Widespread assimilation of a seawater-derived component at Loihi Seamount, Hawaii

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Abstract—Many tholeiitic and transitional pillow-rim and fragmental glasses from Loihi seamount, Hawaii, have high Cl contents and Cl/K2O ratios (and ratios of Cl to other incompatible components, such as P2O5, H2O, etc.) relative to other Hawaiian subaerial volcanoes (e.g., Mauna Loa, Mauna Kea, and Kilauea). We suggest that this results from widespread contamination of Loihi magmas by a Cl-rich, seawater-derived component.

Assimilation of high-CI phases such as saline brine or CI-rich minerals (halite or iron–hydroxychlorides) with high Cl/H2O ratios can explain the range and magnitude of Cl contents in Loihi glasses, as well as the variations in the ratios of Cl to other incompatible elements. Brines and CI-rich minerals are thought to form from seawater within the hydrothermal systems associated with submarine volcanoes, and Loihi magmas could plausibly have assimilated such materials from the hydrothermal envelope adjacent to the magma chamber. Our model can also explain semiquantitatively the observed contamination of Loihi glasses with atmospheric-derived noble gases, provided the assimilant has concentrations of Ne and Ar comparable to or slightly less than seawater. This is more likely for brines than for Cl-rich minerals, leading us to favor brines as the major assimilant. Cl/Br ratios for a limited number of Loihi samples are also seawater-like, and show no indication of the higher values expected to be associated with the assimilation of CI-rich hydrothermal minerals.

Although CI enrichment is a common feature of lavas from Loihi, submarine glasses from other Hawaiian volcanoes show little (Kilauea) or no (Mauna Loa, Mauna Kea) evidence of this process, suggesting that assimilation of seawater-derived components is more likely to occur in the early stages of growth of oceanic volcanoes. Summit collapse events such as the one observed at Loihi in October 1996 provide a ready mechanism for depositing brine-bearing rocks from the volcanic edifice into the top of a submarine summit magma chamber. Copyright © 1999 Elsevier Science Ltd

I. INTRODUCTION

An important issue in the study of ocean island basalts (OIBs) is the degree to which chemical heterogeneity within and between volcanoes is influenced by high-level (i.e., lithospheric and/or crustal) contamination processes, rather than representative of geochemical variations in mantle source regions (Davidson and Bohrson, 1998). Interactions between ascending magma and the lithospheric mantle, the oceanic crust, and the volcanic edifice itself can all leave imprints on a magma’s chemical and isotopic composition (e.g., Patterson et al., 1990; Martin et al., 1994; Eiler et al., 1996; Garcia et al., 1998a; Reiners, 1998). Since the primary goal of many geochemical studies of OIB is to investigate the chemical and isotopic compositions of their mantle sources (e.g., Staudacher et al., 1986; Zindler and Hart, 1986; Honda et al., 1991; Hoffman, 1997), it is important to be able to recognize and, if possible, to correct for magmatic compositional variations that are due to assimilation and contamination.

One potential source of contamination for oceanic magmas is sea water, and many mid-ocean ridge basalts (MORB) appear to have experienced contamination by seawater-derived components (Michael and Schilling, 1989; Jambon et al., 1995; Michael and Cornell, 1998). There are also several lines of evidence from OIB, particularly from Hawaii, that suggest that such components can also be incorporated into magmas in these environments. Noble gases with atmospheric or near-atmospheric isotopic compositions indicate the addition of atmospheric components to magmas from Loihi seamount and to submarine Kilauea magmas prior to eruption (Patterson et al., 1990; Honda et al., 1991, 1993). In glasses from a suite of submarine Kilauea lavas, Kyser and O’Neil (1984) observed a correlation between δD and H2O, and Chaussidon and Jambon (1994) observed a correlation between δD and δ18B. Both sets of authors suggested that the correlations resulted from assimilation of seawater or seawater-altered basalt during magma propagation along the East Rift Zone. Clague et al. (1995) noted that Cl concentrations in some submarine glasses from Kilauea are higher than expected from crystal fractionation and suggested that this could be due to assimilation of seawater-altered basalt near the top of the summit magma chamber. Finally, Kent et al. (1999) suggested that two unusually H2O-, Cl-, and B-rich samples from Loihi represent magmas that assimilated a seawater-derived component; olivine-hosted glass inclusions from these samples also show evidence of this process, and variations in their H2O, Cl, and B contents suggest...
variability in the composition of the assimilant. Kent et al. (1999) also speculated that the high Cl contents reported in other pillow-rim glass samples from Loihi could be another manifestation of contamination by CI-rich, seawater-derived components and that assimilation of seawater-derived components could be a widespread process at this and other oceanic volcanoes. In this study, we examine this hypothesis using new chemical and isotopic analyses of Loihi glasses and data compiled from the literature.

2. ANALYTICAL TECHNIQUES

Major elements and Cl were analysed by a JEOL 733 electron probe at Lawrence Livermore National Laboratory and at the California Institute of Technology using a 5 to 10 nA electron beam, a 10 μm beam size, and an accelerating voltage of 15 kV. Data were reduced with the CITZAF correction algorithms using natural and synthetic standards (Armstrong, 1995). Analytical precision for electron probe analyses, based on counting statistics for the compositions measured, were <2% for SiO₂, Al₂O₃, CaO, MgO, FeO; <10% for Na₂O, K₂O, TiO₂; <20% for Cl and P₂O₅, and <50% for MnO and Cr₂O₃. Data represent the average of 5 to 10 individual analyses taken from 3 to 5 separate glass chips from each sample. Glass chips free from alteration products were selected using the procedure outlined in Kent et al. (1999), and secondary standards were monitored to ensure the comparability of data from the two different electron probes used. Cl analyses were made with reference to CI-rich scapolite and sodalite with count times of 90 to 120 s and background counts determined during each analysis. The detection limit for Cl was 70 to 80 ppm. All uncertainties stated in this paper, unless otherwise noted, are ±2σ.

