CO₂ content beneath northern Iceland and the variability of mantle carbon

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ABSTRACT

Primitive basalt melt inclusions from Borgarhraun, northern Iceland, display large correlated variations in CO₂ and nonvolatile incompatible trace elements (ITEs) such as Nb, Th, Rb, and Ba. The average CO₂/ITE ratios of the Borgarhraun melt inclusion population are precisely determined (e.g., CO₂/Nb = 391 ± 16; 2σM [two standard errors of the mean], n = 161). These data, along with published data on five other populations of undegassed mid-oceanic ridge basalt (MORB) glasses and melt inclusions, demonstrate that upper mantle CO₂/Ba and CO₂/Rb are nearly homogeneous, while CO₂/Nb and CO₂/Th are broadly correlated with long-term indices of mantle heterogeneity reflected in Nd isotopes (¹⁴⁷Nd/¹⁴⁴Nd) in five of the six regions of the upper mantle examined thus far. Our results suggest that heterogeneous carbon contents of the upper mantle are long-lived features, and that average carbon abundances of the mantle sources of Atlantic MORB are higher by a factor of two than those of Pacific MORB. This observation is correlated with a similar distinction in water contents and trace elements characteristic of subduction fluids (Ba, Rb). We suggest that the upper mantle beneath the younger Atlantic Ocean basin contains components of hydrated and carbonated subduction-modified mantle from prior episodes of Iapetus subduction that were entrained and mixed into the upper mantle during opening of the Atlantic Ocean basin.

INTRODUCTION

Magmas deliver carbon from Earth’s upper mantle and release it to the atmosphere and oceans as CO₂. The presence of carbon in the mantle can influence the depth of melting within the mantle (Dagaut and others, 2013), and CO₂ bubbles in magmas can influence the style of explosive eruptions (Hekinian and others, 2000; Clague and others, 2009). The release of CO₂ into the atmosphere also affects long-term global climate and may provide a positive feedback mechanism to volcanism (Huybers and Langmuir, 2009) that may also influence the response of mid-ocean ridge magmatism to glaciation (Maclellan, 2002) and possibly sea-level changes (Burley and Katz, 2015; Tolstoy, 2015). However, the solubility of carbon in silicate melt decreases strongly with decreasing pressure (Dixon and others, 1995), and so most magmas arrive at Earth’s surface having lost most of their carbon via degassing. To circumvent the effects of the degassing process, in this study we examine silicate melt inclusions, which are tiny samples of quenched magma (typically <200 μm diameter) trapped in crystals that grow in the magma prior to eruption. By virtue of being enclosed within their crystal hosts, melt inclusions are prevented from degassing their volatiles during volcanic eruptions, and can be used to study the carbon content of magmas at the time and depth at which the inclusions were trapped. Despite this advantage, nearly all melt inclusion studies that have determined carbon contents, with two exceptions (Saal and others, 2002; Le Voyer and others, 2016), find that the magmas represented by melt inclusions have still lost carbon by degassing prior to entrapment (e.g., Moore and others, 2015). As a result, it has been very difficult to determine the original carbon content of magmas prior to degassing, and thus to use mantle-derived magmas to estimate the carbon content of Earth’s interior.

RESULTS

The average major element compositions of the melt inclusion populations from each of the three phenocrysts phases are within error of each other and the Borgarhraun whole-rock compositions, indicating minimal postentrapment modification. Unlike most other melt inclusion studies, we found that most of the melt inclusions (84%) did not display shrinkage bubbles, which can form within melt inclusions due to differential shrinkage of melt and crystal during cooling and result in exsolution of a vapor phase within the melt inclusion while it is still molten (e.g., Moore and others, 2015; Maclellan, 2017). Most of the NAL709 inclusions that contain shrinkage bubbles were found to have trace element compositions with >2 ppm Nb.

The correlation of CO₂ concentrations with the incompatible trace elements Nb, Th, Rb, and Ba is observed in melt inclusions from all three crystal phases and is independent of the presence or absence of a shrinkage bubble. The correlation of CO₂ with nonvolatile trace elements demonstrates that these melt inclusions were trapped before the magma became saturated in a CO₂-rich vapor phase. The maximum CO₂ concentrations indicate minimum trapping depths of 8–10 km for the

GSA Data Repository item 2018012, methods, data comparisons, mantle CO₂ abundance and flux estimates, and full data tables, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.
initiation of magma crystallization, using the H₂O-CO₂ solubility model of Dixon et al. (1995). This is consistent with CO₂–trace element correlations indicating that the melts had not degassed significantly at the time the inclusions were trapped.

