



A decade of exploring a submarine intraplate volcano: Hydrothermal manganese and iron at Lō'ihi volcano, Hawai'i

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[1] Decadal time series observations of hydrothermal fluid emissions from Lō'ihi volcano were initiated in 1992 using a combination of submersible and shipboard sampling strategies. Magmatic-tectonic processes associated with a spectacular seismic event in July–August 1996 led to the collapse of Pele's Vents (31°C) near the volcano summit into a new pit crater (Pele's Pit) inundated by high-temperature ($T_{\max} = 198^{\circ}\text{C}$) focused and lower-temperature ($<95^{\circ}\text{C}$) diffuse fluid discharge. Variations in the concentrations and relative abundances of vented Fe and Mn characterize the precollapse, summit collapse, and postcollapse periods. The precollapse plume emanating from Pele's Vents had a low rise height (~ 35 m) and concentration intensity (<5 nmol/L TDMn, 70 nmol/L TDFe, ~ 1.8 km distant) and dispersed to the southwest. Plumes coeval with the 1996 summit collapse were characterized by extreme metal concentrations within Pele's Pit (up to $\sim 10,000$ nmol/L DMn and 400,000 nmol/L TDFe) and nearby East Pit ($\sim 34,000$ nmol/L DMn and 120,000 nmol/L TDFe). An intense hydrothermal plume dispersed predominantly to the southwest of the several hundred meter deep pits with concentration anomalies as high as 236 nmol/L DMn and 3,800 nmol/L TDFe measured 9 km distant. Iron and Mn concentrations within the pits decreased >30 - to 200-fold ~ 1.5 months postcollapse and, during the following year, decreased a further twofold to threefold at Pele's Pit and ~ 30 -fold at East Pit. While a steady concentration of ~ 400 nmol/L TDFe prevailed throughout the remaining years of this study at Pele's Pit, a gradual and threefold decrease in the concentration of DMn to about 15 nmol/L was observed. High-temperature fluids (128 – 198°C 1997–1999, $\sim 90^{\circ}\text{C}$ 2001) venting simultaneously from different orifices within Pele's Pit had distinguishable Fe/Mn ratios that can be attributed to different seafloor origins. Fe/Mn ratios characteristic of fluids moderated by high-temperature water-rock reaction had low values in 1997–1998 (1.6 ± 0.7), increasing to about 7 in 1999. Fluids moderated by magmatic degassing of CO_2 had much higher Fe/Mn ratios, increasing from 24 ± 15 in 1997–1998 to 50 in 1999 and 63–87 in 2001. Fe/Mn values of dispersing plumes at Lō'ihi reflect an admixture of these sources and a relative Fe abundance that is consistently high compared to mid-ocean ridge systems. The pulsed injection of Mn and Fe into the surrounding ocean associated with the 1996 tectonic-magmatic event at Lō'ihi was massive. Our decadal observations confirm that Mn and Fe are useful markers of the magnitude and evolution of the effects of magmatic perturbation on hydrothermal systems influenced by chronic magmatic degassing.

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1. Introduction

[2] Lō'īhi is the youngest manifestation of the Hawai'i hot spot and probably will be the next Hawaiian island to arise from Moana Pākīpika, the Pacific Ocean. Because Lō'īhi is unique among intraplate submarine volcanoes regarding its easy access from a major oceanographic research institution (here, School of Ocean & Earth Science & Technology, University of Hawai'i) it is a prime candidate for long-term monitoring of submarine volcanic and hydrothermal processes. The presence of hydrothermal discharge at Lō'īhi was first detected in 1983 as water column anomalies in ³He and methane located near the summit of Lō'īhi seamount [Kim *et al.*, 1983; Horibe *et al.*, 1983]. A more comprehensive survey of hydrothermal plumes near the Lō'īhi summit was made in 1985 [Sakai *et al.*, 1987; Gamo *et al.*, 1987]. Using samples collected during nine oceanographic expeditions between 1985 and 1994, Lupton [1996] demonstrated that the far-field helium plume from Lō'īhi extended 400 km north of the island of Hawai'i and 2000 km to the west. By association with this distal He plume, Boyle *et al.* [2005] interpreted increases in Fe and Mn concentrations within intermediate waters (1000–1500 m) at Hawai'i Ocean Time series (HOT) station ALOHA, located 463 km northwest of Lō'īhi, as deriving from hydrothermal systems at Lō'īhi. Submersible mapping and sampling of the vent fields, fluids and biota commenced in 1987 using ALVIN [Craig *et al.*, 1987; Edmond *et al.*, 1987; Karl *et al.*, 1988, 1989; McMurtry *et al.*, 1987; Sedwick and McMurtry, 1987] with subsequent dives by Pisces V in 1990, 1992, and 1993 [Sedwick *et al.*, 1992, 1994; Sansone *et al.*, 1994]. A cataclysmic magmatic-tectonic event occurred at Lō'īhi summit in 1996 that resulted in the formation of a high-temperature vent field [Duennebieer *et al.*, 1997]. Changes in sulfide mineralogy [Davis and Clague, 1998], source magma composition [Garcia *et al.*, 1998] and hydrothermal fluid chemistry [Sansone

et al., 1998; Hilton *et al.*, 1998; Wheat *et al.*, 1998, 2000] coincident with the 1996 event at Lō'īhi have been reported.

[3] In this paper we present previously unreported observations of Fe and Mn that span a decade at the Lō'īhi hydrothermal system. The distributions of Fe and Mn were mapped to delineate the dispersal of hydrothermal effluent from Lō'īhi and to track changes in Fe/Mn value that are diagnostic of seafloor processes extant before, during, and after a seafloor magmatic event. While the results we report for plumes reflect the integrated output from multiple vent sites located about Lō'īhi summit, we focus our attention on the evolution of fluid emanations from two summit pits (Pele's and East), where the seafloor hydrothermal systems were significantly perturbed during the course of this study.

2. Background

2.1. Geological Setting

[4] The summit of the Lō'īhi submarine volcano lies at a water depth of 969 m and is located 34 km south of the Island of Hawai'i (Figure 1). Lō'īhi sits on the Kaho'olawe-Hualalai-Mauna Loa volcanic line and is less than one-half million years old [Malahoff, 1987]. Lō'īhi is seismically active, with the foci of activity forming a vertical column beneath the summit, which is separate from the column of foci beneath the neighboring Kilauea volcano [Klein, 1982]. Petrological studies of volcanic rock from Lō'īhi summit show it to be composed of tholeiitic to tholeiitic-alkalic transitional alkali basalts and basanites [Moore *et al.*, 1982]. The geology of Lō'īhi has been extensively mapped using photogeological, multibeam acoustical and submersible-based sampling and photographic techniques [Malahoff *et al.*, 1982]. The data assemblage shows the presence of a 31-km northwest to southeast striking rift along which volcanism is active. Magnetic data suggest that the

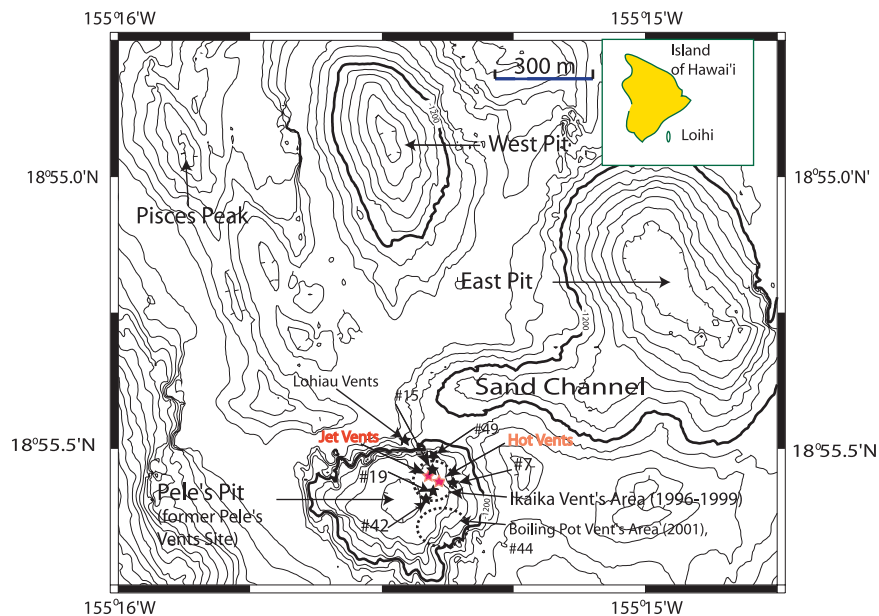


Figure 1. Multibeam bathymetric map (25 m contour interval) of Lō'īhi volcano summit area following the 1996 magmatic-tectonic event. Locations of pit craters are defined by bold 1200 m contour lines. The approximate positions of seafloor vents at Pele's Pit are indicated. The inset shows the location of Lō'īhi volcano relative to the island of Hawai'i.

bulk of the edifice below the summit has a temperature $>550^{\circ}\text{C}$ [Malahoff, 1987]. Geophysical studies suggest that the continuous seismicity of Lō'īhi is volcanogenic [Klein, 1982] with shallow seismic swarms located beneath the summit area resulting from magmatic intrusion and extrusion [Klein et al., 1987; Cooper and Duennebie, 1988]. Volcanic extrusions on Lō'īhi are variously expressed as pillows, tubes, sheet flows, pahoehoe and aa flows and scattered pillow cones [Malahoff, 1987]. Active volcanic intrusives such as dikes are likely to provide the heat source that drives hydrothermal circulation on Lō'īhi. Prior to 1996 the summit had two pit craters: East and West Pit (Figure 1). The main cluster of hydrothermal venting was located on a summit cone on the south flank of Lō'īhi at a site known as Pele's Vents.

[5] The largest earthquake swarm ever recorded at a Hawai'ian volcano was centered beneath the Lō'īhi summit and began on 16 July 1996 [Duennebie et al., 1997]. Over 4000 separate earthquakes were detected between 17 July and 12 August. A rapid response cruise (RRC) organized by University of Hawai'i researchers to investigate the geological effects of the Lō'īhi earthquakes was deployed during the final days of the seismic event (5–10 August). Popping noises recorded by sonobuoys suggest that eruptive events were ongoing at the summit during the RRC [Duennebie et al., 1997]. Most significantly, a multibeam bathymetric resurvey of the summit during the RRC revealed that a pit

crater 600 m in diameter had formed at the site of the former Pele's Vents, renamed Pele's Pit due to the ~ 320 m deeper seafloor now at this site (Figure 1).

2.2. Lō'īhi Hydrothermal Vent System

[6] Seawater penetrates the Lō'īhi edifice and encounters hot dikes beneath the summit and along the South Rift of Lō'īhi that drive localized hydrothermal circulation cells. The ascent of heated water through the porous pillow lavas and talus covering the rift zones results in a hydrology system conducive to diffuse flow that is commonly expressed through multiple outlets having different thermal and venting velocity regimes [Malahoff, 1993]. This was first evidenced during a 1985 survey that detected vertically complex hydrothermal plumes over the Lō'īhi summit area [Sakai et al., 1987; Gamo et al., 1987]. Close examination of the geochemical results from this survey reveal Fe/Mn values that range 6–17, (mol/mol, and everywhere hereafter) [Sakai et al., 1987] that are elevated compared to MOR fluids and an early hint that the hydrothermal system here is enriched in Fe.