H₂O, Be, and B were analysed using a modified Cameca 3f ion microprobe at Lawrence Livermore National Laboratory following the procedures outlined in Kent et al. (1999). Uncertainties for H₂O, Be, and B are based on the reproducibility of 3 to 6 individual analyses on the same glass chips analysed for major elements and are typically ±15% for H₂O and ±20% for Be and B.

Analytical techniques for noble gas analyses are described in Honda et al. (1993). Reproducibility of noble gas data was evaluated by analyzing two aliquots for each sample: one heated in several intermediate temperature steps (600, 1500, and 1600°C for LO-02-02; 700 and 1600°C for LO-02-04), and one where all gas was extracted at 1500°C. Dredging locations for noble gas data for pillow-rim glass and olivine separates from these samples are given in Valbracht et al. (1997).

Table 3 reports on H₂O, Cl, Be, and B contents of 15 pillow-rim glasses (from six alkalic lavas and nine tholeiitic and transitional basalts collected by submersible from 3 to 5 km depth on Loihi’s south rift. Measured Cl and H₂O contents for these glasses range between 0.049 and 0.103 and 0.39 and 0.68 wt.%.

Table 3 reports Cl and H₂O concentrations and isotopic ratios for pillow-rim glass from 110 Loihi samples (41 alkalic, 69 tholeiitic and transitional). These include two samples analysed for Ne concentration and isotopic composition by Staudacher et al. (1986) and one sample analysed for Ar concentration and isotopic composition by Staudacher et al. (1986) and Sarda et al. (1988); Garcia et al. (1989, 1993, 1995, 1998b), and Honda et al. (1993). Including the samples studied here, we have major element electron microprobe analyses of pillow-rim glass from 110 Loihi samples (41 alkalic, 69 tholeiitic and transitional). H₂O and Cl analyses are available for 44 of these (12 alkalic, 32 tholeiitic and transitional); and H₂O, Cl, and noble gas data are available for 26 glasses (eight alkalic, 18 tholeiitic and transitional). These include two samples analysed for Ne concentration and isotopic composition by Staudacher et al. (1986) and one sample analysed for Ar concentration and isotopic composition by Sarda et al. (1988); the Cl contents of these were reported by Byers et al. (1985). Unpublished data are for fragmental glasses collected by piston core and submersible from glass-rich sand layers from the summit and flanks of Loihi (Clague et al., 1997; Clague et al., in press). These glasses, which sample a wide range of magma types, represent quench granulation and bubble wall fragments produced during submarine volcanic eruptions. We have also compiled major element and Cl analyses of submarine glasses from Kilauea (Garcia et al., 1989; Dixon et al., 1990; Clague et al., 1991, 1995; Honda et al., 1993); the North Arch volcanic field (Dixon et al., 1997); and Mauna Kea and Mauna Loa (Garcia et al., 1989). Degassing of Cl is thought to be insignificant at water depths of 700 m and greater (e.g., Michael and Norman and Garcia (1999). The noble gases in these samples are of particular interest because their matrix glasses and many glass inclusions in olivine phenocrysts have high H₂O, Cl, and B concentrations (Kent et al., 1999). As expected (since a seawater-derived assimilant would contain atmospheric isotopic ratios of the noble gases), the ²⁰Ne/²²Ne and ⁴⁰Ar/³⁶Ar ratios of these glasses are close to atmospheric values (Table 1). In contrast, the ³⁶Ar/⁴⁰Ar ratios of these samples (as with many other Loihi samples; e.g., Kurz et al., 1983; Honda et al., 1991, 1993) are unambiguously of mantle origin (~27–32 K for total fusion and up to 40 K for He released during individual heating steps; Table 1).

Table 2 lists major element, H₂O, and Cl analyses of pillow-rim glasses from one alkalic and five tholeiitic and transitional basalts collected by submersible from 3 to 5 km depth on Loihi’s south rift. Measured Cl and H₂O contents for these glasses range between 0.049 and 0.103 and 0.39 and 0.68 wt.%.
Table 1. Noble gas isotopic compositions of glass separates from two tholeiitic basalts from the south rift of Loihi from the study of Kent et al. (1999) and Norman and Garcia (1999). Following convention, stated errors are ±1σ.

