentration of CO_2 in the suboceanic mantle: Inferences from undegassed ocean ridge and ocean island basalts

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ABSTRACT

In order to better determine the behavior of CO_2 relative to incompatible elements, and improve the accuracy of mantle CO_2 concentration and flux estimates, we determined CO_2 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. Fifteen contained no vesicles and were volatile undersaturated for their depth of eruption. Thirty-six contained vesicles and/or were slightly oversaturated, and so may not have retained all of their CO_2. If this latter group lost some bubbles during emplacement, then CO_2/Ba calculated for the undersaturated group alone is the most reliable and uniform ratio at 98 ± 10, and CO_2/Nb is 283 ± 32. If the oversaturated MORBs did not lose bubbles, then CO_2/Nb is the most uniform ratio within the entire suite of ultradepleted MORBs at 291 ± 132, while CO_2/Ba decreases with increasing incompatible element enrichment.

Additional constraints on CO_2/Ba and CO_2/Nb ratios are provided by published estimates of CO_2 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, CO_2/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, CO_2/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 CO_2 contents of MORBs, with an overall average CO_2/Ba = 105 ± 9. Atlantic, Pacific and Indian basalts have similar values. Gakkel Ridge has lower CO_2/Ba because of anomalously high Ba, and is not included in our global averages.

Using the CO_2/Ba ratio and published compilations of trace elements in average MORBs, the CO_2 concentration of a primary, average MORB is $2085^{+473}/_{-427}$ ppm, while primary NMORB magmas (>500 km from ocean island hotspots) have 1840 ppm CO_2. 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. This amount is equivalent to approximately 0.3% of the anthropogenic addition of CO_2 to Earth's atmosphere. NMORB mantle has 183 ppm CO_2 (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 CO_2 in the depleted mantle: around 60–130 ppm CO_2, with large uncertainties that are more related to melting models than to CO_2/Ba. CO_2/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 CO_2/Ba ratios, showing that these regional high Ba anomalies are not accompanied by correspondingly high CO_2 concentrations.

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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; Michael, 1988; Saal et al., 2002). 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 H_2O/Ce ratio (Dixon et al., 1988; Michael, 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 (Dixon et al., 1995; Gerlach, 1989; Stolper and Holloway, 1988). 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 (Cartigny et al., 2008; Scaillet and Pichavant, 2004). 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 (Graham and Sarda, 1991; Pineau et al., 2004; Sarda and Graham, 1990). 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., 2014).

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 CO_2 flux estimates with those derived from comparison to noble gases, especially helium (Marty and Tolstikhin, 1998). Indirect estimates of CO_2 in MORB by noble gas degassing calculations also broadly support the constancy of CO_2/Nb (Burnard et al., 2014).

Here we present new CO_2 and trace element data from additional ultradepleted mid-ocean ridge basalts (UD-MORBs) to determine how variable the CO_2/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 (Hirano et al., 2006; Okumura and Hirano, 2013) in order to determine if there are consistent relationships between incompatible elements and CO_2 for enriched rocks. We discuss the question of bubble accumulation and loss in such rocks, and in MORBs in general. Recent studies of CO_2 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; Hauri et al., 2002; Neave et al., 2014) provide additional data that we evaluate as proxy elements for CO_2. With the development of more accurate proxies for CO_2, we then calculate revised values for CO_2 flux from the mantle, consider mantle CO_2 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 K_2O. Two-sigma precision, based on multiple three-spot analyses of the same basalt glass, was ±0.004% K_2O.

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