[7] Prior to the 1996 event the most vigorous, hence well-studied vent field on Lō'īhi was Pele's Vents, located between 960–978 m depth on the southern flank of the summit [Karl et al., 1988]. This vent field consisted of hundreds of small vents (within an approximately 250 square meter area), 20 cm or less in diameter, discharging clear water at an estimated

Table 1. Lō'īhi Expedition Logistics: 1992–2001

Year	Period	Sampling Mode	Location
1992	Aug.–Sept.	7 submersible dives	Pele's Vents
1993	Sept.–Oct.	2 submersible dives	Pele's Vents
1995	29 March to 1 April	14 hydrocasts	Lō'īhi summit, adjacent sea
1996	RRC 5–10 Aug.	4 hydrocasts + tow-yo	Pele's Pit, East Pit, Lō'īhi summit
	PRRC 23–30 Sept.	3 submersible dives, 11 hydrocasts	Pele's Pit, East Pit, Lō'īhi summit, adjacent sea
1997	Aug.–Sept	6 submersible dives, 6 hydrocasts	Pele's Pit, East Pit, Lō'īhi summit
1998	Sept.–Oct.	2 hydrocasts, 2 submersible dives	Pele's Pit, Lō'īhi summit
1999	Sept.	1 hydrocast, 3 submersible dives	Pele's Pit, South rift
2001	Oct.	9 submersible dives	Pele's Pit

rate of 10 cm/sec with a maximum temperature of 31°C [Karl *et al.*, 1989; Sedwick *et al.*, 1991, 1992, 1994]. In comparison with vents on MORs, hydrothermal fluid from Pele's Vents was found to be enriched in total dissolved CO₂ (up to 418 mmol/kg) and dissolved iron (up to 1460 μmol/kg) and had an unusually high Fe/Mn value of ~30 attributed to “chemical weathering” of wall rock by magmatic volatiles entrained in the circulating hydrothermal fluids [Karl *et al.*, 1988; Sedwick *et al.*, 1992]. Additional venting sites, characterized by a gelatinous carpet of iron-encrusted bacterial mat and low-temperature fluid discharge (<35°C), have been observed deeper along the flanks of Lō'īhi: Kaupo's Vents (1230 m) [Karl *et al.*, 1988], Maximillian Vents (1249 m) [Cremer, 1994] and the Mir Vents (4800 m) [Malahoff, 1992]. Active vent orifices frequently have a white precipitate mask identified by Karl *et al.* [1988] as elemental sulfur. Sites of inactive venting, such as the Thousand Fingers Field (1010 m), are marked by iron-oxide and nontronite deposits [Malahoff *et al.*, 1982].

[8] Significant changes in hydrothermalism at Lō'īhi have been attributed to the magmatic-tectonic event there in 1996. The newly formed Pele's Pit (Figure 1) and previously hydrothermally inactive adjacent East Pit were discovered to contain (and in the case of Pele's Pit, leak to the adjacent ocean) intensely concentrated hydrothermal plumes [Duennebieer *et al.*, 1997]. The first direct observations of seafloor venting at Pele's Pit were made ~1.5 months after its formation. Compared to Pele's Vents, last sampled in 1993, venting discovered at Pele's Pit had higher discharge velocity and fluid temperature (200°C measured, T_{max} sampled = 77°C, at Lohiau Vents on the upper wall of Pele's Pit, Figure 1), decreased CO₂ content and CO₂/³He values [Hilton *et al.*, 1998] and decreased alkalinity and Fe/Mn values [Wheat *et al.*, 1998, 2000]. These data were interpreted to signal a reduced flux of magmatic volatiles

(primarily CO₂) from Lō'īhi volcano [Hilton *et al.*, 1998] and hence a reduced abundance of Fe in vent fluids due to diminished leaching of wallrock by carbonic acid [Wheat *et al.*, 1998, 2000]. A fresh sulfide mineral assemblage recovered near Lohiau Vents provides circumstantial evidence that fluids with even higher temperatures (>250°C) had recently mixed with seawater in this region [Davis and Clague, 1998]. Following the 1996 seismic event, new low-temperature (15–77°C), diffuse flow sites were also discovered elsewhere along the south flank of Lō'īhi: Ula (1099 m), Naha (1325 m), Pohaku (1196 m) and Keiki (1714 m) vents [Hilton *et al.*, 1998; Wheat *et al.*, 1998, 2000].

3. Methods

3.1. Water Sampling

[9] Water samples were collected on nine separate occasions between 1992 and 2001 using a combined submersible (*Pisces V*) and surface ship (R/V *Kaimikai-o-Kanaloa*, beginning in 1995) sampling strategy (Table 1).

[10] During the early years of this study, fluids rising buoyantly from the seafloor were collected by submersible in a 3-L Niskin sampler fixed forward in the sample basket and 0.8 m above the base of the submersible skids. Additional near-seafloor samples were collected in 1-L Niskin bottles fixed to a specially constructed 16-position rosette sampler mounted on the submersible sail.

[11] Neutrally buoyant, horizontally dispersing hydrothermal plumes were sampled by surface ship using conventional vertical cast and tow-yo protocols. A General Oceanics 12-position rosette sampler fitted with 3- and 10-L Niskin bottles and a Sea Bird 911 CTD was used for most operations. Due to a system malfunction during the 1996 RRC expedition (Table 1), a single cast at East Pit was conducted using a Sea Bird SEACAT Model 19

Profiler equipped with a Sea Tech transmissometer and Beckman-style sensor for dissolved oxygen.

[12] Vent fluids discharging directly from the seafloor were collected in 1997, 1998, 1999 and 2001 using hydraulically activated 750 ml titanium syringe samplers [Von Damm *et al.*, 1985]. Subsamples were drawn into acid-cleaned polyethylene bottles. Aliquots for dissolved manganese (DMn) and iron (DFe) were filtered through polycarbonate membranes (0.40 μm pore diameter). Dissolved Mn was analyzed shipboard within ~ 4 hours of recovery with the residual volume acidified to pH 2 using ultra pure HCl pending shore-based determination of DFe. Unfiltered samples were acidified to pH 2 upon collection and stored for shore-based determinations of total dissolvable Fe (TDFe) and total dissolvable Mn (TDMn).

3.2. Temperature Measurement

[13] Fluid temperatures near the seafloor were measured using a Seabird SEACAT Profiler (resolution 0.001°C) mounted on the submersible frame behind the sample basket and 0.8 m above the submersible skids. Temperature surveys were routinely conducted during submersible traverses made ~ 1 m above the seafloor and during ascents from vent fields. Temperature anomalies were assessed as the absolute difference between ambient and locally elevated temperature values.

[14] Temperature within neutrally buoyant plumes was measured using a Seabird SBE 3 temperature sensor (nominal resolution 0.0003°C). Temperature anomalies were assessed as deviations from a linear depth versus temperature relation for the water column bounding the anomaly field.

[15] Vent fluid temperatures were measured using a Logan Enterprises temperature probe ($\pm 1^\circ\text{C}$ resolution). The probe was variously positioned within each vent using the submersible manipulator to insure that the maximum measurable temperature was attained.

3.3. Analytical Procedures

[16] An initial aliquot from all plume samples was used to measure pH by conventional potentiometric procedures. Calibration was relative to NBS buffers and the estimated precision was ± 0.01 pH units.

[17] The concentrations of Mn and Fe were determined using flow injection analysis (Tecator™

FIASStar 5010) and colorimetric detection following kinetic oxidation of *N,N*-Diethylaniline by potassium periodate, catalyzed by Mn [Kolotyrkina *et al.*, 1991] and the oxidation of *N,N'*-Dimethyl-*p*-phenylenediamine by hydrogen peroxide, catalyzed by Fe [Kolotyrkina *et al.*, 1995]. For low concentrations of Mn, on-line preconcentration using DETATA (diethylenetriaminetetraacetic acid) was employed [Tsysin *et al.*, 1991]. The detection limit for Mn was 0.04 nmol/L, the operational range 0.2 nmol/L to 400 nmol/L, and the R.S.D. ranged 5–8%. The detection limit for Fe was 0.5 nmol/L, the determination range 2–3000 nmol/L, and the R.S.D. range 2–8%.

[18] Magnesium in vent fluid samples was determined by EDTA-EGTA titration with R.S.D. of $\pm 1\%$. Silica was determined by ICP-OES with a nominal R.S.D. of $\pm 3\%$.

4. Plumes

4.1. Hydrothermal Venting at Lō'ihī Prior to Summit Collapse

4.1.1. Early Temperature Anomalies Along the South Flank of Lō'ihī Summit

[19] Temperature data obtained during earlier (1988–1991) “pathfinding” submersible surveys along the South Rift zone of Lō'ihī demonstrate a broad depth distribution for hydrothermal discharge with the highest temperature anomalies ($+5.5^\circ\text{C}$) located at Pele's Vents (962–978 m) (Figure 2; A. Malahoff, unpublished data).

4.1.2. Pele's Vents Hydrothermal Plume 1992–1993

[20] Water samples were collected during submersible ascents from Pele's Vents in 1992 and 1993 for determinations of DMn, TDFe and pH (Table 2). While the rise height of the chemical plume was only a few 10s of m above the seafloor, very high concentrations of Mn and Fe (755 nmol/L and 21,800 nmol/L, respectively) and a large anomaly in pH (-1.8 pH units) were observed a meter above the seafloor (Figure 3). The Fe/Mn value for the two years of combined data, 35 ± 1 , $n = 20$, was indistinguishable from the individual year results and similar to that for vent fluids recovered from this site in 1987, 1990, and 1993 with mean values of 35, 30, and 23, respectively) [Sedwick *et al.*, 1992; Wheat *et al.*, 2000].

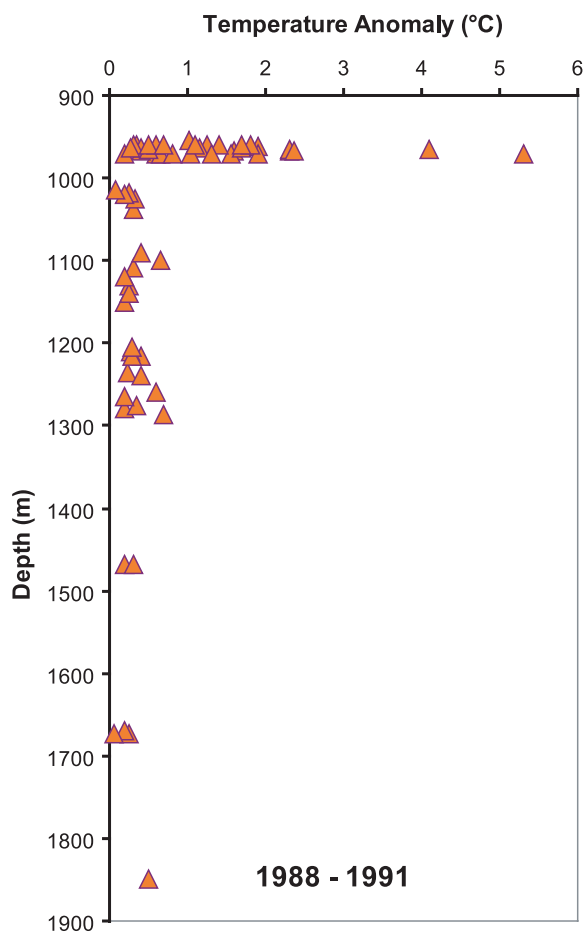


Figure 2. Temperature anomalies detected near the seafloor during submersible surveys of the summit and south flank of Lō'īhi volcano between 1988 and 1991. The highest density of vent sites and the largest anomalies in temperature were located in the Pele's Vents area at about 970 m depth.

4.1.3. Plume Dispersal 1995

[21] A grid of 14 vertical cast stations was occupied over the course of ~ 1.5 days in 1995 to assess the dispersal pattern of the Pele's Vents plume (Figure 4, circled station numbers). Vertical profiles for stations (gray-shaded in Figure 4) where moderate to weakly discernable Mn and Fe plume anomalies were detected are shown in Figure 5. A vertically complex plume distributed between 940 and 1200 m depth dispersed predominantly to the southwest of Lō'īhi summit. Representative values for the plume sampled 1.8 km southwest of the Pele's Vents area are listed in Table 2. Numerous venting sites along the South Rift, as reported in the historical literature and detected during our earlier submersible surveys (see above), undoubtedly

contribute to the irregular vertical plume distributions.

4.2. Lō'īhi Summit Collapse, Rapid Response Cruise (RRC), August 1996

[22] Hydrocasts were obtained within and near Pele's Pit and within East Pit during the RRC. In addition, a 9-km-long tow-yo trending southwest from the summit of Lō'īhi was conducted.

4.2.1. Pele's Pit

[23] A vertical cast penetrated Pele's Pit to a depth of 1207 m, ~ 40 m below its effective sill depth of ~ 1165 m, revealing significant hydrographic and chemical anomalies (Figures 6a and 7a). Compared to ambient seawater at 1100 m, a huge temperature anomaly ($+2.9^\circ\text{C}$) and a moderately elevated salinity ($+0.14$ PSU) were observed. The thermal anomaly is consistent with a magmatic intrusion or extrusion in the Pele's Pit region and heating of the fluid confined within the pit basin. The increase in salinity is impossible to ascribe to mixing with ambient seawater and is equivalent to an increase in chloride concentration of 2.1 mmol/kg (or 0.4% compared to the regional seawater value of 539 mmol/kg), which matches the sense of Cl anomalies ($+20$ to $+50$ mmol/kg) reported by *Wheat et al.* [2000] for fluids sampled on the upper north wall of Pele's Pit at Lohiau vent (1173 m) \sim two months after the seismic event. In contrast, chloride concentrations at the former Pele's Vents were equal to or less than seawater values [*Sedwick et al.*, 1992]. Assuming the pit fluids were well-mixed (consistent with observations of severe turbidity made during submersible dives at this time and also the vertical profiles for hydrographic properties below pit sill depth as shown in Figure 6a), the positive anomaly in salinity within the large volume of the Pele's Pit argues for venting of a brine-like fluid, possibly the remnant conjugate phase resulting from an earlier de-gassing event, as alluded to by *Hilton et al.* [1998].