<table>
<thead>
<tr>
<th>Sample Temperature</th>
<th>$^4$He</th>
<th>$^3$He/$^4$He</th>
<th>$^{22}$Ne</th>
<th>$^{20}$Ne/$^{22}$Ne</th>
<th>$^{36}$Ar</th>
<th>$^{38}$Ar/$^{40}$Ar</th>
<th>$^{84}$Kr</th>
<th>$^{130}$Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-6}]</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-12}]</td>
<td>[× 10^{-12}]</td>
</tr>
<tr>
<td>600</td>
<td>31.0 ± 0.30</td>
<td>45.6 ± 1.1</td>
<td>32.6 ± 0.8</td>
<td>10.7 ± 0.25</td>
<td>9.99 ± 0.07</td>
<td>0.0294 ± 0.0004</td>
<td>125 ± 4</td>
<td>0.1870 ± 0.0009</td>
</tr>
<tr>
<td>1500</td>
<td>229.7 ± 2.30</td>
<td>43.9 ± 0.9</td>
<td>31.4 ± 0.6</td>
<td>23.3 ± 0.55</td>
<td>9.99 ± 0.07</td>
<td>0.0309 ± 0.0004</td>
<td>10919 ± 319</td>
<td>0.1876 ± 0.0003</td>
</tr>
<tr>
<td>1600</td>
<td>2.66 ± 0.03</td>
<td>56.6 ± 2.8</td>
<td>40.4 ± 2.0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>28 ± 1</td>
<td>0.1878 ± 0.0015</td>
</tr>
<tr>
<td>Total</td>
<td>263.00 ± 2.00</td>
<td>44.3 ± 0.8</td>
<td>31.6 ± 0.6</td>
<td>34.0 ± 0.58</td>
<td>9.99 ± 0.05</td>
<td>0.0304 ± 0.0003</td>
<td>11073 ± 319</td>
<td>0.1875 ± 0.0003</td>
</tr>
<tr>
<td>Loihi LO-02-02 b</td>
<td>246 ± 14</td>
<td>41.5 ± 2.8</td>
<td>29.7 ± 2.0</td>
<td>23.3 ± 1.1</td>
<td>10.27 ± 0.11</td>
<td>0.0308 ± 0.0004</td>
<td>2728 ± 181</td>
<td>0.1886 ± 0.0005</td>
</tr>
<tr>
<td>Loihi LO-02-04 a</td>
<td>23.3 ± 0.24</td>
<td>43.2 ± 1.3</td>
<td>30.8 ± 0.9</td>
<td>25.7 ± 0.63</td>
<td>9.94 ± 0.05</td>
<td>0.0294 ± 0.0004</td>
<td>241 ± 7</td>
<td>0.1872 ± 0.0007</td>
</tr>
<tr>
<td>700</td>
<td>181.10 ± 1.85</td>
<td>41.9 ± 0.8</td>
<td>29.9 ± 0.6</td>
<td>24.46 ± 0.55</td>
<td>9.93 ± 0.08</td>
<td>0.0292 ± 0.0004</td>
<td>20410 ± 596</td>
<td>0.1868 ± 0.0003</td>
</tr>
<tr>
<td>1500</td>
<td>164 ± 10</td>
<td>38.5 ± 2.6</td>
<td>27.5 ± 1.9</td>
<td>18.8 ± 0.9</td>
<td>10.00 ± 0.14</td>
<td>0.0303 ± 0.0002</td>
<td>10143 ± 674</td>
<td>0.1884 ± 0.0005</td>
</tr>
<tr>
<td>Air</td>
<td>1.4</td>
<td>1.0</td>
<td>9.8</td>
<td>0.029</td>
<td>10143 ± 674</td>
<td>0.1880</td>
<td>295.5</td>
<td></td>
</tr>
</tbody>
</table>

a $R_A$, the $^3$He/$^4$He ratio of the atmosphere, is $1.4 \times 10^{-6}$.

b N.D. = below blank.

* Noble gas amounts are in cm$^3$ STP/g.
Table 2. Major element, Cl, and H₂O contents of pillow-rim glasses from samples from the study of Valbracht et al. (1997) from the south rift zone of Loihi.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ (wt%)</th>
<th>TiO₂ (wt%)</th>
<th>Al₂O₃ (wt%)</th>
<th>Cr₂O₃ (wt%)</th>
<th>FeO₄ (wt%)</th>
<th>MnO (wt%)</th>
<th>MgO (wt%)</th>
<th>CaO (wt%)</th>
<th>Na₂O (wt%)</th>
<th>K₂O (wt%)</th>
<th>P₂O₅ (wt%)</th>
<th>Cl (wt%)</th>
<th>H₂O (wt%)</th>
<th>Total (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2341-2</td>
<td>a²</td>
<td>47.28</td>
<td>3.14</td>
<td>14.54</td>
<td>0.01</td>
<td>11.85</td>
<td>0.18</td>
<td>5.19</td>
<td>10.86</td>
<td>3.46</td>
<td>1.07</td>
<td>0.45</td>
<td>0.098</td>
<td>0.61</td>
</tr>
<tr>
<td>2341-1</td>
<td>tr²</td>
<td>48.66</td>
<td>3.18</td>
<td>13.81</td>
<td>0.01</td>
<td>12.00</td>
<td>0.17</td>
<td>5.41</td>
<td>10.74</td>
<td>3.01</td>
<td>0.72</td>
<td>0.38</td>
<td>0.103</td>
<td>0.60</td>
</tr>
<tr>
<td>2335-6 (i)</td>
<td>tr²</td>
<td>48.39</td>
<td>2.96</td>
<td>13.96</td>
<td>0.03</td>
<td>10.67</td>
<td>0.16</td>
<td>6.27</td>
<td>11.49</td>
<td>2.92</td>
<td>0.74</td>
<td>0.37</td>
<td>0.097</td>
<td>0.59</td>
</tr>
<tr>
<td>2335-10 tr¹</td>
<td>48.46</td>
<td>3.07</td>
<td>14.53</td>
<td>nd²</td>
<td>10.53</td>
<td>nd²</td>
<td>6.72</td>
<td>12.28</td>
<td>2.78</td>
<td>0.98</td>
<td>0.39</td>
<td>0.075</td>
<td>0.68</td>
<td>100.68</td>
</tr>
<tr>
<td>2338-2 tr¹</td>
<td>48.79</td>
<td>2.79</td>
<td>13.12</td>
<td>0.04</td>
<td>11.29</td>
<td>0.17</td>
<td>6.97</td>
<td>11.74</td>
<td>2.54</td>
<td>0.55</td>
<td>0.32</td>
<td>0.078</td>
<td>0.39</td>
<td>98.79</td>
</tr>
<tr>
<td>2337-3b tr¹</td>
<td>49.59</td>
<td>2.76</td>
<td>13.52</td>
<td>0.02</td>
<td>11.45</td>
<td>0.17</td>
<td>6.17</td>
<td>11.08</td>
<td>2.56</td>
<td>0.50</td>
<td>0.31</td>
<td>0.049</td>
<td>0.47</td>
<td>98.65</td>
</tr>
</tbody>
</table>

