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Francis J. Sansone

Joseph A. Resing

Gordon W. Tribble

Peter N. Sedwick

Old Dominion University, Psedwick@odu.edu

Kevin M. Kelly

See next page for additional authors

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Authors

Francis J. Sansone, Joseph A. Resing, Gordon W. Tribble, Peter N. Sedwick, Kevin M. Kelly, and Ken Hon

LAVA-SEAWATER INTERACTIONS AT SHALLOW-WATER SUBMARINE LAVA FLOWS

Francis J. Sansone¹, Joseph A. Resing¹, Gordon W. Tribble^{1,2}
Peter N. Sedwick¹, Kevin M. Kelly¹, and Ken Hon³

Abstract. Hydrothermal plumes associated with nearshore lava flows from Kilauea Volcano, Hawaii were studied on five occasions during 1989-1990 to address the current lack of data on direct lava-seawater interactions. The following enrichments were found in the sea-surface hydrothermal plumes above the active underwater lava flows: H₂, 15,000x ambient seawater concentrations; Mn, 250x; and Si, 20x. Water temperatures reached 46°C. Lower concentrations and temperatures were observed in the plumes with increasing distance from shore, with H₂, Si, and Mn concentrations linearly related to seawater temperature. Unlike deep sea spreading center hydrothermal plumes, no CH₄ enrichment was observed. The elevated H₂ is likely to be from water-rock reactions, rather than from the release of magmatic gas. The plume mass/heat ratios presented here suggest that submarine flood basalts, although aurally large, should be relatively small immediate contributors to oceanic geochemical cycles compared to hydrothermal circulation through the crust.

Introduction

Direct lava-seawater interactions in the vicinity of Kupapau Point on the southeast coast of the island of Hawaii (19°20'N, 155°1'W) were studied on five occasions. The eruption responsible for these flows from Kilauea Volcano has been extruding lava at an average rate of $4.5 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ since mid-1983 (Wolfe *et al.*, 1987). The magma reaches the surface at Puu Oo cinder cone, where the bulk of magmatic volatiles is vented to the atmosphere (Gerlach and Taylor, 1990). Subsurface tubes then supply this lava to downslope flows, some of which extend offshore (Greenley, 1987).

Five modes of lava-seawater interaction have been observed at this site (Tribble, 1991): 1) shoreline lava flows, 2) submarine pillow lavas, 3) submarine channelized lava flows, 4) hydrothermal jets from seawater contact with buried submarine lava tubes, and 5) explosions at the surface of fluid underwater flows, thought to be caused by the ignition of hydrogen-rich gases produced by lava-seawater reactions (see below). The hot water from these processes forms $\leq 3\text{-m}$ thick surface plumes that can be observed to extend seaward from the shore (Sansone *et al.*, 1990b).

These plumes have a distinct greenish-gray color, with the hottest water being light brown. Very sharp gradients exist between the plume and the clear blue surrounding seawater. A colored plume typically extends a kilometer or less alongshore, and may stretch more than a kilometer offshore depending on the nearshore currents. This altered seawater has high levels of suspended black glass fragments released during the fracturing of hot lava in contact with seawater. On several occasions large concentrations of gelatinous zooplankton were also observed. The light attenuation anomalies in the surface plume can reach values of 9 m^{-1} (10%

light transmission over 25 cm) (data not shown). Finally, it is not uncommon for several lava outbreaks to occur along a few km of shoreline, with individual plumes emanating from each outbreak.