[24] The corresponding profiles of Fe and Mn for the plume within Pele's Pit (Figure 7a) illustrate concentration anomalies that are unprecedented in their magnitude, approximately 30–40-thousand-times the respective background seawater values (Table 2). The fraction of iron in the particulate phase was high (80–95% of TDFe) and the TDFe/TDMn ratio (42 ± 7) was elevated over vent fluids previously reported at Lō'īhi and less than the mean whole rock value of 58 for this volcano [*Frey and Clague*, 1983] or 62 for basaltic breccia

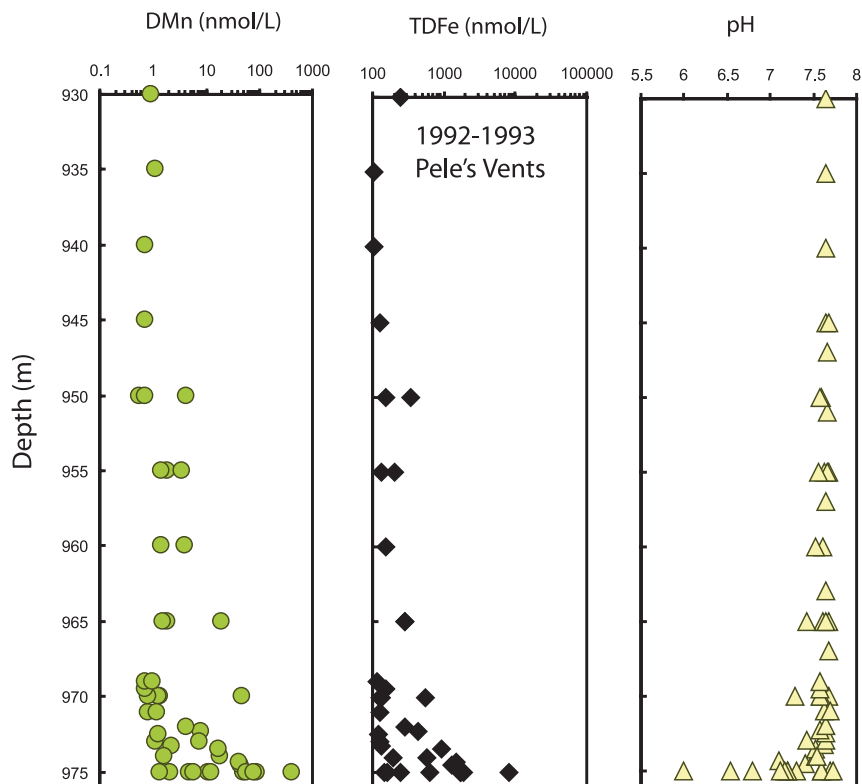


Figure 3. Distributions of dissolved manganese (DMn), total dissolvable iron (TDFe), and pH within the near-bottom water above Pele’s Vents as sampled from the submersible *Pisces V* in 1992 and 1993. Note that log scales for DMn and TDFe are required to accommodate the large ranges in concentration detected when sampling close to the seafloor.

and 75 for basaltic glass delivered to the seafloor as part of a 1996 magma eruption at northwest Lō’ihi summit [Garcia *et al.*, 1998]. The Mn/heat value within Pele’s Pit (Table 3) was within the range of values observed for hydrothermal discharge at northeast Pacific MORs, while the Fe/heat value is much larger [e.g., Massoth *et al.*, 1994, 1995, 1998]. The pH of the water filling Pele’s Pit was 5.6–6.0, rising to 6.0–6.5 above pit sill depth, giving a maximum pH anomaly of –2.1 pH units, consistent with recent or ongoing local injection of a high volume of magmatic acid volatiles (most probably CO₂ and minor sulfur gases based on the basaltic composition of the magma).

4.2.2. East Pit

[25] Although hydrothermal discharge had been previously unobserved within East Pit, seismic and sonobouy data collected during the 1996 event suggested recent seafloor activity in this region [Duennebieer *et al.*, 1997]. A hydrocast to 1230 m depth within East Pit detected even larger anomalies

in temperature (+3.4°C) and salinity (+0.38 PSU, equivalent to an anomaly in chloride concentration of 5.9 mmol/kg) than were observed at Pele’s Pit (Figure 6a). Especially when the substantially larger volume of East Pit is considered, our observations require that either the inputs of heat and salt were greater here than at Pele’s Pit, or mixing with the ambient ocean less dynamic. Auxiliary sensors on the back-up CTD system deployed here quantify the high turbidity noted during submersible dives attempted at this same time (light transmission was reduced from 96% to less than 10%) and attest to the anoxic state of water confined within East Pit (the concentration of dissolved oxygen decreased from the regional value of about 1 mL/L to zero, Figure 6b).

[26] The maximum observed TDMn concentration (~34,000 nmol/L) within East Pit was about three times higher than that at Pele’s Pit, while in contrast, the iron abundance (TDFe ~120,000 nmol/L) was only about one-third that within Pele’s Pit (Figures 7a and 7b, Table 2). Almost

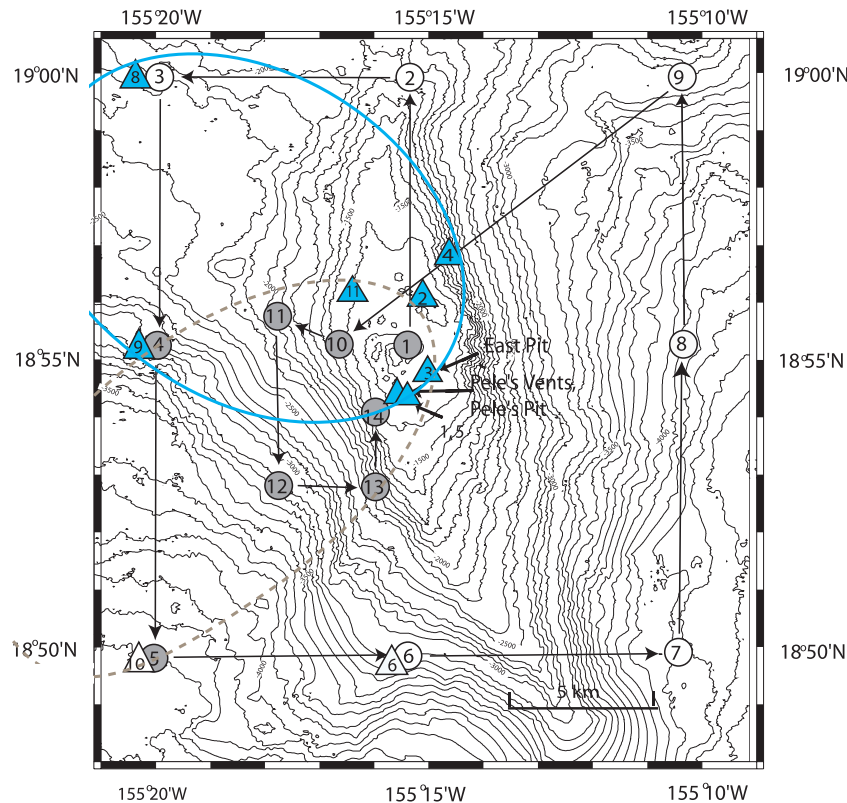


Figure 4. Bathymetric chart (100 m contour interval) showing sampling grids occupied in March 1995 (circles with station numbers) and September 1996 (triangles) (PRRC) to map the dispersal of hydrothermal plumes away from Lō'īhi volcano. Stations where hydrothermal plumes were detected in 1995 are shaded gray, and those detected in 1996 are blue. The inferred dispersal envelope for 1995 is shown as a gray dashed line and for 1996 is shown as a blue line.

all of the Fe within East Pit was in the dissolved phase, consistent with the anoxic state there. While both Mn/heat and Fe/heat ratio values were high compared to MOR standards (Table 3), the TDFe/TDMn value was MOR-like [Von Damm, 1995] and low (3.6 ± 0.4) relative to historical vent fluid and plume data for Lō'īhi. A substantial pH anomaly (-1.6 pH units) was also observed within East Pit.

4.2.3. Dispersal of Lō'īhi Hydrothermal Plume During the Collapse Event Period

[27] A vertical cast conducted 0.5 km west of Pele's Pit during the RRC identified the intense lens (~ 50 m in thickness) of a hydrothermal plume dispersing at the sill depth of Pele's Pit (Figure 8a). The TDFe/TDMn value (40.6), matched that observed within Pele's Pit, while the magnitude of the pH anomaly had decreased to -1.0 pH units, about half that observed within Pele's Pit, or an order-of-magnitude in terms of hydrogen ion activity. More

distal sampling of this plume 3.6 km west (Figure 8b, Table 2) provided a TDFe/TDMn value of ~ 17 , suggesting considerable fallout of a particulate Fe phase during plume dispersal over this distance, possibly as freshly formed iron sulfides or hydroxides. The pH anomaly here was -0.7 pH units, reflecting \sim twofold dilution between these off-site stations, consistent with that for DMn, which has been shown to behave conservatively over these short spatial scales [Lavelle *et al.*, 1992].

[28] A tow-yo extending 9 km southwest of the summit provides a cross-sectional view of the dispersing plume, seen as a temperature anomaly distribution in Figure 9. Metal concentrations and thermal anomaly values for discrete samples numbered in Figure 9 are given in Table 4. The dispersing hydrothermal plume sampled 9 km distant from Lō'īhi summit (identified as sample 2 in Figure 9) had unprecedented high metal concentrations this far from a source (236 nmol DMn and 3,800 nmol/L TDFe). Six samples col-

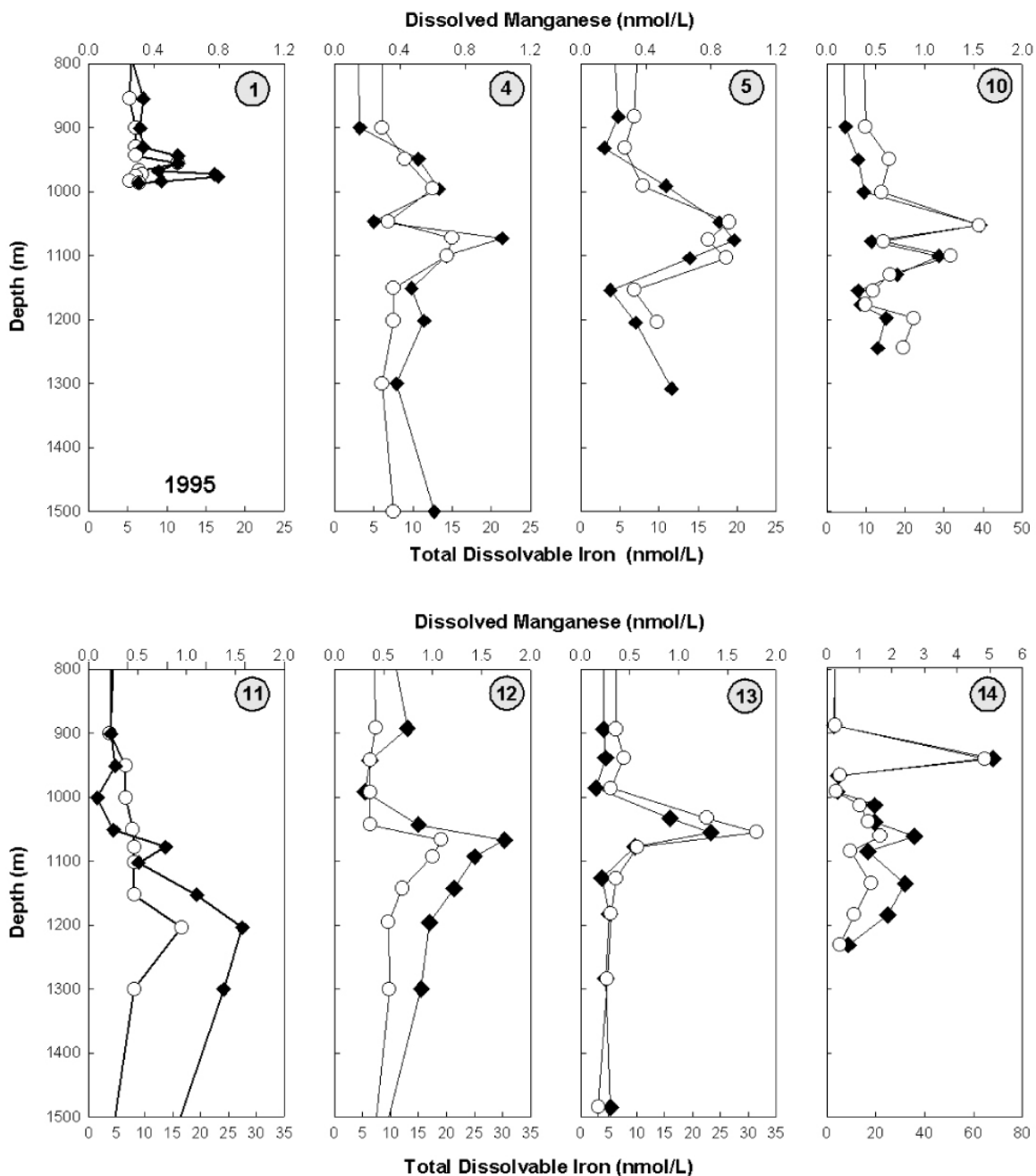


Figure 5. Vertical profile distributions of DMn (open circles) and TDFe (solid diamonds) for stations located away from the Lō’ihi volcano summit area in 1995 (Figure 4) where anomalies in these tracers of hydrothermal discharge were detected. All concentrations are nmol/L. The complex vertical structures attest to the presence of multiple sources along the flanks of Lō’ihi that contribute to the composite distal plume. The station closest to the summit (14) has the most intense plume signal, coincident with the depth of Pele’s Vents.