* All analyses reported in weight percent and are from glass chips provided by P. Valbracht and A. Malahoff.

² Fe expressed as total FeO.
³ nd = not determined.
⁴ tr = transitional basalt.
⁵ t = tholeiitic basalt.

Table 3. Cl, H₂O, Be, B contents of Loihi pillow-rim glasses for which major element and noble gas compositions were analyzed by Honda et al. (1993).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cl (wt%)</th>
<th>H₂O (wt%)</th>
<th>Be (ppm)</th>
<th>B (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KK 15-4</td>
<td>0.122</td>
<td>0.97</td>
<td>2.0</td>
<td>4.9</td>
</tr>
<tr>
<td>KK 17-11 a²</td>
<td>0.070</td>
<td>0.74</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td>KK 21-3 a²</td>
<td>0.043</td>
<td>0.63</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>KK 29-13 a²</td>
<td>0.063</td>
<td>0.47</td>
<td>0.8</td>
<td>1.7</td>
</tr>
<tr>
<td>KK 30-6 a²</td>
<td>0.066</td>
<td>0.60</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td>KK 31-9 a²</td>
<td>0.039</td>
<td>0.58</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>KK 20-13 tr²</td>
<td>0.036</td>
<td>0.57</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>HW 2-16 r²</td>
<td>0.029</td>
<td>0.41</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>KK 20-2 r²</td>
<td>0.062</td>
<td>0.44</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>KK 22-2 r²</td>
<td>0.042</td>
<td>0.57</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>KK 22-20 r²</td>
<td>0.030</td>
<td>0.47</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>KK 22-4 r²</td>
<td>0.041</td>
<td>0.56</td>
<td>0.9</td>
<td>1.7</td>
</tr>
<tr>
<td>KK 23-9 r²</td>
<td>0.040</td>
<td>0.42</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>KK 26-4 r²</td>
<td>0.093</td>
<td>0.49</td>
<td>0.9</td>
<td>1.7</td>
</tr>
<tr>
<td>KK 29-4 r²</td>
<td>0.039</td>
<td>0.38</td>
<td>0.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* a — basanite.
  b — alkali basalt.
  tr = transitional basalt.
  t = tholeiitic basalt.

Schilling, 1989), so we have focused our compilation on samples from depths greater than this.

Note that throughout we refer to samples as either “alkalic” (including alkali basalts, basanites, and hawaiites) or “tholeiitic and transitional” (all basalts), following the classifications of Macdonald and Katsura (1964) based on total alkalis vs. silica.

4. DISCUSSION

4.1. Cl in Loihi Glasses

A distinctive feature of many tholeiitic and transitional glasses from Loihi is that they have higher Cl concentrations than submarine glasses from other Hawaiian volcanoes. For example, numerous tholeiitic and transitional pillow-rim and fragmental glasses from Loihi have Cl concentrations in excess of 0.10 wt.% (up to a maximum of 0.18 wt.%), compared to a range of <0.01 to 0.06 wt.% Cl in submarine glasses from Kilauea, Mauna Loa, and Mauna Kea (Fig. 1). Alkalic pillow-

rim and fragmental glasses from Loihi also have high Cl contents (up to 0.13 wt.%), however the overall range of Cl concentrations in submarine alkalic glasses is similar to that of submarine glasses from the North Arch field (Fig. 1; Dixon et al., 1997). The large range of Cl contents evident in Loihi tholeiitic and transitional glasses, including the anomalously high values evident in many samples, are not matched by concomitant variations in the concentrations of other incompatible elements (e.g., K, P, H, Be, and B), suggesting that Cl has been decoupled from these elements in tholeiitic and transitional magmas. This is evident both in large variations in the ratios of Cl to other incompatible components (as shown for Cl/K₂O in Fig. 2) compared to ratios that do not involve Cl (e.g., P₂O₅/K₂O ratios for all Loihi glasses vary by a factor of ~2-5, whereas Cl/K₂O and Cl/P₂O₅ ratios vary by factors of ~6–7) and in poor correlations between Cl and other incompatible components for tholeiitic and transitional samples (compared to generally good correlations between incompatible components other than Cl; Fig. 3).

Decoupling between Cl and other incompatible components is less evident in alkaline glasses from Loihi; these have Cl/K₂O ratios that are less elevated and variable than tholeiitic and transitional glasses (Fig. 2), and Cl is reasonably well correlated with other incompatible components in alkaline samples (Fig. 3). However, in comparison to alkaline glasses from the North Arch, alkaline glasses from Loihi have higher maximum Cl/K₂O ratios (0.15 compared to 0.12) and a larger range in Cl/K₂O (a factor of ~4 compared to a factor of ~2).

