Geochemistry of Atmospheric Aerosols Generated from Lava-Seawater Interactions

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Geochemistry of atmospheric aerosols generated from lava-seawater interactions

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[1] Trace elements were measured in the aerosol plume produced by lava-seawater interactions along the shoreline of Kilauea volcano, Hawaii. Plume concentrations were normalized relative to Hawaiian basalt composition and showed a linear log-log co-variation with their emanation coefficient (an indicator of element volatility). Normalized aerosol concentrations also consistently covaried with corresponding normalized concentrations in dilute fumarolic gas from Kilauea volcano and fumarolic gas condensates from Kudryavy and Merapi volcanoes, despite different mechanisms of element volatilization. Conservatively estimated regional ocean deposition rates of Cu, Cd, Ni, Pb, Mn, Zn, Fe and P were >50 times background rates. Thus, upper ocean volcanism may be an important source of both toxic and nutrient elements to the surrounding ocean. It appears unlikely, however, that shallow ocean volcanism can exert a significant impact on the global ecosystem, even during massive lava emplacements.

INDEX TERMS: 8409 Volcanology: Atmospheric effects (0370); 4825 Oceanography: Biological and Chemical: Trace elements; 1630 Global Change: Impact phenomena

1. Introduction

[2] Significant inputs to the atmosphere are known to occur from terrestrial volcanism [e.g., Lantzy and Mackenzie, 1979] and may play a role in modulating climate by injecting large quantities of particles and magmatic gases into the atmosphere, potentially affecting the earth’s albedo and influencing the global biogeochemical cycling of many elements [e.g., Caldeira and Rampino, 1991]. Sub-aqueous volcanism at the ocean surface also has the potential to introduce a variety of environmentally important chemical species to the atmosphere through lava-water interactions; this process was likely important in the geological past when near-surface ocean volcanism was more common. For example, volcanism near the ocean surface was a predominant process during the emplacement of large igneous provinces (LIPs) [e.g., Coffin and Eldholm, 1994] and during the opening of the current oceanic basins [e.g., White and McKenzie, 1989]. LIPs have volumes of up to tens of million km³ of mafic rock, with mean emplacement rates of up to tens of km² y⁻¹ [e.g., Coffin and Eldholm, 1994]. In addition, LIP generation occurred during periods of rapid species extinction, such as the 67 MA Cretaceous-Tertiary boundary and the 248 MA Permian extinction, heightening the importance of understanding the mechanisms and geochemical effects of these large events.

[3] There are few data available on the direct lava-seawater interactions that occur during upper ocean LIP emplacement. However, lava from Kilauea volcano (19° 20’N, 155° 00’W) on the island of Hawaii has been flowing into the ocean almost continuously since 1986 [Mattox and Mangan, 1997], providing a convenient means for studying such processes. Although the physical and geochemical effects of this lava entry on the adjacent ocean have been previously reported [Sansone and Resing, 1995; Resing and Sansone, 1999, in press], the composition of the aerosol (“steam”) plume associated with the lava entry has not previously been determined.

2. Methods

[4] On the day of sample collection (16 July 2000) lava tubes released lava into the surface ocean either at the steep edge of the shoreline lava bench or underwater with little contact with the atmosphere before water contact. The resulting boiling of seawater produced a visible atmospheric aerosol plume that was transported parallel to the coastline by the winds on that day. Subaerial volcanic inputs to the aerosol plume were minimized by both the wind direction and the small amount of subaerial lava extrusion along the shoreline.

[5] Plume aerosols were sampled using an active mesh collector (impactor) consisting of an air pump that pulled 151 L min⁻¹ of air through 0.18 m² of tightly folded plastic screen (0.5 mm opening) located in the top of a 4-L wide mouth polyethylene bottle. The collector was suspended below a Hughes 500D helicopter using 60 m of synthetic fiber rope; aerosol entered through four 1-cm diameter holes in the bottle wall, coalesced on the mesh, and was collected in the bottom of the bottle. The buoyant portion of the aerosol plume was sampled for 22 min, ~15 m downwind of the lava entry and at an altitude of ~10 m above sea level. Visual observation showed that turbulence from the helicopter’s rotor did not disturb the aerosol plume in the vicinity of the sampler. The collection efficiency of the sampler was close to 100%, as evidenced by the absence of visible liquid or solid inside the tubing connecting the outlet of the mesh with the air pump after sampling. Prior to use, all apparatus were washed, soaked in 10% HCl, triply rinsed with 18-MΩ deionized water and stored in cleaned polyethylene bags. After collection, samples were transferred to 30-mL polypropylene bottles.