lected within the plume core had a TDFe/DMn ratio of 15.5 ± 2.6 and DMn/heat and TDFe/heat values of 0.42 ± 0.13 nmol/J and 6.3 ± 1.9 nmol/J, respectively (Table 4). Since both vented manganese and heat are expected to behave conservatively

during plume dilution [e.g., Massoth *et al.*, 1995], the similarity in DMn/heat values for Pele’s Pit (the “signature” source site) and the dispersing plume is not surprising (Tables 3 and 4). By comparison, the relatively low values for TDFe/heat

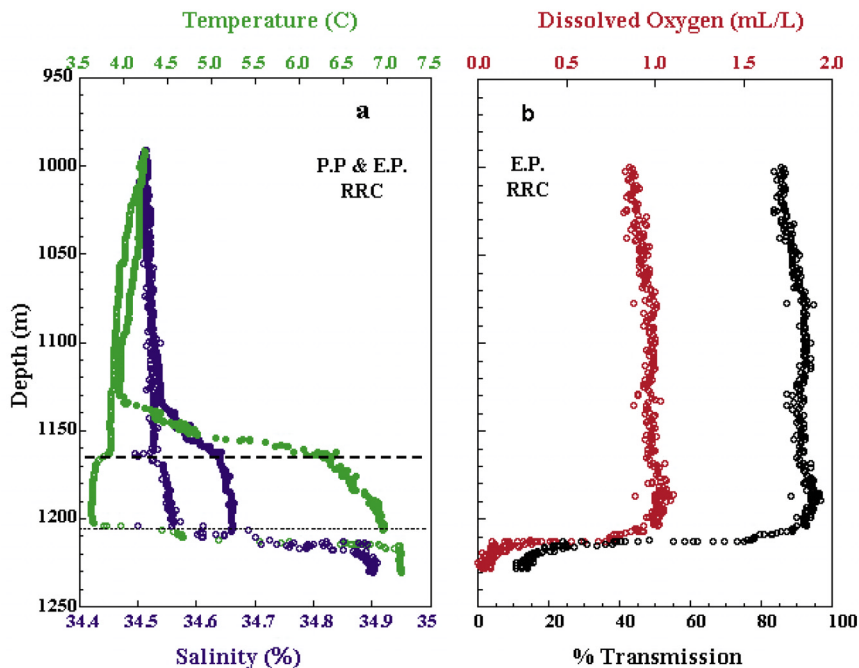


Figure 6. Hydrographic profiles obtained in Pele's and East Pits during the Rapid Response Cruise (RRC) 5–10 August 1996. (a) The vertical distributions of temperature ($^{\circ}\text{C}$, green symbols) and salinity (PSU, blue symbols) for the adjacent Pele's Pit (P.P., closed circles) and East Pit (E.P., open circles). The effective sill depths for these pits are marked as heavy (Pele's Pit, 1165 m) and light (East Pit, 1205 m) dashed lines. Because different CTD sensors were used for these deployments, the results have been normalized at about 1000 m depth using the sensor with results most similar to historical data for this region (WOCE P16C Station 324, located 37 km distant from Lō'ihi; <http://whpo.ucsd.edu/data/onetime/pacific/p16/p16c/p16chy.txt>) for normalization. Slightly cool, salty water can be seen immediately above the sill depths, suggesting that deeper ambient seawater may be flowing into the pits areas (and possibly flushing them). The large magnitudes of the thermal and salt anomalies are discussed in the text. (b) Vertical profiles of dissolved oxygen (mL/L, red symbols) and % transmission (of light, black symbols) within East Pit (E.P., complementary data for Pele's Pit is not available). Although the profile penetrated only the uppermost layer of East Pit, the data suggest the basin is well-mixed, anoxic, and extremely turbid.

throughout the towpath support the notion of rapid settling of particulate Fe close to the source region.

4.3. Post Summit Collapse

4.3.1. Pele's and East Pits ~1.5 Months Postcollapse

[29] A Post Rapid Response Cruise (PRRC: 23–30 September) commenced six weeks after the conclusion of the RRC (Table 1). Three submersible dives into the newly formed Pele's Pit were conducted and a grid of ten water sampling stations was occupied to quantify hydrothermal anomalies within Pele's and East Pits and to map plume dispersal away from the Lō'ihi summit area (Figure 4, grid stations are shown as triangles). Multiple venting sites and unstable terrain were observed during the submersible dives.

While safety concerns precluded direct sampling of vent fluids (visibility was less than 3 m), buoyant plume waters collected atop the submersible when positioned near the Jet Vents site at Pele's Pit (Figure 1) had low pH values (6.1–6.6) and high and variable DMn (255–473 nmol/L), DFe (464–1218 nmol/L), and TDFe (857–1705 nmol/L) concentrations, providing our first insight that venting sources with Fe/Mn values much lower than were observed for the RRC plume were now operative here.

[30] Dramatic reductions in the thermal and chemical intensities of the plumes contained within Pele's and East pits during the short sampling hiatus (Figures 8 and 10, Table 2) confirm the pulsed nature of the huge injections of heat and mass associated with the 1996 magmatic event at Lō'ihi. Temperature anomalies (0.1°C – 0.2°C) and

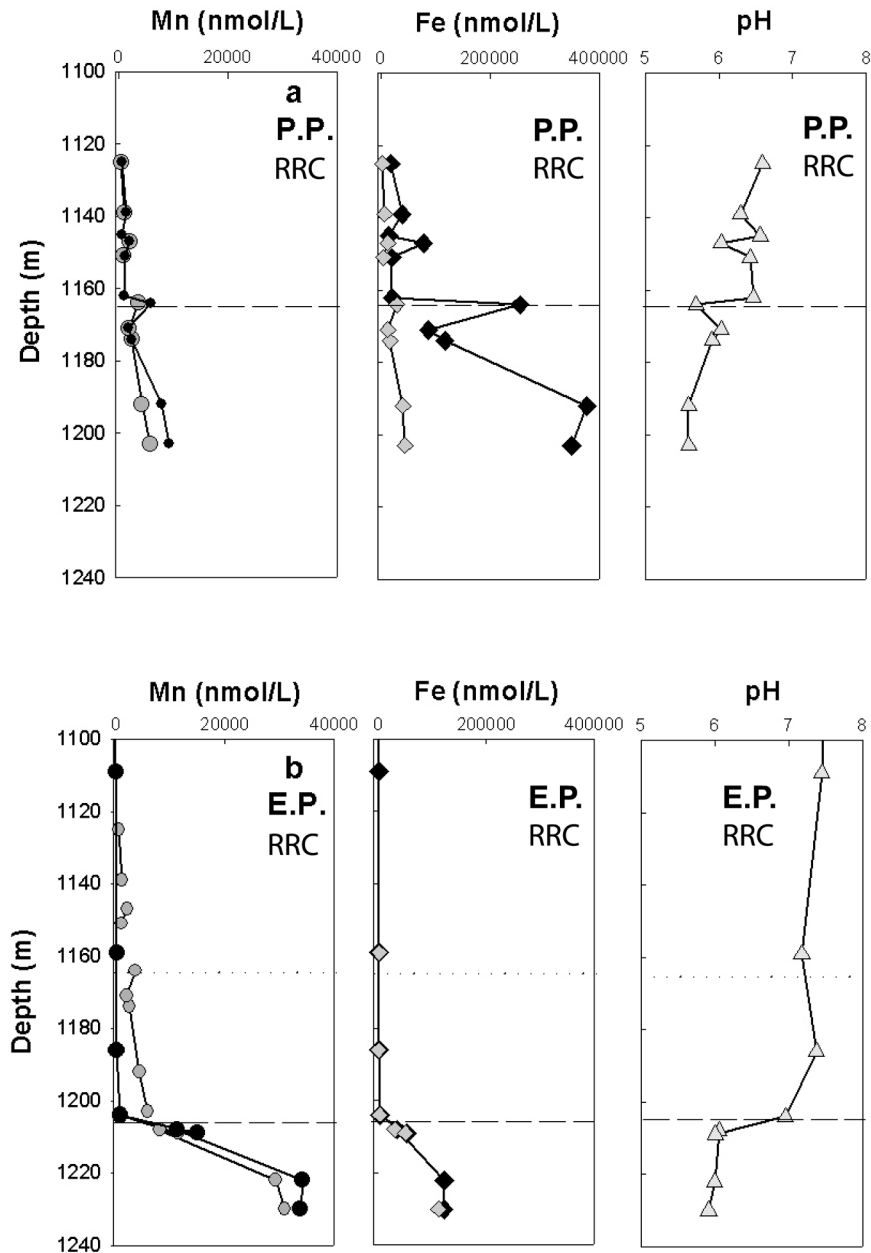


Figure 7. Discrete sampling profiles for DMn and TDMn (open and closed circles, respectively), DFe and TDFe (open and closed diamonds), and pH obtained in (a) Pele's Pit (P.P.) and (b) East Pit (E.P.) during the Rapid Response Cruise (RRC) in August 1996. The data were obtained during the "up cast" following the downward hydrographic profiles shown in Figure 6. The sill depths for the respective pits are shown as dashed lines. Pele's Pit has considerably less Mn and more Fe than East Pit, with the phase distribution of Fe in East Pit unusually skewed toward a very high dissolved Fe fraction. Both pits have intense pH anomalies, with water immediately above Pele's Pit sill depth reflecting buoyant vertical advection, in contrast to the case for East Pit. The single most astonishing feature of this figure is the intensity of the concentration maxima for all parameters shown ($\text{pH} = -\log [\text{H}^+]$).

Fe and Mn concentrations had decreased ~30- to 300-fold. At Pele's Pit a buoyant plume with Fe and Mn concentrations equal to those within the pit rose ~100 m above sill depth (Figure 10). While a plume with similar chemical magnitudes was also

evident over East Pit, order-of-magnitude greater concentrations were observed immediately above of the pit floor (Figure 10). A substantial pH anomaly (−0.7 pH units) persisted within Pele's Pit, while within East Pit the pH had rebounded to

Table 3. Metal/Heat Values at Pele's and East Pits During RRC Expedition and Representative Range for Hydrothermal Plumes at Northeast Pacific Spreading Centers^a

	Pele's Pit	East Pit	NEPAC Spreading Centers
DMn/heat, nM/J	0.42 ± 0.05 (n = 7)	1.96 ± 0.29 (n = 4)	0.10 – 1.02
TDFe/heat, nM/J	22.0 ± 4.8 (n = 7)	8.3 ± 0.8 (n = 4)	0.13 – 1.78

^aMassoth et al. [1994, 1995, 1998].