A hull-mounted thermistor (precision = $\pm 0.05^\circ\text{C}$) was used to measure the temperature of the surface plumes. Positioning was obtained ($\pm 2 \text{ m}$) with a Motorola Mini-Ranger Falcon-IV. Samples were collected with a 2.5-liter Go-Flo bottle. H₂ was measured ($\pm 15\%$) within one day of collection by gas-chromatography(GC)/UV-photometry (Bullister *et al.*, 1982). CH₄ was determined ($\pm 1\%$) by cold-trap/GC (Brooks *et al.*, 1981). Dissolved inorganic nutrients (PO₄ ($\pm 0.02 \mu\text{M}$); NH₄, NO₃ + NO₂, and Si ($\pm 0.03 \mu\text{M}$)), dissolved organic P ($\pm 0.04 \mu\text{M}$), and dissolved organic N ($\pm 0.6 \mu\text{M}$) were measured on filtered samples (0.2 μm pore size) using standard techniques (Parsons *et al.*, 1984) with a Technicon AutoAnalyzer II, except for September 1990 Si samples, which were measured ($\pm 3\%$) by flow injection analysis. Mn and Li in filtered samples were determined ($\pm 10\%$) by direct injection furnace atomic absorption spectroscopy (Carnrick *et al.*, 1981). Class-100 conditions were used for trace element sample preparations; acid-washed polypropylene and polycarbonate apparatus were used for sample collection and filtration; North Atlantic Standard Seawater and Coastal Atlantic Standard Seawater (National Research Council, Canada) were used as standards.

Results and Discussion

The surface seawater temperature for the Kupapau Point region on 11 June 1989 shows the localized nature of the lava activity on this day (Figure 1a); the maximum surface water temperature recorded was 38°C approximately 100m offshore of the shoreline lava flows. Vigorous underwater lava flows were also observed by SCUBA divers below this point. In contrast, lava-induced surface seawater temperature anomalies were seen six weeks later across a 3-km length of coast (Figure 1b), the result of major nearshore and shoreline lava flows at the ends of this section, with smaller flows in between. The maximum surface water temperature measured on this day was 44°C.

The dissolved H₂ and CH₄ concentrations of surface seawater samples collected from thermal plumes on the five sampling dates are plotted vs. water temperature anomaly (ΔT) in Figure 2. An extrapolation of the H₂ regression line to $\Delta T = 110^\circ$ (135°C, the boiling point of seawater at the $\sim 21 \text{ m}$ depth of the major nearshore lava-seawater contact (Stoughton and Lietzke, 1967)) yields a hypothetical "endmember" H₂ concentration of 11 μM . This value is within the range of 1-1700 μM found in endmember fluids from spreading center (deep-sea) hydrothermal vents (Welhan and Craig, 1983; Lilley *et al.*, 1983). In contrast, CH₄ concentrations in the Kupapau plumes were not significantly greater than the low nM levels typically found in nearshore Hawaiian waters (Figure 2). This result is in marked contrast to the elevated CH₄ levels (50-1400 μM) reported for endmember fluids from spreading center hydrothermal vents (M.D. Lilley, pers. comm.; Welhan and Craig, 1983; Lilley *et al.*, 1983).

Note that our use of 135°C as the temperature of the hydrothermal "endmember" in our system does not imply that this is necessarily the temperature of the water-rock reactions. The

¹Department of Oceanography, University of Hawaii at Manoa²Water Resources Division, U.S. Geological Survey³Hawaiian Volcano Observatory, U.S. Geological Survey

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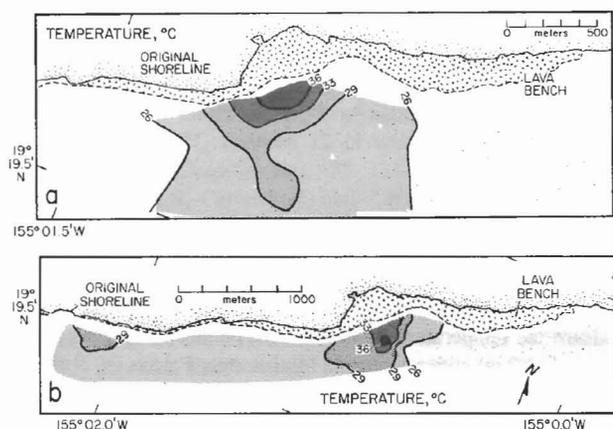


Fig. 1. The temperature distribution in surface seawater at Kupapau Point on a) 11 June 1989 and b) 26 July 1989. The shading indicates the areas surveyed (cruise track interval ≤ 100 m).

contact between incandescent lava and seawater undoubtedly results in temperatures well in excess of the ambient boiling point, and likely results in high temperature steam-lava/steam-rock reactions (see below). SCUBA divers at this site regularly observe the release of what appears to be steam from the seawater-lava contact; the steam rises several cm from the contact before it is quenched by the surrounding seawater (Sansone *et al.*, 1990a). The 135°C "endmember" is used in this study to determine the composition of the seawater immediately above the seawater(-steam)-lava contact.