[6] Cl⁻, SO₄²⁻, Mg²⁺ and K⁺ were determined (±5%) by ion chromatography (IC); Na (±7%) by ICP-AES; Ca by both IC and ICP-AES; Fe (±2%) and Al (±8%) by direct-injection flow injection analysis (FIA) [Resing, 1997]; Hg (±5%) by cold vapor atomic absorption spectroscopy; NO₃⁻ + NO₂⁻, NH₄⁺ and Si (±0.03 μM) by AutoAnalyzer; arsenate (±5%) and soluble reactive P (SRP) (±2%) by spectrophotometry [Hansen and Koroleff, 1999]; and total dissolved P (TDP) (±150 nM) by acid persulfate oxidation [Hansen and Koroleff, 1999]. Other trace elements were determined (±0.2–6%) by FIA-ICP-MS [Resing, 1997]. pH was measured (±0.5) in the field with pHydroin indicating pH paper.

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The aerosol plume temperature was measured (±0.6°C) with an Onset Optic StowAway temperature logger mounted next to the sample impactor.

3. Results and Discussion

[7] The aerosol plume temperature at the point of sampling was ~36°C, and the collected aerosol had a pH value of 1.0. The aerosol/seawater concentration ratios for Na, Mg, K, SO₄²⁻, (calculated per-mass; data not shown) were 0.62 (<0.01):1, suggesting that the aerosol was 62% seawater. In contrast, however, Cl⁻ had a significantly larger ratio of 0.69, presumably due to the production of HCl [Resing and Sansone, 1999]. Ca²⁺ had a ratio of 0.83, which remains enigmatic, but which does not appear to be an analytical artifact, as Ca was determined by two separate analytical methods.

Among the minor and trace elements, Fe, which is thought to be a limiting nutrient in many oligotrophic marine environments [e.g., Martin et al., 1991], was particularly elevated in the plume (13 mg kg⁻¹, Table 1), as was TDP (2.3 mg kg⁻¹), indicating the potential for the plume to be a source of nutrients for terrestrial and marine environments downstream. In contrast, no evidence was found for enriched fixed N levels in the aerosol plume.

[8] Using the major element data, we can assume that the aerosol is 62% seawater. We can then use the concentrations of minor and trace elements in seawater [Libes, 1992] to correct their aerosol concentrations by subtracting the seawater contributions from the aerosol concentrations. When this is done, we find that Rb and Sr are mostly derived from seawater; however the remainder of the elements are significantly enriched over their seawater values and must have the lava as their source.

[9] The “corrected” concentrations were then normalized to the respective concentrations of the elements in Hawaiian basalt (BHVO; Govindaraju, 1994). The results of this calculation show that Hg, Cd, Pb, Mo, and Zn display a much greater relative enrichment than do the other trace elements. These same elements have also been shown to be greatly enriched in fumarolic gases and gas condensates from a variety of volcanoes; thus, when our data are compared with corresponding normalized concentrations in dilute fumarolic gas from Kilauea volcano and gas condensates from Kudryavy volcano (Figure 1), there is a strong linear covariation between these systems, even though these volcanoes are geologically dissimilar and there are different mechanisms of element volatilization (lava-seawater interactions vs. magma degassing). A similar relationship can be seen with Merapi gas condensate data [Symonds et al., 1987] (data not shown). Note that

### Table 1. Concentrations of Trace Elements in the Aerosol Plume, Estimated Aerosol-plume Atmospheric Input Rates, Estimated Aerosol-plume and Tropical North Pacific Background Ocean Deposition Rates, and the Aerosol-plume/Background Deposition Rate Ratios. Dashes Indicate Data Not Available