SYSTEMATICS OF CO₂ AND NONVOLATILE TRACE ELEMENTS

The undegassed nature of the Borganhraun melt inclusions is an exceedingly rare occurrence, previously observed at only two other locales, the Siqueiros transform on the East Pacific Rise (Saal et al., 2002) and the equatorial Mid-Atlantic Ridge (MAR) (Le Voyer et al., 2016). The well-correlated abundances of CO₂ and incompatible trace elements (ITEs) result in tightly constrained CO₂/ITE ratios for this population of melt inclusions (e.g., CO₂/Nb = 391 ± 16, 2σM [two standard errors of the mean], n = 161; Fig. 2). Separate averages of data for melt inclusions trapped in olivine, diopside, and Cr-spinel all overlap each other within errors, and agree with the CO₂/Nb ratio of the entire melt inclusion population within errors. Similarly precise ratios are obtained for CO₂/Th (7300 ± 540), CO₂/Rb (787 ± 36), and CO₂/Ba (48.3 ± 2.7).

When comparing the Borganhraun CO₂/ITE ratios with other sample suites, a limiting factor is the generally large scatter in the estimated pre-eruptive abundances of CO₂. Thus any comparison of our data to published data must be limited to specific subsets of the global data that report correlated CO₂ and ITE abundances and thus well-constrained CO₂/ITE ratios. Among the published data, only 4 sample populations meet the criteria for determination of CO₂/Nb with a precision better than 20% (relative); 2 are from the eastern Pacific (Saal et al., 2002; Shimizu et al., 2016) and the other 2 are from the Atlantic Ocean (Cartigny et al., 2008; Le Voyer et al., 2016). In addition to these four populations, we compare our data with vapor-undersaturated submarine MORB glasses identified from published volatile data using the PetDB petrologic database (http://www.earthchem.org/petdb), using only samples with CO₂ data obtained by Fourier-transform infrared spectroscopy or ion microprobe with corresponding data for Rb, Ba, Nb, or Th on the same sample (n = 161). This compilation includes samples from the global data set of Michael and Graham (2015) whose global average CO₂/Nb is also precisely determined (±9% 2σM). The ratios CO₂/Ba and CO₂/Rb show a limited range of values; average CO₂/Rb ratios are nearly the same among the six populations of MORB (±26% 2σ), while CO₂/Ba varies by ±56% (Table 1; Fig. 3). These results are consistent with the previously observed limited variation of Rb/Ba ratios in global MORB (Hofmann and White, 1983; Jenner and O’Neill, 2012; Kelley et al., 2013).

The situation is different when comparing CO₂ abundances with Nb and Th in these sample suites. The CO₂/Nb ratio of 391 ± 16 for Borganhraun is significantly higher than the CO₂/Nb ratio determined for MORB.
from the eastern Pacific; melt inclusions from the Siqueiros Fracture Zone on the East Pacific Rise (Saal et al., 2002) have CO2/Nb = 230 ± 12 (n = 100), while undegassed submarine glasses from the eastern Pacific (Shimizu et al., 2016) also demonstrate a correlation of CO2 with Nb yielding a CO2/Nb ratio of 277 ± 14 (n = 19). Similar differences are seen in CO2/Th.

The Borgarhraun CO2/Nb and CO2/Th ratios are significantly higher than the Pacific suites, and closer to the high-precision measurements of MORB melt inclusions from the equatorial MAR (Table 1; Fig. 3), which yield CO2/Nb = 557 ± 34 and CO2/Th = 825 ± 760 (n = 21) (Le Voyer et al., 2016). Submarine glass samples from the 14°N segment of the MAR, that include the pipping rock 2pID43, have CO2/Nb = 534 ± 90 and CO2/Th = 9770 ± 1560 (n = 6) (Cartigny et al., 2008). It thus appears that the Atlantic locales (Borgarhraun included) are uniformly higher than the Pacific locales; a simple averaging by ocean basin yields a CO2/Nb for the Atlantic (414 ± 17) that is 70% higher than CO2/Nb for the Pacific (243 ± 11); the Atlantic CO2/Th ratio (7550 ± 460) is more than twice the Pacific CO2/Th (3310 ± 220).