The enrichment in Cl that we describe in tholeiitic and transitional lavas appears to be a widespread feature of Loihi magmas. High Cl and Cl/K₂O ratios are evident in samples taken from throughout the summit region, as well as from the southern and northern rift zones of the volcano. In addition, high Cl and Cl/K₂O are common in fragmental glasses taken from sand layers (Figs. 1 and 2), which, because of their large variations in major element composition, are thought to sample many eruptions (Clague et al., in press). This suggests that high Cl and high Cl/K₂O (and ratios of Cl to other incompatible elements) in Loihi lavas, and whatever process or processes produce them, are widespread features of magmatism at Loihi seamount.
Fig. 1. Variation of Cl with MgO for Loihi pillow-rim and fragmental glasses. Symbols are explained in the legend. H$_2$O-rich samples studied by Kent et al. (1999) are marked by small horizontal arrows. Representative ±2σ error bars are given at top right. Dashed lines show model Cl concentrations of a representative parental tholeiite (from Garcia et al., 1995 and Kent et al., 1999 and shown as a filled star) during crystal fractionation. The model is based on fractionation of olivine (by removal of increments of olivine in Fe-Mg equilibrium) between 16 and 8 wt.% and 75% clinopyroxene (using the composition “CPX4” from by Garcia et al., 1995), 20% anorthite (An$_{70}$) and 5% olivine (Fo$_{86}$) between 8% and 4% MgO. (A) Pillow rim glasses. Data for Loihi samples are from Tables 2 and 3 and Byers et al. (1985), Garcia et al. (1989, 1998b), and Kent et al. (1999). Fields for Mauna Loa and Mauna Kea pillow-rim glasses (shown as a single field), for glasses from the North Arch volcanic field, and for Kilauea pillow-rim glasses are from Byers et al. (1985), Garcia et al. (1989, 1998b), Honda et al. (1993), Clague et al. (1995), and Dixon et al. (1997). (B) Comparison between pillow rim glasses from (A) and fields for fragmental glasses from Loihi and Kilauea. Data for Loihi fragmental glasses from D. A. Clague and A. Davis (unpublished data); data for Kilauea fragmental glasses from Clague et al. (1995).
Fig. 2. Cl/K₂O (wt.%) vs. MgO for Loihi pillow-rim and fragmental glasses. Dashed line shows Cl/K₂O (which remains constant) during crystal fractionation of a representative parental Loihi tholeiite (Garcia et al., 1995; Kent et al., 1999). Symbols and data sources as for Fig. 1. Representative ±2σ error bars are given at top right. (A) Pillow-rim glasses; (B) Comparison between pillow-rim glasses from (A) and fields for fragmental glasses.
Fig. 3. Variations of concentrations of selected incompatible elements and oxides in Loihi pillow-rim glasses. Symbols and data sources as for Fig. 1, with additional data for K$_2$O and P$_2$O$_5$ from Garcia et al. (1993, 1995). Representative ±2σ error bars are given at bottom right in each panel. (A) K$_2$O vs. P$_2$O$_5$; (B) Cl vs. P$_2$O$_5$; (C) K$_2$O vs. H$_2$O; (D) Cl vs. H$_2$O; (E) Be vs. B; (F) Cl vs. B.
4.1.1. Origin of Cl enrichment in Loihi glasses

High concentrations of Cl in basaltic lavas can be the result of magmatic processes such as low-degree partial melting and/or crystal fractionation. However, these processes also enrich the concentrations of other incompatible elements, and thus cannot explain the observed decoupling of Cl from other incompatible components at Loihi. As shown in Fig. 1, crystal fractionation of olivine, clinopyroxene, and plagioclase from a representative tholeiitic parental melt is incapable of producing the highest observed Cl contents of tholeiitic and transitional lavas (Fig. 1). Byers et al. (1985) and Garcia et al. (1989) suggested that Cl enrichment is a primary feature of the mantle sources of Loihi magmas. However, this would require an unusual kind of enrichment process affecting only Cl in order to explain the lack of correlation between Cl and other incompatible elements that typically accompany it in “enriched” sources (e.g., Schilling et al., 1980).

Lavas from Loihi do not appear to have degassed significant water, S, or halogens (Dixon and Clague, 1997), and Dixon et al. (1990) suggested that Loihi lavas are not enriched in Cl, but rather that subaerial volcanoes, such as Kilauea and Mauna Loa, have been depleted in Cl by degassing of Cl from their summit magma reservoirs. However, if this were the case, then Cl would behave in Loihi glasses like an involatile incompatible element, and the observed lack of correlation between Cl and other incompatible components such as K2O and P2O5 (Figs. 2 and 3) could not be readily explained.

Submarine alteration and weathering is also known to increase the concentrations of components such as K2O, H2O, Cl, and B in altered basaltic glasses (e.g., Staudigel and Hart, 1984; Smith et al., 1995; Staudigel et al., 1996), and if alteration preferentially enriched Cl relative to other incompatible components (including K2O, P2O5, and H2O), this could explain the observed Cl enrichments. However, given that all glasses in this study were selected to be free of visible alteration phases, that the Cl contents of each glass were homogeneous to within analytical uncertainty, and that there is an absence of H2O enrichment in nearly all samples, it is unlikely that the high Cl concentrations in Loihi glasses directly reflect submarine weathering. Moreover, high Cl contents and Cl/K2O ratios have also been observed for melt inclusions within fresh olivine phenocrysts in some Loihi samples (Kent et al., 1999).