<table>
<thead>
<tr>
<th>Element</th>
<th>Aerosol plume conc (µg/kg)</th>
<th>Seawater conc (µmol/kg)</th>
<th>Aerosol-plume atmospheric input rate (kg/mol/a)</th>
<th>Even distribution model deposition rate (g/m²/y)</th>
<th>Dispersion model deposition rate (g/m²/y)</th>
<th>Background ocean deposition rate (mg/m²/y)</th>
<th>Even distribution aerosol plume/background deposition rate</th>
<th>Dispersion model aerosol plume/background deposition rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>17200</td>
<td>1.0 x 10⁻³</td>
<td>1700</td>
<td>99</td>
<td>113</td>
<td>440</td>
<td>–</td>
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<tr>
<td>Fe</td>
<td>13000</td>
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<td>75</td>
<td>87</td>
<td>340</td>
<td>5.6</td>
<td>16000</td>
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<td>Al</td>
<td>7320</td>
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<td>740</td>
<td>42</td>
<td>10</td>
<td>37</td>
<td>0.7</td>
<td>14000</td>
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<td>1480</td>
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<td>150</td>
<td>8.6</td>
<td>10</td>
<td>3</td>
<td>–</td>
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</tr>
<tr>
<td>NPP</td>
<td>820</td>
<td>–</td>
<td>84</td>
<td>4.8</td>
<td>5.6</td>
<td>18</td>
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<td>3100</td>
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<td>TDP</td>
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<td>2.3 x 10⁰</td>
<td>234</td>
<td>13.4</td>
<td>16</td>
<td>55</td>
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<tr>
<td>Sr</td>
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<td>8.7 x 10¹</td>
<td>410</td>
<td>23</td>
<td>27</td>
<td>100</td>
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<td>–</td>
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<tr>
<td>Zn</td>
<td>1840</td>
<td>6 x 10⁻³</td>
<td>190</td>
<td>11</td>
<td>13</td>
<td>48</td>
<td>0.67</td>
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<tr>
<td>Cu</td>
<td>1170</td>
<td>4 x 10⁻³</td>
<td>120</td>
<td>6.7</td>
<td>8.0</td>
<td>30</td>
<td>0.089</td>
<td>90000</td>
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<td>Mn</td>
<td>275</td>
<td>5 x 10⁻³</td>
<td>28</td>
<td>1.6</td>
<td>1.9</td>
<td>7.1</td>
<td>0.09</td>
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<tr>
<td>Pb</td>
<td>241</td>
<td>1 x 10⁻⁵</td>
<td>24</td>
<td>1.4</td>
<td>1.6</td>
<td>6.2</td>
<td>0.078</td>
<td>23000</td>
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<td>Ni</td>
<td>142</td>
<td>8 x 10⁻⁴</td>
<td>14</td>
<td>0.82</td>
<td>0.93</td>
<td>3.7</td>
<td>0.023</td>
<td>40000</td>
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<tr>
<td>V</td>
<td>99</td>
<td>2.5 x 10⁻²</td>
<td>10</td>
<td>0.57</td>
<td>0.67</td>
<td>2.6</td>
<td>0.078</td>
<td>8600</td>
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<tr>
<td>Rb</td>
<td>98</td>
<td>1.4 x 10⁰</td>
<td>10</td>
<td>0.56</td>
<td>0.67</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ba</td>
<td>58</td>
<td>1 x 10⁻¹</td>
<td>5.9</td>
<td>0.34</td>
<td>0.39</td>
<td>1.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cr</td>
<td>46</td>
<td>4 x 10⁻³</td>
<td>4.7</td>
<td>0.27</td>
<td>0.31</td>
<td>1.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cd</td>
<td>34</td>
<td>7 x 10⁻⁴</td>
<td>3.5</td>
<td>0.20</td>
<td>0.23</td>
<td>0.88</td>
<td>0.0035</td>
<td>66000</td>
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<tr>
<td>Mo</td>
<td>28</td>
<td>1.1 x 10⁻¹</td>
<td>2.8</td>
<td>0.16</td>
<td>0.19</td>
<td>0.72</td>
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<td>–</td>
</tr>
<tr>
<td>Co</td>
<td>18</td>
<td>3 x 10⁻⁵</td>
<td>1.8</td>
<td>0.10</td>
<td>0.12</td>
<td>0.45</td>
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<tr>
<td>Ce</td>
<td>5.5</td>
<td>2 x 10⁻⁵</td>
<td>0.56</td>
<td>0.032</td>
<td>0.037</td>
<td>0.14</td>
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<td>–</td>
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<tr>
<td>As</td>
<td>5.2</td>
<td>2.3 x 10⁻²</td>
<td>0.53</td>
<td>0.030</td>
<td>0.035</td>
<td>0.14</td>
<td>0.0056</td>
<td>6200</td>
</tr>
<tr>
<td>La</td>
<td>2.9</td>
<td>3 x 10⁻⁵</td>
<td>0.29</td>
<td>0.017</td>
<td>0.019</td>
<td>0.074</td>
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<tr>
<td>Ag</td>
<td>2.4</td>
<td>2.5 x 10⁻⁵</td>
<td>0.24</td>
<td>0.014</td>
<td>0.016</td>
<td>0.062</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hg</td>
<td>2.2</td>
<td>5 x 10⁻⁶</td>
<td>0.22</td>
<td>0.013</td>
<td>0.015</td>
<td>0.037</td>
<td>0.006</td>
<td>2500</td>
</tr>
<tr>
<td>Nd</td>
<td>1.8</td>
<td>2 x 10⁻⁵</td>
<td>0.18</td>
<td>0.010</td>
<td>0.012</td>
<td>0.047</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Y</td>
<td>1.5</td>
<td>1 x 10⁻⁴</td>
<td>0.15</td>
<td>0.0085</td>
<td>0.010</td>
<td>0.038</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>U</td>
<td>0.90</td>
<td>1.3 x 10⁻²</td>
<td>0.091</td>
<td>0.0052</td>
<td>0.006</td>
<td>0.023</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NO₃⁺+NO₂⁻+N₂O&lt;₁₁₀</td>
<td>3 x 10¹⁰</td>
<td>&lt;11</td>
<td>&lt;6.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NH₄⁺+N&lt;₁₁₀</td>
<td>3 x 10¹⁰</td>
<td>&lt;11</td>
<td>&lt;0.63</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*Libes [1992]
*Calculated assuming a plume production rate of 40,000 m³ min⁻¹ at the ocean lava entry we sampled.
*Calculated assuming a Kilauea lava production rate of 320,000 m³ d⁻¹, with 15% entering the ocean at the lava entry we sampled.
*Graham and Duce [1979, 1981], Arimoto et al. [1985], and Duce et al. [1991]: Ni and As data estimated from Pb deposition rates divided by Pb/Ni and Pb/As crustal abundance ratios [Li, 2000], respectively.
*NPP = TDP – SRP
offsers in the regressions are likely due to differences in sample dilution.