Large numbers of gas bubbles were released to the overlying seawater, with some reaching the atmosphere. The major sources of gas bubbles included the contact of incandescent channelized lava flows and pillow lavas with seawater, underwater hydrothermal jets, and explosions occurring on fluid lava flows. Five samples of bubbles were collected immediately over a variety of lava flows by divers with inverted bottles. The bubbles were 14-25% H_2 (v/v), 19-22% O_2 , 49-64% N_2 , 1-9% CO_2 , and 40-79 ppm CH_4 (T. Lorenson and W. Evans, pers. comm.).

These high levels of H_2 cannot solely result from the release of magmatic gas because the latter contains much lower H_2 levels: Kilauea magmatic gas is 0.1-1.5% H_2 (Greenland, 1987). We believe that the H_2 in the seawater plume and the gas bubbles is primarily due to water-rock reactions (*e.g.*, Christie *et al.*, 1986). Note that such processes are not limited to liquid-solid reactions: the production of H_2 from Fe oxidation by steam at 700°C and 1 atm is well established (Deming, 1935). Finally, our hypothesis is also consistent with the above-mentioned venting of volatiles from Kilauea magma at Puu Oo before it is extruded at the shore.

The low CH_4 levels in the bubbles are similar to those in Kilauea magmatic gas (*e.g.*, Greenland, 1987). It is likely that the low CH_4 levels in the surface plumes simply reflect the low CH_4 concentrations existing during rock-water equilibria at elevated temperature and low pressure (Gerlach, 1980). This would also explain the significantly higher levels of CH_4 observed in deep sea hydrothermal fluids, because rock-water CH_4 production is significant only under elevated hydrostatic pressures (Gerlach, 1980). Note, however, that H_2 production is not similarly constrained by pressure (T.M. Gerlach, pers. comm.).

Except for a marked increase in dissolved Si (Figure 2), there was not a significant change in organic or inorganic nutrients in the surface plumes from ambient seawater levels (data not shown). Li also remained at background nearshore levels (~ 25 $\mu\text{mole/kg}$, data not shown). In contrast, dissolved Mn was significantly enriched in the plumes (Figure 2). Extrapolation of the Si (solid line) and Mn regressions in Figure 2 to $\Delta T = 110^\circ$ (135°C) yields hypothetical