Our preferred explanation for the enrichment of Cl in Loihi glasses is that Loihi magmas frequently assimilate seawater-derived, Cl-rich components. Assimilation of Cl-rich seawater-derived components can explain the elevated Cl contents and the large range in Cl concentrations and Cl/K2O ratios characteristic of the Loihi data set, as well as the lack of correlation between Cl and elements such as K and P not enriched in seawater. This idea is not new: Clague et al. (1995) explained elevated Cl contents in submarine Kilauea lavas in the same way. Michael and Schilling (1989), Jambon et al. (1995), and Michael and Cornell (1998) proposed that the same process occurs in mid-ocean ridge environments. For Loihi, Kent et al. (1999) proposed the same hypothesis based on a detailed study of two samples (including glass inclusions in olivine phenocrysts).

Potential assimilants include not only seawater, but also the saline brines and complementary H2O-rich fluids derived from seawater (e.g., Bischoff and Rosenbauer, 1987), altered basalt, and Cl-rich minerals such as halite and iron–hydroxychlorides (e.g., Seyfreid et al., 1986; Berndt et al., 1988; Berndt and Seyfried, 1997) that may form within submarine hydrothermal systems. Highly saline brines (e.g., up to ~50 wt.% NaCl) and iron–hydroxychloride and halite are thought to exist in the submarine hydrothermal systems associated with MORB (Seyfreid et al., 1986; Kelley and Delaney, 1987; Bischoff and Rosenbauer, 1987; Berndt et al., 1988; Berndt and Seyfried, 1990; 1997; Butterfield et al., 1997) and have also been proposed to occur in hydrothermal systems associated with oceanic volcanoes such as Loihi (e.g., Fournier, 1987). Loihi’s summit is almost 1000 m below sea level (Moore et al., 1982), and hydrothermal systems in the volcanic edifice are dominated by circulation of seawater (Fournier, 1987; Karl et al., 1988; Davis and Clague, 1998). Interaction between magmas and either seawater-derived fluids and/or altered rocks from the hydrothermal system could introduce a Cl-rich component into the magma.

The potential assimilants can be distinguished by their Cl/H2O ratios and absolute Cl concentrations. Figure 4 compares Cl/K2O and H2O/K2O ratios of Loihi pillow-rim glasses with fields for submarine glasses from Kilauea, Mauna Loa, Mauna Kea, and the North Arch. Also shown are mixing lines between a representative Loihi tholeiite with MgO = 8 wt.% and five

Fig. 4. Cl/K2O vs. H2O/K2O for pillow-rim glasses from Loihi. Data sources and symbols as for Fig. 1. Fields show data for pillow-rim glasses from Mauna Loa and Mauna Kea (as a single field), Kilauea, and the North Arch volcanic field. Lines show mixing trends between a representative parental Loihi tholeiite (from Garcia et al., 1995 and Kent et al., 1999) calculated to MgO = 8 wt.% (shown as a hollow star and containing 0.44 wt.% H2O, 0.47 wt.% K2O, 0.013 wt.% Cl) and either altered basalt (containing 5 wt.% H2O, 1 wt.% K2O, 0.1 wt.% Cl), seawater, 15 wt.% and 50 wt.% NaCl brine, or halite. Compositions of the assimilant endmembers are detailed in Kent et al. (1999). Numbers on mixing lines show percentages of Cl-rich components added to basalt in wt.%. Representative ±2σ error bars are given at top right.
potential assimilants: sea water, 15 and 50 wt.% NaCl brines, altered basalt, and halite. With the exception of the two unusually water-rich samples described by Kent et al. (1999), pillow-rim glasses from Loihi form a near vertical array, with little or no variation in H2O/K2O with increasing CI/K2O; i.e., the Loihi data are not consistent with the addition of assimilants with low CI/H2O ratios such as seawater, 15% NaCl brine, a complementary H2O-rich fluid formed by phase separation (not shown in Fig. 4), or altered basalt. Also, even if the absence of H2O enrichment was disregarded, bulk assimilation of altered basalt is unlikely to explain the high CI contents of Loihi glasses because of the large quantities of this material that would be required to elevate CI contents and the CI/K2O ratios (Fig. 4).

Based on Fig. 4, both saline brines and Cl-rich minerals such as halite have high enough CI contents and CI/H2O and CI/K2O ratios to qualify for the required assimilant. The total range of CI/K2O ratios of tholeiitic and transitional basalts can be explained by the addition of small amounts of these materials (e.g., ~0.4 wt.% of 50 wt.% NaCl brine or halite, or <1 wt.% of Fe2[OH]3Cl; Rucklidge and Patterson, 1977). Assimilation could result from direct incorporation of these phases into the magma or from assimilation of small amounts of rock containing these phases. Note that except for the two samples studied by Kent et al. (1999), H2O and B contents beyond those expected from crystal fractionation of parental melts have not been observed in other Loihi glasses; the assimilants required to explain these two samples would have to be anomalously H2O- and B-rich, although still with CI/H2O greater than that of seawater, suggesting a variability in the nature of the CI enrichment process operating at Loihi.