[10] A compilation of fumarolic data from eight different volcanoes was used to calculate emanation coefficients [Lambert et al., 1985/1986] for 44 different elements [Rubin, 1997]. Corrected, normalized aerosol concentrations also correlate linearly on a log-log basis with the emanation coefficients of the elements (Figure 2). Thus, more volatile elements are preferentially enriched in the aerosol plume relative to Hawaiian basalt. A similar enrichment of volatile elements was observed in seawater in contact with lava at the shoreline entry and in precipitation (rain) from the aerosol plume [Resing and Sansone, in press]. However, these samples had higher relative concentrations of the least volatile elements (e.g., Al, La, Mn, Fe) than we observed in the aerosol, apparently due to congruent dissolution from the basalt into seawater and the aerosol plume rain. The dashed line in Figure 2 is the linear regression for elements with emanation coefficients >10–3; elements with lower emanation coefficients fall noticeably above the line.

[11] Although the extent and distribution of deposition from the Kilauea aerosol plume remains uncertain, sulfate aerosols from Kilauea’s terrestrial vents have been detected over 1000 km away [Porter and Clarke, 1997]. As a result, we attempted to model the atmospheric plume deposition rates to the adjacent ocean, which is potentially affected by inputs of nutrients such as Fe and P, and toxic trace elements such as Pb and Cu.

[12] Using visual analysis of video images of the aerosol plume during our sampling, we estimate the plume height to be ≈300 m and the plume production rate to be ≈730 m³ s⁻¹. The Kilauea lava production rate was 320,000 m³ d⁻¹, with ≈10–20% entering the ocean at the Waha’ula lava entry where we sampled (J. Kauahikaua, pers. comm., 2001). These values allow atmospheric input rates to be calculated for each trace element on both an absolute and a lava-normalized basis (Table 1); these are likely to be minimum estimates, as it was not possible to keep the sampler located in the core of the aerosol plume at all times during sampling.