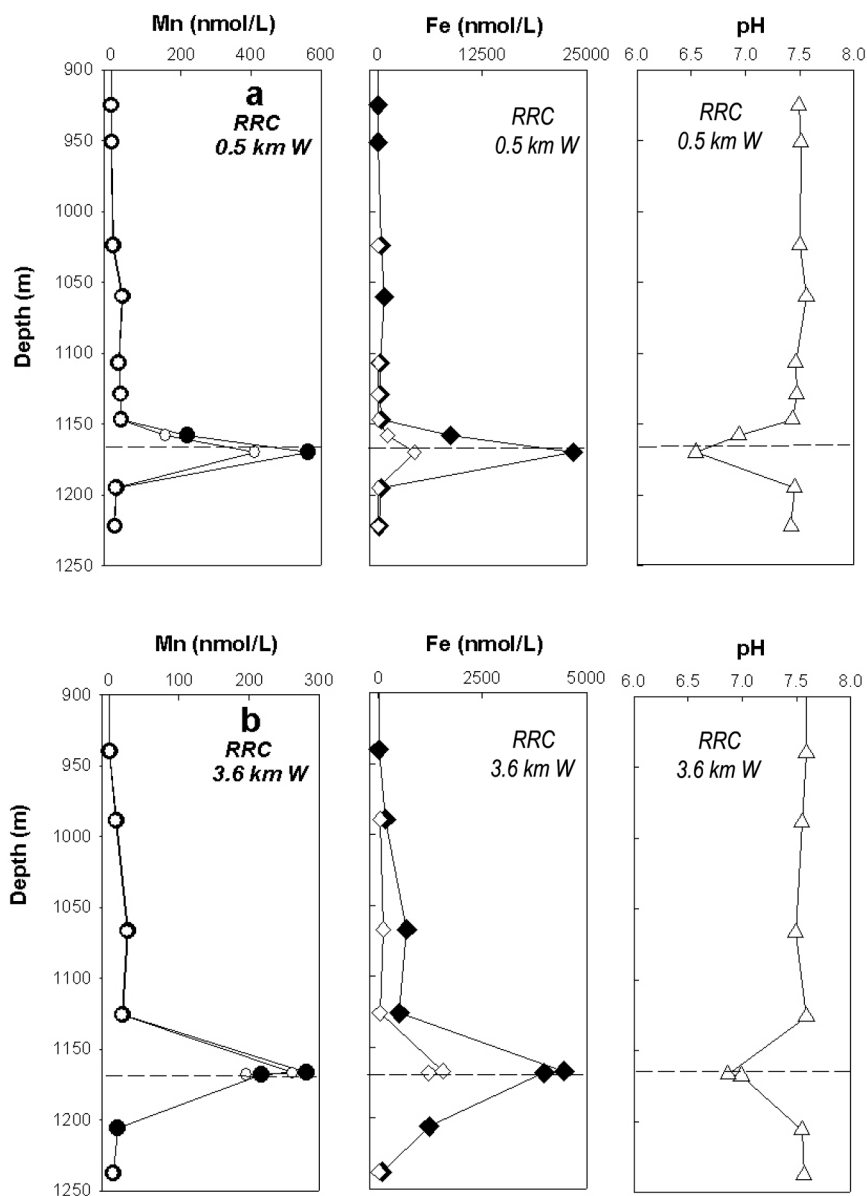


Figure 8. Vertical profiles of DMn and DFe (open symbols), TDMn and TDFe (solid symbols), and pH, obtained during the RRC, 1996: (a) ~0.5 km west of the newly formed Pele's Pit crater and (b) 3.6 km west. Dashed lines reflect the effective sill depth of Pele's Pit. Note that the low fraction of DFe is consistent with Pele's Pit being the main source of these plumes. The reduced magnitudes of the concentration axes compared to those for Figure 7 highlight the considerable plume dilution that occurs over these spatial scales.

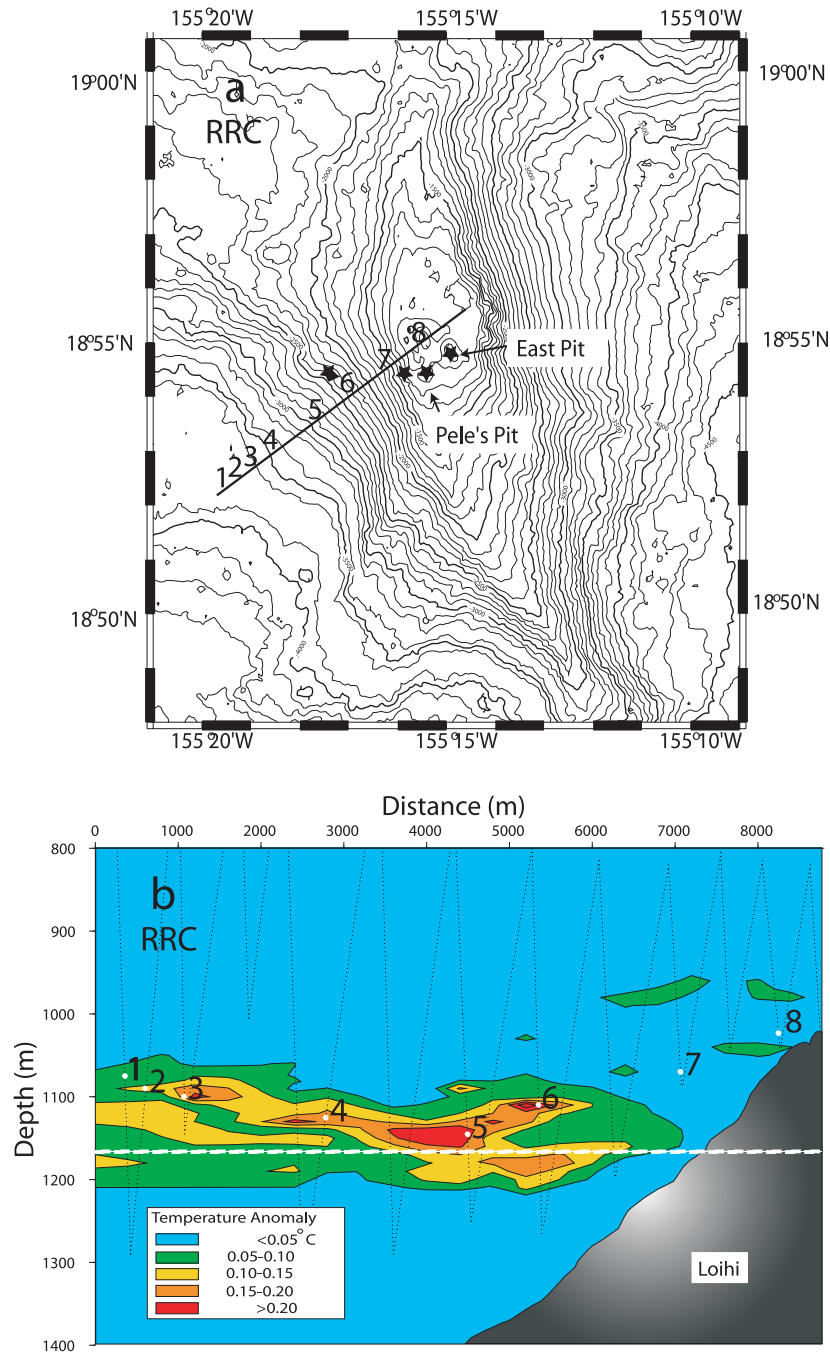


Figure 9. (a) Bathymetric chart showing tow-path (9 km in length) and sampling locations for a tow-yo extending southwest of Lō'ihi summit during the Rapid Response Cruise (RRC), 5–10 August 1996. Stars indicate locations of Pele's Pit and East Pit and the positions of stations occupied 0.5 km and 3.6 km west of Pele's Pit (profile distributions shown in Figure 8). (b) Thermal plume dispersing away from Lō'ihi summit, as contoured from tow-yo data acquired along the saw-tooth towpath indicated by the dotted lines and shown in planar form in Figure 9a.

near-ambient seawater values (Table 2). Interestingly, the short-term temporal trends for Fe/Mn values have opposite senses within the neighboring pits: an ~fourfold decrease within Pele's Pit, to values approximately equal to the upper limit of

those associated with magmatic intrusion events at MORs [Massoth *et al.*, 2003], and a fivefold increase at East Pit, from MOR-like values to relative Fe enrichments typical of the CO₂-moderated systems previously described at this volcano.

Table 4. Chemical and Thermochemical Values for Discrete Samples, RRC Tow-yo

Sample	DMn, nM	DFe, nM	TDFe, nM	TDFe/DMn, mol/mol	ΔT , °C	Mn/Heat, nM/J	TDFe/Heat, nM/J
1	72	377	1251	17.3	0.08	0.22	3.8
2	236	-	3804	16.1	0.16	0.36	5.8
3	465	2785	7304	15.7	0.22	0.51	8.0
4	335	1438	6214	18.5	0.16	0.51	9.5
5	327	1223	5982	18.3	0.25	0.32	5.9
6	560	4607	7250	12.9	0.28	0.49	6.3
7	49	-	571	11.7	0.02	0.61	7.1
8	27	-	354	13.1	0.02	0.32	4.2

The dramatic but ephemeral effects of magmatic intrusion on the hydrothermal systems at these pits appear to be giving way to chronic controls governed more by a cooling dike at Pele's Pit and more by pervasive magmatic degassing at East Pit.

4.3.2. Plume Dispersal From Lō'ihī ~1.5 Months Postcollapse

[31] Vertical profiles of Mn and Fe at the PRRC grid stations with hydrothermal anomalies (blue-shaded triangles in Figure 4) are also displayed in Figure 10. For the sectors sampled, our data suggest the horizontally dispersing neutrally buoyant plume extended NNW of Lō'ihī and was ~200 m in vertical dimension. The large plume anomalies at station 11, located 2.7 km NW of Pele's Pit, for DMn, TDFe, and pH (-0.3 units) (Table 2) demonstrate that a highly enriched chemical plume continued to disperse from the summit of Lō'ihī volcano. Plume maxima for Fe and Mn located at the most distant stations (8 and 9) were enhanced fourfold to tenfold over similarly distant stations sampled prior to the summit collapse event (Stations 4 and 5, Figures 4 and 5).

4.3.3. Evolution of the Lō'ihī Hydrothermal Venting System: 1997–2001

[32] Combined surface ship and submersible sampling at Lō'ihī resumed one year after the PRRC (27 August to 6 September 1997, Table 1). Five submersible dives were made to venting sites within Pele's Pit during which both vent fluid and plume samples were collected. Variable but large anomalies for our hydrothermal tracers were observed: DMn 20–100 nmol/L; TDFe 250–600 nmol/L; and pH 7.0–7.6. Two hydrocasts within Pele's Pit resulted in uniform profile distributions within the pit and had similar anomaly magnitudes to the submersible data, which were about one-half the PRRC values (Figure 11, Table 2). While a buoyant plume persisted above

Pele's Pit, with a rise height similar to that observed a year previously, it had a stepped structure with lower concentrations between 1100 and 1050 m. It is noteworthy that a large fraction of the Fe within Pele's Pit was in the dissolved phase (60–80%), suggesting a continued high input of hydrothermal Fe coupled with a rapid flushing rate.

[33] A hydrocast at East Pit shows profile maxima in the 1050–1180 m depth range (Figure 11) that most likely reflect the advected buoyant plume from nearby Pele's Pit. The concentrations of Fe and Mn within East Pit were reduced by about 60-fold from values detected there in 1996 and the Fe/Mn value was slightly elevated over values in this pit one year previously (Table 2). No hydrothermal activity was observed during a single submersible reconnaissance dive at East Pit.

[34] A vertical cast conducted 1 km west of Pele's Pit in 1997 reveals a plume significantly diminished in chemical intensity compared to our preceding postevent observations in this same area and also highlights the relative plume contributions from sources located deeper on the flanks of Lō'ihī (Figure 11). Consistent with measurements of vent fluid Fe and Mn at some of these deeper sites [Wheat *et al.*, 2000], the plume results indicate a higher Fe/Mn ratio than determined for the plume dispersing at sill depth from Pele's Pit (Table 2).

[35] Continued time series observations of the Pele's Pit plume were made in 1998, 1999, and 2001. The data trends show a gradual decrease in the concentration of DMn, a uniform level of TDFe, and consequently increasing TDFe/DMn values (Table 2).