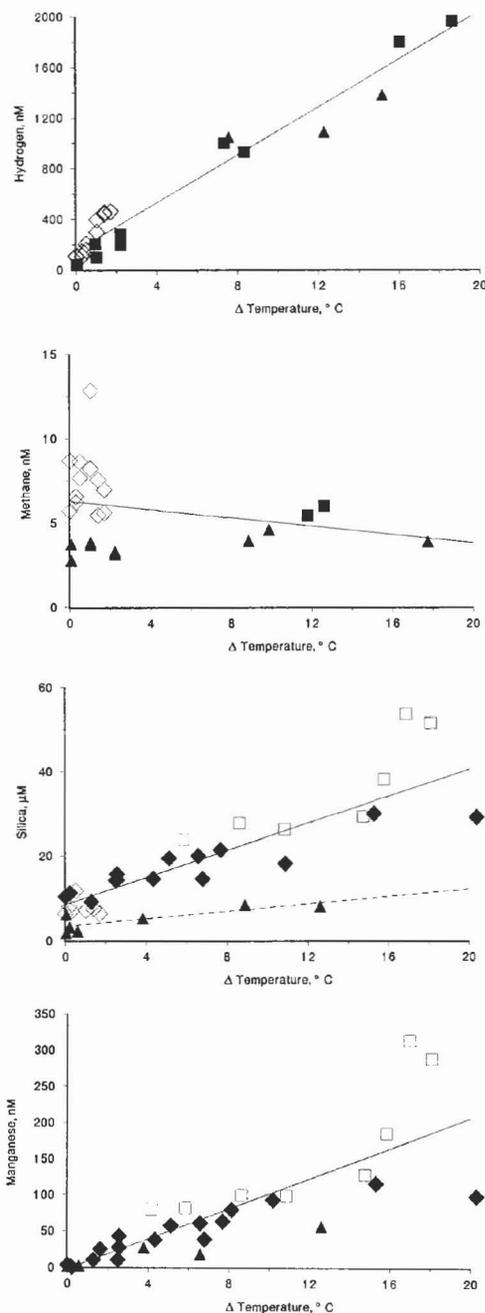


Fig. 2. Dissolved H_2 , CH_4 , Si and Mn vs. ΔT (with respect to offshore surface seawater) for surface seawater samples. Data from (\blacktriangle) 11 June 1989, (\blacksquare) 26 July 1989, (\diamond) 20 March 1990, (\blacklozenge) 23 Sept 1990, and (\square) 24 Sept 1990. Lines indicate least square linear regressions with the following slopes: H_2 , 95 nM $^\circ\text{C}^{-1}$; CH_4 , -0.12 nM $^\circ\text{C}^{-1}$; Si, 0.44 μM $^\circ\text{C}^{-1}$ (dashed line, June 1989 data), 1.6 μM $^\circ\text{C}^{-1}$ (solid line, all other data); and Mn, 11 nM $^\circ\text{C}^{-1}$.

"endmember" concentrations of 190 μM Si and 1.2 μM Mn. Both values are several orders of magnitude lower than those reported for high temperature spreading center hydrothermal vent endmembers (*e.g.*, Von Damm *et al.*, 1987). It is likely that this difference is largely due to the very short water-rock reaction time in our system. For example, Seyfried *et al.* (1984) found that Li concentrations in seawater in contact with basalt glass at 150° and 500 bar do not increase until after 30 hours.

TABLE 1. Ranges of mass/heat ratios for seawater alteration at deep sea hydrothermal systems and Hawaiian surface plumes.

Hydrothermal system	H ₂ /heat (pmol/J)	CH ₄ /heat (pmol/J)	Si/heat (nmol/J)	Mn/heat (pmol/J)	Reference
Spreading center high-T vent fluid	184-858*	18-34*	7-23	290-3500	Welhan and Craig, 1983; Von Damm <i>et al.</i> , 1985, 1987
Spreading center low-T vent fluid	0.5-4.7*	65-220*	14	360-930	Corliss <i>et al.</i> , 1979; Lilley <i>et al.</i> , 1983
Spreading center plume		9.5-1600		170-840	Baker and Massoth, 1986; Baker <i>et al.</i> , 1987; Charlou <i>et al.</i> , 1988; Kadko <i>et al.</i> , 1990
Spreading center megaplume			10	88	Baker <i>et al.</i> , 1987
Mid-plate plume (Loihi, Hawaii)		78-88			Gamo <i>et al.</i> , 1987
Hawaiian surface plumes	22	~ 0	0.10-0.38	2.5	This work

High-T ratios calculated using heat capacity data of Bischoff and Rosenbauer (1985); surface plume ratios from regressions in Figure 2.

*Calculated assuming excess heat = 1.9×10^{17} J/mol-³He (Jenkins *et al.*, 1978).

The "endmember" concentrations computed from our samples are similar to those of seawater emanating from hydrothermal jets located at ~21 m depth at this site (Sedwick *et al.*, 1991). These waters had lowered pH values (~6.5) and had dissolved Si and Mn concentrations of 9-143 $\mu\text{mole kg}^{-1}$ and 73-1290 nmol kg^{-1} , respectively. This heated seawater was apparently subjected to boiling, as evidenced by the steam observed in the jets' effluent, and chloride enrichment in the heated seawater (up to 19.13 g kg^{-1} , as compared to an ambient concentration of 19.02 g kg^{-1}).