Assimilation of a Cl-rich component can also explain why CI/K2O ratios (and the ratios of CI to other incompatible elements) range to higher values and are more variable in tholeiitic and transitional glasses than in incompatible glasses from Loihi (Figs. 2 and 3). Alkalic magmas have higher primary concentrations of CI (and all other incompatible elements) than tholeiitic and transitional magmas, and thus their CI/K2O ratios will be less affected by the addition of CI. For example, the addition of 0.4 wt.% of a 50 wt.% NaCl brine (the estimated amount of assimilant required to produce the highest CI/K2O ratios observed in tholeiitic and transitional magmas) to an alkalic magma with preassimilation K2O and Cl concentrations of 1.0 and 0.03 wt.% would produce a CI/K2O ratio of 0.16, compared to 0.30 in a tholeiitic magma with preassimilation K2O and Cl contents of 0.50 and 0.015 wt.% (Kent et al., 1999). The maximum CI/K2O ratios observed in alkalic glasses are ~0.15, and are thus consistent with the addition of similar amounts of a 50 wt.% NaCl brine as required for tholeiitic and transitional glasses. Assimilation of such components by alkalic magmas is also consistent with indications that alkaline lavas contain atmosphere-derived noble gases (see below).

If our hypothesis is correct, assimilation of seawater-derived CI-rich components must be a widespread process at Loihi. In contrast, the low CI/K2O ratios of submarine glasses from Mauna Loa and Mauna Kea (Fig. 2) suggest that lavas currently exposed on the flanks of these volcanoes have not been significantly affected by this process. Kilauea may be an intermediate case, as there is some variation of the CI/K2O ratio in pillow-rim glasses from the submarine portion of the East Rift Zone (Fig. 2), consistent with assimilation of seawater-altered basalt (Clague et al., 1995). However, this is not a universal feature of Kilauea samples (for example numerous pillow-rim glasses and high-MgO fragmental glasses from Kilauea show no evidence of Cl enrichment; Dixon et al., 1990; Clague et al., 1991, 1995) and it is less pronounced than in Loihi samples when it does occur (Fig. 2).

The small amounts of assimilation of brines or Cl-rich minerals (<1%) required to produce the CI contents and CI/K2O ratios in tholeiitic, transitional, and alkalic glasses from Loihi (Fig. 4), suggests that this process would be unlikely to affect the concentrations and isotopic compositions of most petrologically important lithophile elements (e.g., rare-earth element, Sr, Pb). Tests of the assimilation hypothesis must instead focus on elements and/or isotopes that are significantly enriched in seawater-derived materials, such as B, Cl, and H (although, as emphasized above, relatively few Loihi samples are enriched in H2O and B). Another possibility is the isotopic ratios of the heavy noble gases (Ne, Ar, Kr, Xe), which are enriched in concentration in seawater by several orders of magnitude relative to Loihi glasses (Patterson et al., 1990; Valbracht et al., 1997). In Sec. 4.2, we explore the consistency of noble gas isotopic data from Loihi samples with our hypothesis that there has been widespread contamination of Loihi magmas by seawater-derived components.

4.2. Contamination of Noble Gases

Glasses and phenocrysts from Loihi have been contaminated by atmosphere-derived noble gases: i.e., the Ne and Ar isotopic ratios of such samples range between atmospheric and mantle-derived values (Patterson et al., 1990; Honda et al., 1991; 1993; Valbracht et al., 1997). Although much of the study of noble gases from Loihi has been aimed at defining the nonatmospheric mantle-derived component (e.g., Staudacher et al., 1986; Sarda et al., 1988; Honda et al., 1991; 1993; Valbracht et al., 1997), our interest is in whether the atmospheric noble gas signature in samples from Loihi is correlated with CI enrichment, as would be expected if both were introduced during assimilation of seawater-derived components.

In Fig. 5 we compare the Ne and Ar isotopic compositions and CI/K2O ratios of the 26 pillow-rim glasses from Loihi for which both classes of data are available. We have also plotted (shown as a field for clarity) data for samples from Kilauea from Honda et al. (1993). Although many Loihi glasses have relatively low CI/K2O and low, roughly atmospheric 20Ne/22Ne and 40Ar/36Ar on Fig. 5, the data extend both vertically (to high CI/K2O at low noble gas isotopic ratios) and horizontally (to high noble gas isotopic ratios at low CI/K2O).

Figure 5 shows the results of three simple mixing calculations. All three calculations take a representative tholeiitic Loihi basalt with MgO = 8 wt.% (calculated from a representative parental tholeiite composition taken from Garcia et al., 1995; Kent et al., 1999) with mantle-like Ne and Ar isotopic compositions (solar Ne [20Ne/22Ne = 13.8] and 40Ar/36Ar = 7000) and Ne and Ar concentrations estimated for Loihi tholeiitic basalt as one end member. Details of the end members used are given in the caption for Fig. 5. Three different Cl- and rare-gas-rich end members were considered: (i) sea water (model 1); (ii) a 50 wt.% NaCl fluid with seawater Ne and Ar concentrations (model 2); and (iii) a 50 wt.% NaCl fluid with an
order of magnitude less $^{20}\text{Ne}$ and $^{36}\text{Ar}$ than sea water (model 3). The assimilants in all three calculations have atmospheric $\text{Ne}$ and $\text{Ar}$ isotopic ratios. Both increased salinity and decreased noble gas concentrations result in more gently curved mixing trends in Fig. 5. The $\text{Cl}$ contents of the $\text{Cl}$-rich assimilant in models 2 and 3 are based on a 50 wt.% NaCl brine but could also represent assimilation of highly $\text{Cl}$-enriched rocks and minerals. The lower noble gas abundance of model 3 is an attempt to illustrate the effects of the expected decrease in noble gas solubility in a high-temperature brine (noble gas solubility in aqueous fluids decreases with increasing temperature and salinity, and formation of a brine by phase separation is expected to partition noble gases out of the brine phase; Ozima and Podosek, 1983; Kennedy, 1988), although remixing between brine and seawater could result in fluids with high $\text{Cl}$ and only moderately depleted noble gas concentrations. The noble gas concentrations of $\text{Cl}$-rich minerals from submarine hydrothermal systems have not been measured, but are likely to be lower than seawater (although we note that $\text{Cl}$-rich minerals could conceivably contain noble gases adsorbed onto mineral surfaces and/or trapped within fluid inclusions).