5. Vent Fluids at Pele's Pit

5.1. Ikaika Vents Area: 1997–1999

[36] Due to safety concerns regarding poor visibility and unstable terrain during our initial dives at

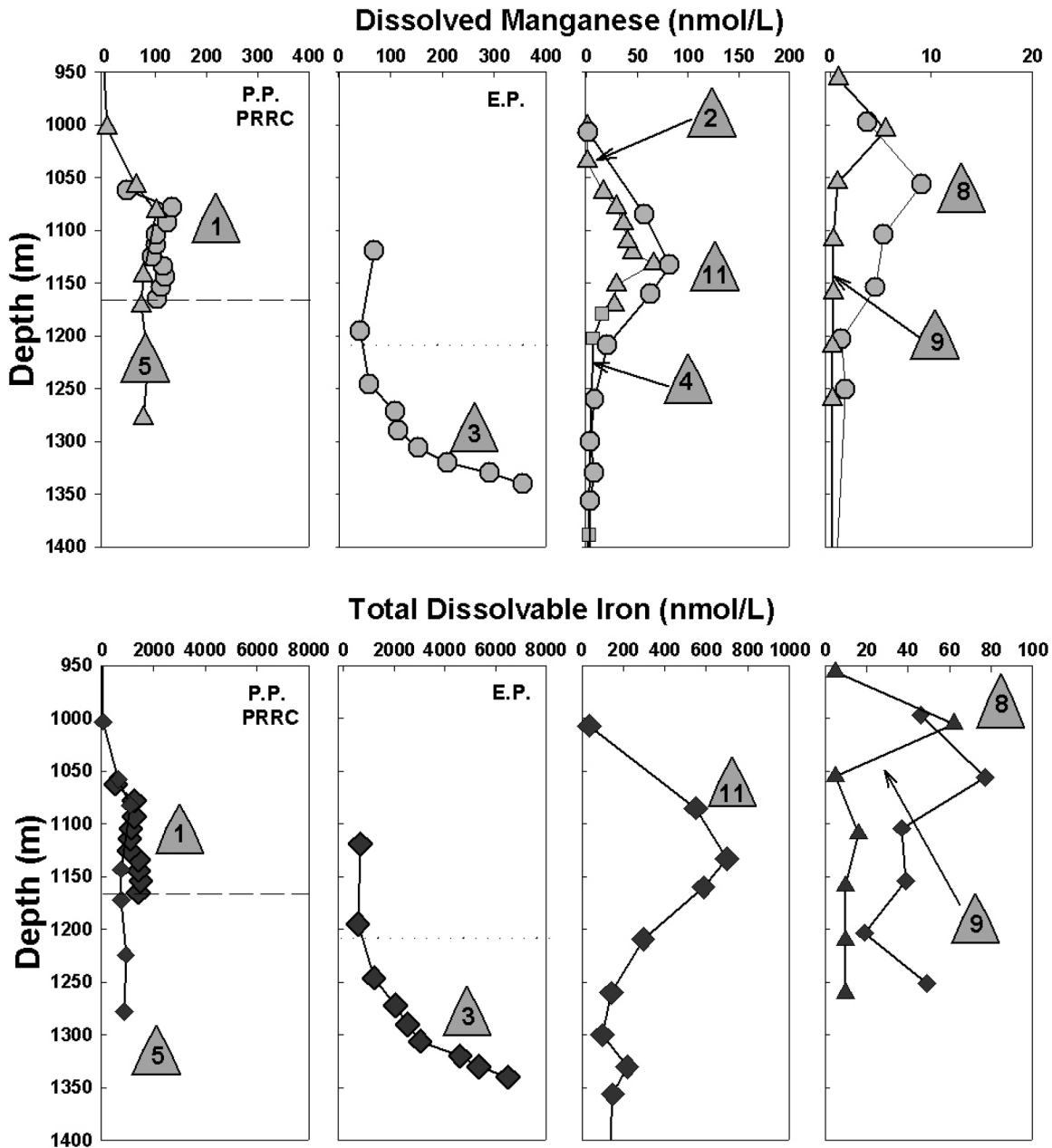


Figure 10. Vertical profiles of DMn and TDFe (nmol/L) within Pele's Pit (P.P., left panels) and East Pit (E.P., left-center panels), and at stations located distal to Lō'īhi volcano (right panels), shown as triangles in Figure 4, during the Post Rapid Response Cruise (PRRC), 23–30 September 1996. Comparison of the concentration axes shown here to those for Figure 7 illustrates the marked decrease in metal abundances that has occurred within the pits over the six weeks since they were last sampled, verifying the pulsed nature of the intense discharge associated with the magmatic event. An interesting perspective on that intensity is obtained by comparison of Figures 5 and 10, where equidistant and most distal plume maxima sampled before (Figure 5, stations 4 and 5) and after (Figure 10, stations 8 and 9) the 1996 event are considerably different, being fourfold to tenfold more enriched following the seismic event at Lō'īhi summit.

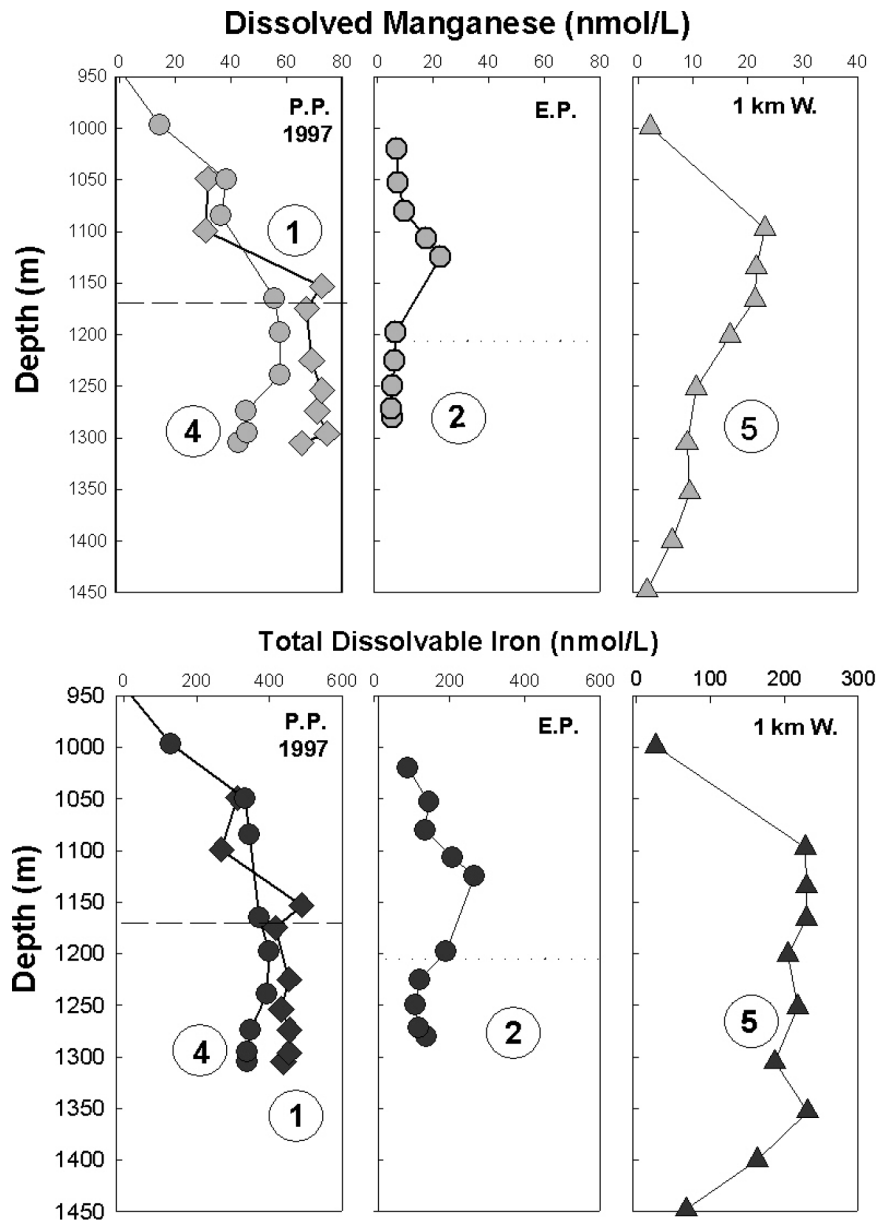


Figure 11. Vertical profiles of DMn and TDFe (nmol/L) obtained in Pele’s Pit (P.P.), in East Pit (E.P.), and 2.5 km west of Pele’s Pit during August–September 1997, approximately one year after the magmatic event at Lō’ihi summit. Dashed lines represent the sill depths at the respective pits. Although a continued reduction in the intensity of the chemical plumes one year after the magmatic event is apparent by comparison to Figure 10, evidence of a relatively more enduring source at Pele’s Pit can be seen. As discussed in the text, plume emissions (with different Fe/Mn signature values) from vents located along the flanks of Lō’ihi volcano are evident in the profile obtained west of the pit area.

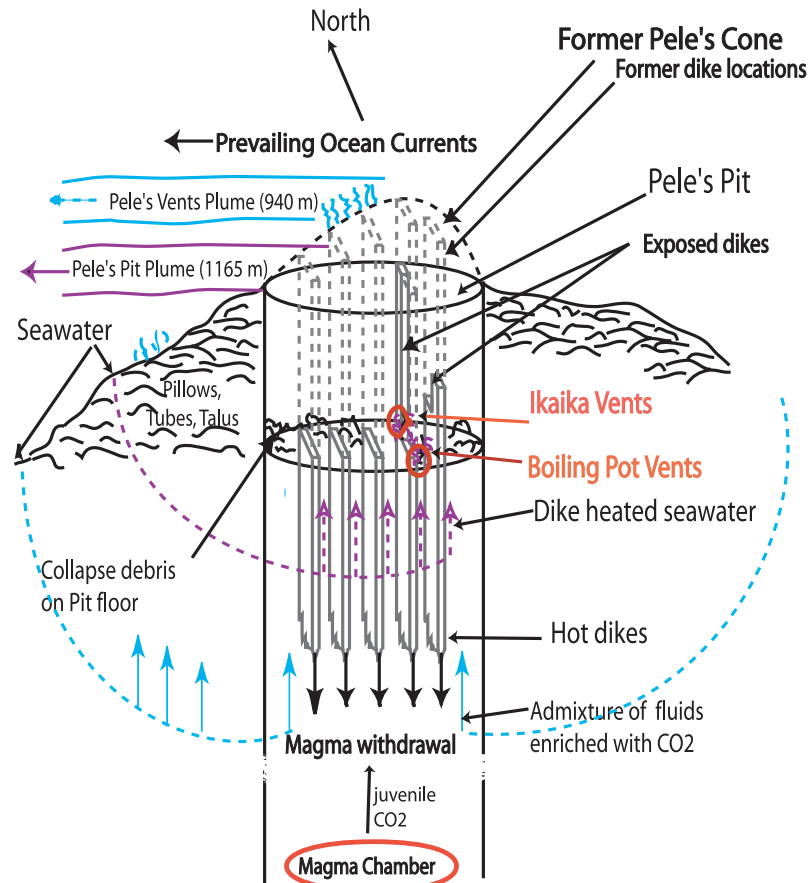


Figure 12. Schematic diagram showing the relative locations of geological features at Pele's Vents and Pit and the underpinning magmatic-hydrothermal processes taking place. Summit collapse followed magma withdrawal, leaving partially exposed and freestanding dike remnants inside the newly formed Pele's Pit. Interaction between seawater and hot dikes generated hydrothermal circulation cells with possible admixture of magmatic fluids rising from deeper within the subseafloor plumbing system.

Pele's Pit in 1996, our vent fluid sampling program was delayed until August 1997, and was focused on the highest-temperature vents located during our dives. In 1997, 1998, and 1999 we returned to the Ikaika (Hawaiian for "strong") Vents area (also known as Forbidden Vents [Hilton *et al.*, 1998]), discovered but not sampled in September 1996 at the intersection of a large collapse block and the north pit floor (1297–1305 m depth, Figures 1 and 12), where we sampled the focused flows discharging from the Hot and Jet Vents in the temperature range 146°C–198°C (Table 5). Several other sites in this area (Marker #s 7, 15, 19, 42, and 49) with less vigorous high-temperature (128°C–179°C) flows were also sampled during this three-year period (Table 5, Figure 1).