**SUBDUCTION ORIGIN FOR MANTLE CO2 VARIATIONS**

The CO2/Rb and CO2/Ba ratios are clearly more homogeneous than CO2/Th and CO2/Nb ratios. Five of the six undegassed MORB populations show correlations between 143Nd/144Nd, CO2/Nb, and CO2/Th (Fig. 3) that suggest that these variations are long-term characteristics of the upper mantle. The more homogeneous CO2/Ba and CO2/Rb ratios do not show correlations with Nd isotopes, indicating that these ratios are similar in isotopically depleted and enriched components in the upper mantle sources of MORB. It is thus likely that the variable mantle CO2 contents originate as a result of variable mixing of depleted mantle sources (high 143Nd/144Nd, low CO2/Nb, and CO2/Th) with small amounts of a subduction component containing elevated abundances of CO2, Rb, and Ba (Fig. 3), a signature characteristic of subduction zone fluids (Elliott et al., 1997; Kessel et al., 2005; Kelemen and Manning, 2015). In addition, the regional differences in mantle CO2 documented here between the Atlantic (high CO2/Nb and CO2/Th) and Pacific (low CO2/Nb and CO2/Th) ocean basins correspond to a similar difference in mantle H2O abundance, as Atlantic MORB has higher H2O/ Ce than Pacific MORB (Michael, 1995). There are similar distinctions in Ba/Nb and Ba/La ratios, with Atlantic MORB being systematically higher than Pacific MORB (e.g., Arevalo and McDonough, 2010; Jenner and O’Neill, 2012; Kelley et al., 2013).

Among the four nonvolatile trace elements we have considered together with CO2, both Nb and Th have low solubility in hydrous fluids from subduction zones (Kessel et al., 2005) that are expected to be enriched in H2O, Rb, and Ba as well as carbonate (Kelemen and Manning, 2015). Thus CO2/Ba and CO2/Rb would be expected to behave similarly to each other in fluid-dominated subduction enrichment processes, and distinct from CO2/Nb and CO2/Th. The high H2O/Ce, Ba/Nb, and Ba/La, and low 143Nd/144Nd are all signatures of mantle enrichment that are characteristic of subduction zone magmas (Elliott et al., 1997; Ruscitto et al., 2012), and by inference high CO2/ITE ratios are also characteristic of this signature.

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**TABLE 1. CO2-ITE RATIOS AND MANTLE SOURCE CO2 ABUNDANCES FOR SIX MID-OCEAN RIDGE SAMPLE GROUPS, ALL-MORB, AND AVERAGES FOR ATLANTIC AND PACIFIC OCEAN BASINS**

<table>
<thead>
<tr>
<th>CO2/Nb</th>
<th>CO2/Th</th>
<th>CO2/Ba</th>
<th>H2O/Ce</th>
<th>Mantle CO2 ppm (Co2/Nb)</th>
<th>Mantle CO2 ppm (CO2/Ba)</th>
<th>Mantle CO2 ppm (CO2/Th)</th>
<th>Average mantle CO2 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>391</td>
<td>7304</td>
<td>48.3</td>
<td>8.78</td>
<td>118 ± 64</td>
<td>129 ± 48</td>
<td>146 ± 33</td>
<td>118 ± 31</td>
</tr>
<tr>
<td>557</td>
<td>8253</td>
<td>96.6</td>
<td>13.11</td>
<td>31 ± 20</td>
<td>48 ± 39</td>
<td>45 ± 15</td>
<td>31 ± 17</td>
</tr>
<tr>
<td>534</td>
<td>2999</td>
<td>105.6</td>
<td>7.19</td>
<td>242 ± 17</td>
<td>39 ± 23</td>
<td>45 ± 22</td>
<td>24 ± 23</td>
</tr>
<tr>
<td>230</td>
<td>4039</td>
<td>74.2</td>
<td>10.36</td>
<td>10 ± 9</td>
<td>15 ± 10</td>
<td>15 ± 9</td>
<td>10 ± 8</td>
</tr>
<tr>
<td>277</td>
<td>4438</td>
<td>99.8</td>
<td>10.31</td>
<td>17 ± 8</td>
<td>15 ± 10</td>
<td>15 ± 9</td>
<td>17 ± 8</td>
</tr>
<tr>
<td>285</td>
<td>7383</td>
<td>63.6</td>
<td>9.74</td>
<td>22 ± 7</td>
<td>15 ± 10</td>
<td>15 ± 9</td>
<td>22 ± 7</td>
</tr>
<tr>
<td>435</td>
<td>5755</td>
<td>101</td>
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<td>414</td>
<td>7306</td>
<td>105.5</td>
<td>76.9</td>
<td>11 ± 4</td>
<td>15 ± 10</td>
<td>15 ± 9</td>
<td>11 ± 4</td>
</tr>
<tr>
<td>243</td>
<td>1300</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Note: ITE—incompatible trace element; MORB—mid-oceanic ridge basalt; MAR—Mid Atlantic Ridge; QDG-NEPR—Quebradenois—Gofar transform and northern East Pacific Rise; MOR—mid-oceanic ridge. Data sources: 1—this study; 2—Le Voyer et al. (2017); 3—Cartigny et al. (2008); 4—Saal et al. (2002); 5—Shimizu et al. (2016); 6—PetDB (Petrological Database, http://www.earthchem.org/petdb; this study).