The Loihi data define overall concave upward fields in Fig. 5. This requires that the $\text{Ne}$ and $\text{Ar}$ concentrations in the high-$\text{Cl}$ endmember are several orders of magnitude greater than in the mantle endmember. This argues against a rare-gas-poor phase (as we expect $\text{Cl}$-rich minerals to be) as the source
of high Cl and atmospheric noble gases in Loihi magmas. The Loihi data are bounded in Fig. 5 by models 1 and 3, suggesting that assimilation of Cl-enriched brines can account for atmospheric contamination of rare-gas isotopic ratios provided the brines have variable rare-gas concentrations that are similar to or somewhat lower than those of seawater. Some Kilauea submarine glasses also display Cl enrichment, although to a smaller extent than Loihi samples, and the largely horizontal trends of the Kilauea tholeiites in Fig. 5 are also consistent with assimilation of a noble gas-bearing and seawater-derived component, but to a consistently smaller degree than most Loihi samples, as inferred above based on their CI/K2O ratios.

Our interpretation that seawater-derived brines are the most likely assimilant is also supported by CI/Br ratios measured in a limited number of pillow-rim glasses from Loihi (Jambon, 1994; A. Jambon, personal communication, 1999). These glasses (with Cl contents of 0.03–0.06 wt.%; i.e., at the low end of the range of samples considered here) have uniform CI/Br ratios (~360) close to that of seawater (290) (and also to average MORB, 400 ± 100; Jambon, 1994). Assimilation of halite or other Cl-rich mineral, even in small amounts, would be expected to substantially elevate CI/Br (Br does not partition into the halite structure; Berndt and Seyfried, 1997, and the same is also probably true for other Cl-rich minerals such as iron–hydroxychlorides; Berndt and Seyfried, 1997). In contrast, formation of brines from sea water does not substantially fractionate the CI/Br ratio (Berndt and Seyfried, 1997).

4.3. Assimilation During Summit Collapse

In October 1996, a ∼600 m diameter section of the summit of Loihi collapsed to form a crater about 300-m deep (Duennebier, 1996; Davis and Clague, 1998; Garcia et al., 1998b). Summit collapse events such as this are thought to occur after removal of magma by eruption leaves the roof of the summit magma chamber unsupported (e.g., Decker, 1987). At Loihi, the collapsed region included several hydrothermally active areas (including the area formerly known as Pele’s vents), and the collapse event changed both the geometry of fluid circulation in the existing summit hydrothermal system and the chemistry of fluids released at summit hydrothermal vents (Duennebier et al., 1996; Davis and Clague, 1998). Collapse events like this could be linked to assimilation of Cl-rich components as they provide a means for brines and rocks (the latter potentially brine-bearing) from deep within the summit hydrothermal systems to collapse into the top of the magma chamber. It is less likely that fluids from the hydrothermal system could enter the magma chamber more directly, as semiductile flow in heated wallrocks around the magma chamber would probably “armor” the magma chamber against the direct entry of fluids (Fournier, 1987).

If summit collapse events are associated with assimilation, then similar processes may operate in other Hawaiian volcanoes, where collapse craters are also common (Decker, 1987). However, our observation that high Cl contents and CI/K2O ratios are largely limited to glasses from Loihi may indicate that assimilation of Cl-rich, seawater-derived components is an important process only in the early stages of the development of oceanic volcanoes, when the summit and/or summit magma chamber is still submerged and summit hydrothermal systems are dominated by seawater. Planned deep drilling into Mauna Kea (Stolper et al., 1996) may allow for more detailed investigation of the role of assimilation in the early stages of volcanic development.

5. CONCLUSIONS

Many pillow-rim and fragmental glasses from Loihi seamount have high Cl and high ratios of Cl to K (and other incompatible elements) relative to submarine glasses from other Hawaiian volcanoes (Mauna Loa, Mauna Kea, and Kilauea). We propose that this reflects widespread assimilation of a seawater-derived, Cl-rich component at this volcano.

Assimilation of seawater-derived Cl-rich phases such as saline brine or Cl-rich minerals (halite or iron–hydroxychlorides) with high CI/H2O ratios can explain the observed Cl contents and large variations in the ratios of Cl to other incompatible elements in Loihi lavas. Brines and Cl-rich minerals are thought to form from seawater within the hydrothermal systems associated with submarine volcanoes, so such phases are plausibly available for assimilation in the magma systems of submarine volcanoes such as Loihi.

Assimilation of seawater-derived, Cl-rich components can also explain the contamination of Loihi lavas with atmospheric-derived noble gases if the assimilant had concentrations of Ne and Ar comparable to, or slightly less than, seawater. This is more likely for brines than for Cl-rich minerals, leading us to favor brines as the major assimilant. In addition, seawater-like Br/Cl ratios in several Loihi pillow-rim glasses also favor seawater-derived brines as the primary assimilant as halite and other Cl-rich minerals strongly fractionate this ratio.

Summit collapse events such as the one observed at Loihi in October 1996, provide a mechanism for depositing brine-bearing rocks and/or Cl-rich hydrothermal minerals from the volcanic edifice into the top of a summit magma chamber.

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