[37] Most of our samples have significantly higher venting temperatures and pure hydrothermal "end-member" fractions (based on Mg values [Von

Damm *et al.*, 1985]) than were observed at Pele's Vents (e.g., $T_{\max} = 31^{\circ}\text{C}$, $\text{Mg}_{\min} = 49.5 \text{ mmol/kg}$ [Sedwick *et al.*, 1992]). While our median and highest Mn concentrations are about ~4-times higher than comparable values for Pele's Vents, our Fe concentrations were lower by ~threefold [Sedwick *et al.*, 1992, Figure 10]. More revealing of source provenance, our Fe/Mn values fall into two distinct groupings: one with range 12–50, encompassing the range (23–35) noted earlier for Pele's Vents, like earlier workers we consider the chemistry of these fluids to be moderated by magmatic degassing of CO₂ [Sedwick *et al.*, 1992; Wheat *et al.*, 2000], and a second, new grouping with distinctly lower Fe/Mn values in the range 0.7–7.4, consistent with the range observed for hydrothermal fluids on MORs [Von Damm, 1995] where the vent fluid chemistry is moderated by high-temperature water-rock reaction (Table 5). Data for other elements in these same

Table 5. Vent Fluid Data for Pele's Pit 1997–2001

Year	Vent	Temp., °C	Mg, mM	Si, mM	Mn, μM	Fe, μM	Fe/Mn, mol/mol
<i>Ikaika Area</i>							
1997	Hot Vents	198	7.2		91.3	102	1.1
1997	Jet Vents	187	29.9	4.93	39.5	111	2.8
1997	Hot Vents	162	41.3	2.43	17.8	12.1	0.7
1997 ^a	#42	179	50.7	2.28	3.5	145	41
1998	Jet Vents	162	16.1		77.3	129	1.7
1998	Hot Vents	153	17.1	7.82	78.7	98.6	1.3
1998	Jet Vents	146	14.6	8.32	75.7	132	1.8
1998	#19	151	29.1		44.9	96.4	2.1
1998 ^a	#49	147	41.2	4.23	17.6	341	19
1998 ^a	#7	128	38.7	5.14	19.1	229	12
1999	Jet Vents	155	30.8	6.61	18.2	135	7.4
1999	#15	165	34.8	5.11	13.6	92	6.8
1999 ^a	#19	139	48.6	1.92	2.3	116	50
<i>Boiling Pot</i>							
2001 ^a	#44	90			1.3	111	87
2001 ^a	#44	89			2.0	126	63
2001 ^a	#44	89			1.2	101	86

^aData represent fluids considered to be moderated by CO₂-rich volatile emissions.

vent fluids support our contention that the groupings derive from separate processes that impose different fundamental controls on fluid chemistry. For example, regressions of Si against Mg for the two groups (Figure 13) suggest that the CO₂-moderated fluids are enriched in one or both of these elements relative to the water-rock moderated fluids, and that the effects of the different controlling processes extend beyond only Fe and Mn.

[38] When the concentrations of Mn and Fe in the water-rock group samples are regressed against the respective Mg concentrations, the 1997–1998 data provide a trend distinct from that for 1999 (Figure 14). Further, the magnitude of the zero Mg “end-member” value based on these trends decreases with time after the magmatic-tectonic event for Mn, but increases for Fe. During 1997–1998 the end-member value for Mn was 107 μmol/L and decreased by more than half in 1999 to 40 μmol/L, whereas for these same periods Fe end-member concentrations almost doubled from 158 to 291 μmol/L.

5.2. Boiling Pot Vents Area: 2001

[39] Sometime after our 1999 observations the Ikaika area vents were obliterated by mass wasting of the north crater wall. When Pele's Pit was revisited in 2001 vigorous but lower temperature ($T_{\max} = 93^{\circ}\text{C}$) hydrothermal discharge was discovered at the Boiling Pot Vents located along the southeast pit wall (Figures 1 and 12). Fluid concentrations here were similar to the CO₂-moderated

fluids previously sampled at Ikaika vents although Fe/Mn values were even higher (63–87 compared to 50 two years earlier) (Table 5).

6. Discussion

6.1. Magmatic Perturbation Effects on Submarine Fluid Discharge at Lō'īhi Volcano

[40] Our decadal observations preceded, were coincident with, and postdated by 5 years a spectacular magmatic-tectonic event at an actively degassing submarine intraplate volcano. Our results for iron and manganese allow an unprecedented and clear view of the varying effects of the magmatic-hydrothermal processes that contribute to the flux of these metals to the ocean from Lō'īhi volcano.

[41] A basic premise of our interpretation is that two processes (water-rock reaction and acid volatile-rock reaction) moderate vent fluid chemistry at Lō'īhi and that these processes vary both spatially and temporally in the extent they control the chemical signatures of fluid emissions. We assume by association (similar seafloor plumbing and rock substrate) that the fluids we have designated as “water-rock moderated” are MOR-like with most Fe and Mn added when the fluids are hottest and hydrothermal flowpaths nearest to a cooling magma body. Experimental results suggest the extraction efficiency of Mn and Fe from basaltic wallrock increases markedly when fluid temper-

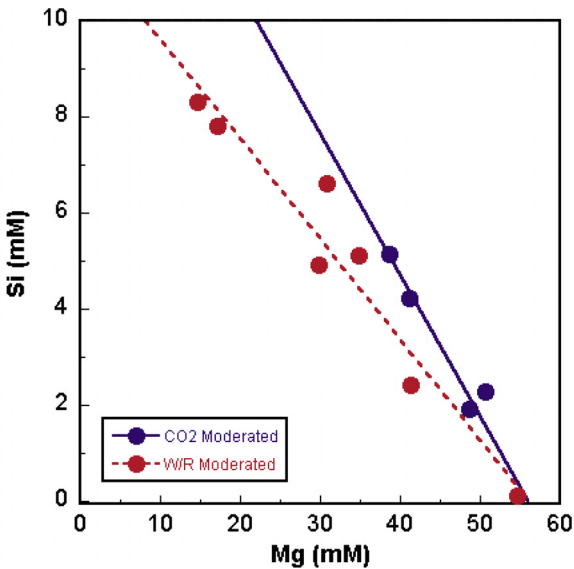


Figure 13. Linear regressions of Si against Mg for CO₂-moderated (blue symbols and solid line) and water-rock moderated (red symbols and dashed line) vent fluid groupings at Pele’s Pit for samples collected in 1997, 1998, and 1999 (Table 5). The different regression lines add support for our vent fluid groupings and suggest that the same processes that control Fe and Mn also affect other major elements within the vent fluids. The regression equation for the CO₂-moderated fluid group is $y = 16.4 - 0.293x$, $R = 0.98$ (intercept error ± 1.7), and for the water-rock moderated group is $y = 11.7 - 0.207x$, $R = 0.97$ (intercept error ± 0.8).

atures exceed 350°C [Seewald and Seyfried, 1990], which is consistent with observations of venting temperature maxima at MORs ($335^\circ \pm 42^\circ\text{C}$ for 33 different vent sites reviewed by Hannington *et al.* [2005]), allowing for subsurface mixing with seawater. End-member vent fluids at 33 unsedimented sites on MORs have a mean Fe/Mn value of 4.2 ± 2.8 (mol/mol) [Hannington *et al.*, 2005]. The low ratio values compared to that for basaltic wallrock (an order of magnitude higher) are commonly attributed to formation of Fe-bearing mineral phases within the subsurface, processes that are apparently ubiquitous at MOR venting systems.

[42] In contrast, hydrothermal pathways inundated by magmatic acid volatiles, in the case of Lō’ihi predominantly CO₂ [Sedwick *et al.*, 1992], may discharge “CO₂-moderated” fluids with Fe/Mn values closer to that of wallrock. Experimental data suggest this is particularly the case when reaction temperatures range between 150°–200°C (i.e., lower than ideal for metal liberation by water-rock reaction) when kinetic and thermodynamic controls combine to significantly enhance the effi-

ciency of wallrock dissolution by carbonic acid [Bischoff and Rosenbauer, 1996]. At higher reaction temperatures, such as at Axial Volcano on the Juan de Fuca Ridge where CO₂-rich fluids discharge at temperatures in excess of 300°C (Fe/Mn ~ 1.0 [Massoth *et al.*, 1989]), CO₂ is relatively unreactive with volcanic rocks [Bischoff and Rosenbauer, 1996], and water-rock reactions and MOR-like Fe/Mn values prevail. We prefer to describe this second grouping of fluids as “CO₂

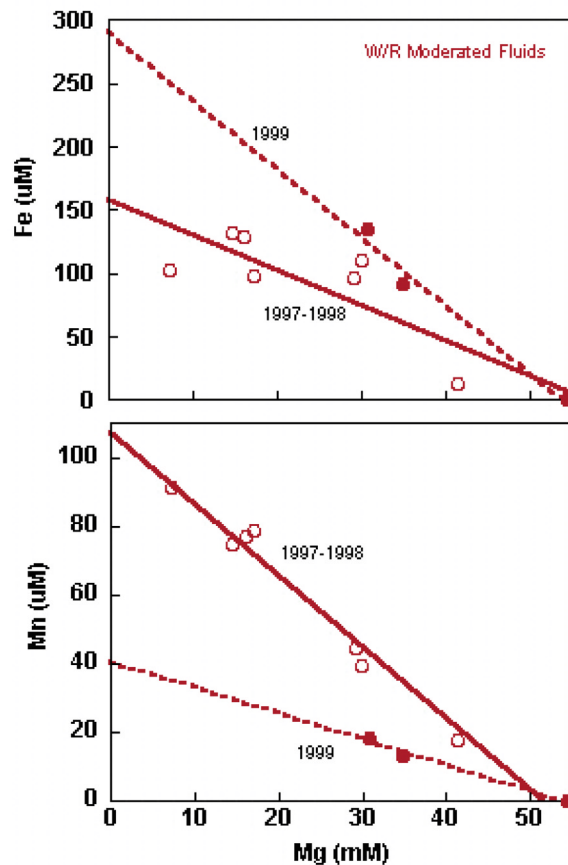


Figure 14. Linear regressions of the concentrations of (top) Fe and (bottom) Mn against Mg for water-rock moderated vent fluids collected within Pele’s Pit. At “zero” Mg concentration, the y intercept values may be considered to be “end-member” vent fluid concentrations [Von Damn *et al.*, 1985]. Open symbols represent data collected during 1997 and 1998, and closed symbols are for fluids sampled in 1999. All data are taken from Table 5, and only fluids with Fe/Mn values less than 8 (thought not to be heavily influenced by CO₂-induced dissolution of wallrock) were used in the regression plots. For Mn, the regression equations were $y = 107 - 2.1x$, $R = 0.99$ and $y = 40 - 0.74x$, $R = 0.99$, for the 1997–1998 and 1999 data groupings, respectively. Similarly, for these same groupings the Fe regression equations were $y = 158 - 2.8x$, $R = 0.86$, and $y = 191 - 5.4x$, $R = 0.99$. See text for discussion.

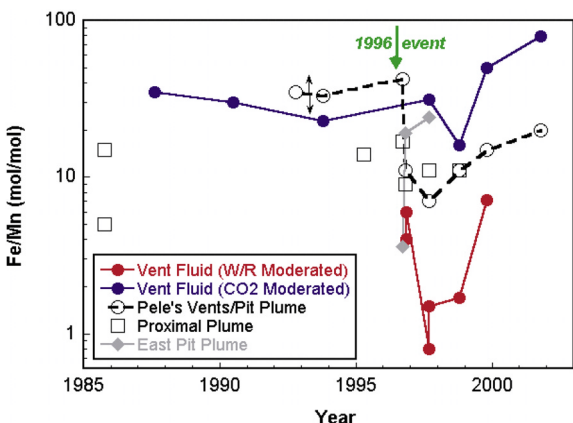


Figure 15. Time series distributions of Fe/Mn (mol/mol) values in vent fluids and plumes from the Pele's Vents and Pit area between 1985 and 2001. Data from the literature are combined with the results presented in this paper to provide a fuller perspective. Proximal plume results for 1985 are from *Sakai et al.* [1987]. Vent fluid results are shown in blue (for CO₂-moderated fluids) and red (for water-rock moderated fluids). CO₂-moderated values for 1987 and 1990 are from *Sedwick et al.* [1992] and for 1993 are from *Wheat et al.* [2000]. The 1996 value for CO₂-moderated fluids is an average of single data points from this study (41) and from *Wheat et al.* [2000] (23). Water-rock moderated results for October 1996 (4 and 6) are from *Wheat et al.* [2000], as is a single data point for 1997 (0.8), similar to a result from this work (Table 5). The thin vertical arrow between the 1992 and 1993 data points for the plume over Pele's Vents represents the standard deviation of the pooled data for those years and is the largest uncertainty for any data grouping on the chart (Table 2). Note log scale of ordinate axis (Fe/Mn). See text for discussion.

moderated" rather than "chemically weathered," as the reaction temperatures for the fluids sampled (Table 5) are considerably higher than commonly considered for subaerial dissolution (so-called "chemical weathering") of igneous silicate and aluminosilicate minerals by carbonic acid [*Garrels and MacKenzie, 1971*].