*ALL-MORB Nd isotopes from Gale et al. (2013); CO2-ITE (incompatible trace element) ratios estimated from correlations with Nd isotopes (CO2/Nb, CO2/Th) or population averages (CO2/Rb, CO2/Ba) of the sample populations. Mantle source ITE concentrations estimated using Nd isotopes from the MORB source mixing model of Shimizu et al. (2016) as for other groups (see text). Dash (−) represents “not determined.”

H2O/Ce ratios for Atlantic and Pacific are the averages of the sample populations discussed in this study.

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**Figure 3.** A: Average CO2/Nb versus Nd isotopes for the six mid-ocean ridge regions that exhibit CO2—incompatible trace element correlations. B: CO2/Th versus Nd. Five of the six regions define a correlation suggesting that CO2/Nb and CO2/Th heterogeneities are long-lived features of mantle sources in the convecting upper mantle. The red curve is a model mixing line between enriched and depleted mid-ocean ridge basalt sources from the model of Shimizu et al. (2016) with CO2/Rb, and Th concentrations in the depleted end member adjusted to best fit the data (see text). Atlantic locales have lower 143Nd/144Nd, higher CO2/Nb, and higher CO2/Th, as well as higher H2O/Ce (Michael, 1995) and higher Ba/Nb (Arevalo and McDonough, 2010), characteristic of subduction-modified mantle.
We therefore suggest that the Atlantic Ocean basin has been polluted by small amounts of mantle wedge material that was hydrated and carbonated during the subduction episodes that characterized the convergent margins surrounding the ancient Iapetus Ocean. Opening of the Atlantic Ocean basin along the preexisting Iapetus suture provided opportunity for Iapetus subarc mantle to become entrained and mixed into the asthenospheric flow that produced the mantle that is sampled today along the MAR. The Pacific Ocean basin, having initially formed during the breakup of the Rodinia supercontinent ~750 m.y. ago (Evans, 2009), is nearly 4 times older than the Atlantic Ocean basin (~200 m.y.; McHone and Butler, 1984) and has thus had a more extended history of upper mantle convection to flush out continent-proximal supra-subduction components. As a result, the eastern Pacific mantle is less affected by mixing with subcontinental subduction-modified mantle, resulting in lower H2O/Co, Ba/Nb, Ba/La, CO2/Nb, and CO2/Th. This conceptual model thus argues for the importance of prior tectonic episodes of subduction in determining the spectrum of volatile, trace element, and isotopic compositions present in the upper mantle beneath ocean basins of different age.

The melt inclusions from Borgarhraun, equatorial MAR, and Siqueiros are the only three documented examples of vapor-undersaturated melt inclusions in existence. However, given that there are regions of the mid-ocean ridge system where MORB magmas erupt with little or no degassing, as documented here and in Shimizu et al. (2016) and Michael and Graham (2015), more vapor-undersaturated melt inclusions are certain to be discovered, and future studies will be very important for constraining the regional distribution of carbon in the upper mantle, the variability of the carbon flux from mid-ocean ridges, and ultimately the origin of carbon throughout the upper mantle.

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