The lava extrusion rate from Kilauea Volcano during mid-1989 was $2.5\text{-}3.0 \times 10^5 \text{ m}^3 \text{ day}^{-1}$, with approximately 20-30% of the lava entering the ocean (Kelly *et al.*, 1989). Assuming a lava temperature of 1130°C (D.M. Thomas, pers. comm.), a lava specific heat of cooling of 3.8 $\text{J cm}^{-3} \text{ deg}^{-1}$, and a lava latent heat of crystallization of 10^3 J cm^{-3} (Baker *et al.*, 1987), this represents a heat input to the ocean of $2.6\text{-}4.7 \times 10^{14} \text{ J day}^{-1}$. This computed heat flux is smaller than those for spreading center hydrothermal "megaplumes" ($6\text{-}60 \times 10^{15} \text{ J day}^{-1}$) (Baker *et al.*, 1989), but is larger than those measured for individual spreading center vents ($4.3 \times 10^{10} \text{ - } 2.2 \times 10^{13} \text{ J day}^{-1}$) (Converse *et al.*, 1984).

The above calculations assume negligible heat losses from the surface plume to the atmosphere. Although these losses cannot be accurately estimated at this time, the very good linearity for ΔT vs. H₂ and Si (Figure 2) argue that temperature must be quite conservative over the time and space scales of our observations.

Using the relationship between ΔT and H₂ (Figure 2), a H₂ flux of $6.2\text{-}11 \times 10^3 \text{ mol day}^{-1}$ can be computed from the heat flux calculated above. Data are not available to compare this H₂ flux with those for spreading center systems, but it is clear that it is small on a global scale: the total flux of H₂ from the ocean to the atmosphere $\sim 3 \times 10^9 \text{ mol day}^{-1}$ (Jørgensen, 1982).

A comparison of mass/heat ratios for a variety of hydrothermal systems shows that there are distinct differences between the Kilauea surface plumes and other systems (Table 1). The very low Si/heat and Mn/heat ratios for the Kilauea plumes indicate that the hydrothermal extraction efficiencies are relatively low for these elements, despite the high reaction temperatures implied by direct lava-seawater contact. The low ratios are likely due to the short contact time of seawater with the lava before the latter is cooled.

These mass/heat ratios can be used to infer the importance of submarine lava-seawater interactions on global geochemical cycles. For example, recent reports have drawn attention to the existence of large scale submarine flood basalts that appear to be of relatively recent origin, and which may have been responsible for large heat inputs to the ocean (*e.g.*, Davis, 1982; Shaw and Moore, 1988). Using a global submarine lava extrusion rate of $3.3 \text{ km}^3 \text{ y}^{-1}$ (Crisp, 1984), a global heat flux of $1.8 \times 10^{19} \text{ J yr}^{-1}$ can be calculated,

which is only 10% of the estimated global spreading center hydrothermal heat flux of $2.1 \times 10^{20} \text{ J yr}^{-1}$ (Jenkins *et al.*, 1978). This result, combined with the low extraction efficiencies computed for lava-seawater interactions (Table 1), suggest that immediate global chemical fluxes due to submarine lava extrusions are much smaller than those for spreading center hydrothermal systems.

Nevertheless, submarine lava extrusions may be geochemically important on a regional scale. For example, as seen here, elements such as Si that are depleted in surface seawater may experience significant enrichment in the vicinity of shallow lava-seawater interactions. Continuing reports of sea surface hydrothermal activity related to shallow water volcanism (*e.g.*, McClelland *et al.*, 1989) suggest that upper ocean volcanism may be relatively widespread.

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- K. Hon, Hawaiian Volcano Observatory, P.O. Box 51, Volcano, HI 96718 (Present address: U.S. Geological Survey, MS-903, Federal Center, Denver, CO 80225).
- K. M. Kelly, J. A. Resing, F. J. Sansone, and P. N. Sedwick, Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Road, Honolulu, HI 96822.
- G. W. Tribble, U.S. Geological Survey, 677 Ala Moana Blvd., Suite 415, Honolulu, HI 96813.

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