[13] Although our meteorological information is limited, we have attempted to make two estimates of the rate of plume aerosol deposition. The first, an “Even distribution model” (Table 1), is intended to put an upper bound on deposition and assumes that concentrations measured within the aerosol plume apply to a 30 km × 0.5 km area of ocean, the region over which the plume is visible. All of the material is deposited within this region. The second estimate is based on a simple plume dispersion model using several assumptions: 1) an average deposition velocity of 0.5 cm s⁻¹ [Williams, 1982], 2) that the concentration of the 9 m³ plume parcel produced each second was distributed evenly from 300 m to the ocean surface in order to apply a mixed boundary layer deposition velocity, 3) a plume expansion rate of 3.6% per hour (or 0.01% s⁻¹), and 4) a plume speed of 7 m s⁻¹ (typical of tradewind conditions). Deposition rates were determined once every second over a distance of 40 km, subtracting the previous amount deposited from the plume concentration with each iteration. Modeled aerosol plume deposition rates rapidly reached background levels at 30 km from the ocean entry point, with the extent of the plume coverage increasing from 81 m² to 1100 m². The total deposition over the first 30 km is given in Table 1 as the “Dispersion model deposition rate”.

[14] The trace element deposition rates from the conservative dispersion model are 10–340 times greater than background tropical North Pacific deposition rates (Table 1). However, deposition from Kilauea’s volcanic plume is primarily via rainout because of the small diameter of the plume aerosols (~0.3 μm, Porter and Clarke [1997]), and thus deposition is likely to be episodic; this would lead to a greater intensity of deposition during rainfall events than is indicated by the above calculation. These
arguments suggest that, at least on a regional scale, volcanic aerosol deposition can have a significant effect on upper ocean biogeochemistry. However, it is not clear at this point what the net effect of these different inputs is on upper ocean biota, as the aerosol plume deposition includes both nutrients (e.g., Si, Fe, P) and potentially toxic elements (e.g., Cu, Cd, Pb). Note that sea-surface lava-seawater interactions also produce large amounts of macroscopic airborne particulate matter that is deposited very close to the lava entry [Resing, 1997]. This hyaloclastic glass is highly soluble [Sicks, 1975], and its dissolution may also contribute significantly to such oceanic processes as “Fe fertilization” [Martin et al., 1991].

[15] Our results can be used to examine whether large scale upper ocean lava extrusions, such as those known to occur during the formation of LIPs, are capable of injecting significant amounts of environmentally sensitive elements into the atmosphere. By assuming geochemical dynamics similar to the Kilauea lava entry (Table 1), a LIP lava extrusion of 500 km³ (approximately the size of the 26.5 ka Oruauni eruption, the largest known “wet” eruption, Wilson [2000]) would be expected to inject 40 Gg of Fe, 20 Gg of Pb, and 0.7 Gg of Pb into the atmosphere. These values represent only 0.1%, 0.5%, and 10%, respectively, of the current annual global nonanthropogenic inputs of these elements to the atmosphere [Lantzy and Mackenzie, 1979; Mackenzie et al., 1993]. Hence, the data suggest that atmospheric inputs to the global ecosystem from shallow ocean volcanism are small, although local/regional effects may be quite pronounced. It remains to be determined whether regional plume deposition is a net positive or negative factor on oceanic primary production.

[16] The Kilauea lava flowing into the ocean is degassed of most of its CO₂, H₂, H₂O, and sulfur-gases. These gases may act as carrier phases for the volatile trace elements [Gerlach, 1989], and their absence from the lava entering the ocean at Kilauea most likely results in a lower flux of volatile elements from the lava to the atmosphere. However, this is not the case for eruptions that occur where volcanoes breach the sea surface. Our estimates, therefore, are very conservative.

[17] Acknowledgments. We thank David Okita for skillful piloting during sampling; Liangzhong Zhang for IC analyses; Media Arts, Inc. for video-recording the sampling operations; Telu Li for discussions of the data; and Jim Kauahikaua for information on the Kilauea lava flow rates; and Taran for discussions of the sampling logistics. The research was supported by the JASON Foundation for Education and the Andrew W. Mellon Foundation. SOEST Contr. No. 5946, PMEL Contr. No. 2249, JISAO Contr. No. 894.

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