[43] Our discussion is focused on the Pele's vents area where magmatic intrusion and collapse have resulted in our most extraordinary chemical observations (and presumably, the greatest flux to the ocean). An overview perspective on changes in hydrothermal Fe and Mn at this site, expressed in terms of Fe/Mn values for the various plumes and vent fluids we and others have sampled, is presented in Figure 15. By relying on elemental ratio values, uncertainties associated with spatial effects on concentration are eliminated, and results from

the various sampling regimes (e.g., vent fluids, buoyant plumes, and neutrally buoyant horizontally dispersing plumes) that comprise the millionfold dilution range for the concentrations of hydrothermal Mn and Fe can be directly compared. We discuss these sampling regimes separately below.

6.2. Vent Fluids

[44] Evidence of a magmatic eruption at Lō'īhi summit during the first half of 1996 and continued magmatic activity possibly coincident with the 1996 seismic swarm [*Garcia et al., 1998*] supports the notion that hot dikes capable of driving hydrothermal circulation and high-temperature water-rock reaction also may have penetrated the Pele's Vents area. Subsequent withdrawal of magmas from the summit area to deeper levels of the volcano [*Davis and Clague, 1998*] resulted locally in formation of Pele's Pit, which also is consistent with magma transport into and out of this area. The upper reaches of fresh dikes exposed along the pit wall testify to the recent presence of shallow subseafloor reservoirs of heat (and fluids) in this area. On the basis of gas data from samples collected in 1996 from the Lohiau vents located on the upper north wall of Pele's Pit, *Hilton et al.* [1998] inferred that a pulsed degassing event may have preceded their sampling. It is conceivable that gases trapped in the very shallow fluid reservoirs associated with the dike intrusions beneath Pele's vents contributed to such an outgassing event and that subseafloor extensions of these dikes may have continued to fuel hydrothermal circulation at Pele's Pit for months to a few years or longer [*Massoth et al., 1998; Baker et al., 2004, and references therein*].

6.2.1. Water-Rock Moderated Fluids

[45] A clear and chronic separation of the water-rock moderated and CO₂-moderated vent fluid groupings is evident on the basis of the time series data shown in Figure 15. The low Mg values observed for vent fluids collected between 1997 and 1999 (Table 5) provide further compelling evidence for high-temperature water-rock reaction beneath Pele's Pit. When our final observations of water-rock moderated vent fluids were made in 1999, three years after the major magmatic event, Fe/Mn values were 6.8–7.4 and on the high end of the range observed for fluids venting on MORs. There the higher Fe/Mn values have been attributed to ephemeral bursts of high acidity following a dike intrusion [*Massoth et al., 1998, and references therein*] or to episodic release of CO₂ [*Wheat et al.,*

2000]. Given the timing of our observations relative to the pulsed event at Lō'īhi, neither explanation is satisfying. *Massoth et al.* [2003] observed similar high Fe/Mn values on arc volcanoes where chronic discharge of fluids with high levels of CO₂ and other magmatic acid volatiles occurs, a situation we consider to be more similar to intraplate volcanoes like Lō'īhi. We believe the shift in 1999 to slightly higher Fe/Mn values at the water-rock moderated vent sites more likely reflects encroachment of CO₂-rich fluids, which we know are pervasive on Lō'īhi summit, into a waning dike-driven hydrothermal plumbing system that feeds these sites. As the dike progressively freezes, we expect venting temperatures to decline even further and Fe/Mn value to increase until the discharge eventually attains a CO₂-moderated character, reflecting communication with a deeper-seated, longer-lived degassing magma source and the chronic venting signature for Lō'īhi volcano. Further support that a magmatic CO₂ overprint has been placed on the water-rock signature in 1999 and that water/rock reaction has waned is provided by opposing trends in the zero-Mg end-member values for Mn and Fe (Figure 14), where Fe concentration increased in 1999 (reflecting acid-CO₂ leaching of the relatively Fe-rich basaltic wall rock, Fe/Mn ~ 54 [*Frey and Clague*, 1983]) and Mn concentration decreased (reflecting a reduced efficiency of water-rock reaction with decreasing temperature).

6.2.2. CO₂-Moderated Fluids

[46] The spatially and temporally coincident discharge of fluids within Pele's Pit with characteristically high Fe/Mn values attests to the chronic presence of acid volatile (CO₂) charged hydrothermal pathways at Lō'īhi, even where the volcano has been locally perturbed by a magmatic intrusion event (Figures 1 and 15, Table 5). The Fe/Mn value for CO₂-moderated vent fluid flowing into Pele's Pit when first sampled a year after the magmatic event (Fe/Mn value was 41 for single sample in Table 5 and ~23 for a single sample reported by *Wheat et al.* [2000], the average of these values is plotted in Figure 15) was not dissimilar to that observed at Pele's Vents before collapse (Figure 15), and may reflect the "steady state" value for quiescent discharge at Lō'īhi. The generally increasing trend in Fe/Mn values to 2001, when the Fe/Mn value exceeded that for the bulk volcanic substrate at Lō'īhi (58 [*Frey and Clague*, 1983]), may be more revealing of collapse-related burial of iron-rich sediments than evolution of the

subseafloor magmatic-hydrothermal system. Dissolution of the basaltic wall rock can not alone achieve the high Fe/Mn values observed in 2001. These high values may be best explained as a consequence of subseafloor dissolution of previously deposited iron oxide and oxyhydroxide sediments. Iron-rich sediments recovered from Lō'īhi, Macdonald, and Teahetia intraplate volcanoes have Fe/Mn values that commonly exceed 200 [*Malahoff et al.*, 1982; *De Carlo et al.*, 1983; *Puteanus et al.*, 1991]. Such deposits were abundant at the former Pele's Vents area [*Karl et al.*, 1989; *Sedwick et al.*, 1992] and at the Lohiau vent in 1996, 1997 [*Wheat et al.*, 2000] and 1998 [*Emerson and Moyer*, 2002], and conceivably are buried in the lava pile beneath Pele's Pit where they could be resolubilized by acid-reducing hydrothermal upflow.

6.3. Pele's Pit Plume

[47] Hydrothermal plumes effectively integrate and reflect the respective volumetric contributions of the local seafloor sources [*Baker et al.*, 1993; *Massoth et al.*, 1994]. Given the remarkably high concentrations of the chemical plumes we have observed at Pele's Pit, the trends seen in Figure 15 for this site are effectively those for Lō'īhi volcano. As our plume observations precede vent fluid sampling by a year and were coincident with event seismic activity, they provide a unique perspective on early-stage geochemical transformations associated with magmatic intrusion (and deflation/pit collapse).

[48] The high Fe/Mn values observed during the RRC (42 ± 7) can be explained by two processes, which may have occurred coincidentally. The first process is magmatic degassing of CO₂ due to rapid decompression of a magma injected as a dike near Pele's Pit, as previously suggested by *Hilton et al.* [1998]. If indeed massive quantities of CO₂ were released during such a pulsed event, isochemical dissolution of the bounding wallrock may have contributed to the high Fe/Mn values. Alternatively, the tectonic collapse event that preceded our plume sampling may simply have resuspended the considerable mass of iron-rich sediments that previously covered the seafloor near Pele's Vents or exposed these deposits to acidic fluids resulting in their rapid dissolution followed by kinetically fast (re)precipitation while trapped within the confines of Pele's Pit where a particulate Fe phase predominated (Table 2) [*Massoth et al.*, 1998; *Field and Sherrell*, 2000]. While we can not discriminate between these processes using Fe/Mn values alone,

the unusually high fraction of total Mn that was particulate (33%, $\leq 4\%$ is common in hydrothermal plumes) and the known slow transformation of vented (dissolved) Mn to a particulate phase [Lavelle *et al.*, 1992], together suggest that resuspension of acid-soluble (pH 2) sediments enriched in Mn had occurred. A resuspension/fallout scenario is also consistent with the results obtained one month after the RRC, when plume concentrations at Pele's Pit had decreased dramatically: 36-fold for DMn and 208-fold for TDFe (Table 4).

[49] The Fe/Mn values within Pele's Pit are bracketed by the patterns for the two vent fluid groupings, strongly suggesting that the Pele's Pit plume is an admixture of these chemically distinct sources with a possible volumetric predominance by water-rock moderated fluids during the immediate aftermath of the 1996 event. While no high-temperature water-rock moderated fluids were sampled in 2001, the trend line for the plume within Pele's Pit clearly indicates the continued presence of such a source. Given decay times for hydrothermal venting of months to a decade following dike intrusions on MORs [Baker *et al.*, 2004, and references therein], it is conceivable that dike-driven hydrothermal circulation initiated in 1996 continued at Pele's Pit into 2001. The increase of Fe/Mn values with time is consistent with progressive waning of water-rock moderated discharge and an increased influence of CO₂-moderated flow at Pele's Pit.

6.4. East Pit Plume

[50] East Pit and Pele's Pit are spatially separated by only ~ 1.2 km (center to center), yet the temporal trends for Fe/Mn at these sites are dramatically different (Figure 15). Our initial observation of Fe/Mn within the East Pit plume (3.6) is consistent with this pit having an independent and dominant high-temperature water-rock moderated source. This notion is supported by the high concentration (and by extension, high inventory, especially when the \sim twofold larger pit volume at East Pit is considered) of Mn within East Pit and the high fractions of Fe and Mn in the dissolved phase (both metals $> \sim 90\%$ dissolved). These observations also argue against sediment resuspension as a source of the East Pit plume. When we returned to East Pit (PRRC) after a six-week sampling hiatus most of the hydrothermal inventory of Fe and Mn had been flushed (or had settled as a particulate phase, which is unlikely based on the slow phase transformation rate for Mn) and a transition to a volumetrically dominant invasion

of CO₂-enriched fluids had occurred that persisted for at least another year (Figures 7, 10, and 15). We believe that East Pit was hydrothermally quiescent prior to the 1996 intrusion, when a dike-related pulse of hot, reduced hydrothermal fluid was injected into the pit, titrating the available oxygen and adding metals to the plume. A pulsed injection of hydrothermal fluids into East Pit followed by basin flushing would explain the rapid decay in plume metal concentrations and the enhanced particulate iron fraction 1.5 months later (on average, 73% compared to 9% during RRC). A possible scenario to explain the increased Fe/Mn value at East Pit (19) after 1.5 months is a shift in the relative inflows of the two types of source fluids: a rapid fall off in the volume of water-rock moderated fluids as the heat content of a small, shallow dike at East Pit is mined to depletion, and significantly enhanced opportunistic inflow of pervasive CO₂-rich fluids, possibly via a fresh fracture network created beneath East Pit as a result of the recent tectonic activity in this area.

6.5. Dispersing Plumes: Implications on Global Hydrothermal Fluxes of Fe and Mn

[51] The similarity of Fe/Mn values for dispersing plumes sampled proximal to Lō'īhi summit (Figure 1) and the vertical plume distributions (Figures 8, 10, and 11, Table 2) suggest P.P (and East Pit per discussion above) has been the volumetrically predominant source of hydrothermal discharge from Lō'īhi since the intrusion event in 1996. Deeper components of the dispersing plume correspond to lower ridge flank vents, which have similar high Fe/Mn values (18–40 [Wheat *et al.*, 2000]). Plume concentrations of Fe and Mn measured 9 km from Lō'īhi summit during the RRC were unprecedented in magnitude for a dispersing hydrothermal plume this distant from a known source region, and demonstrate the significant effect that magmatic event-related discharge can have on the proximal ocean. Significant and detectable elevations in the concentrations of Fe and Mn, respectively, observed more than 450 km northwest of Lō'īhi, ascribed (by virtue covariation with anomalies in ³He) to hydrothermal discharge at this site [Boyle *et al.*, 2005], attest to the transport of plume-borne chemicals beyond the proximal and into the distal ocean. When these spatial observations are coupled with the chronic nature of plumes now observed over almost two decades at Lō'īhi, and the knowledge that, as is the case for $\delta^3\text{He}$ [Lupton, 1996], source fluids here may be chemically enriched in some components

(e.g., high Fe/Mn) relative to vent fluids at MORs, the notion emerges that intraplate volcanoes such as Lō'īhi may contribute significantly to the oceanic hydrothermal budget. While the few available observations at other hydrothermally active intraplate volcanoes demonstrate they also have enriched chemical plumes, e.g., at Macdonald and Teahetia seamounts Fe/Mn values are 38 and 17, respectively [Stuben *et al.*, 1992], and that some also have experienced recent magmatic events, e.g., Macdonald seamount in 1989 [Cheminée *et al.*, 1991] and Vailulu'u seamount between 2001 and 2005 [Vailulu'u Research Group, 2005]), further exploration of additional sites is needed before the magnitude of hydrothermal chemical fluxes from intraplate volcanoes can be reliably estimated. The results presented here suggest such exploration may be very worthwhile.

7. Summary

[52] 1. A decadal time series for Fe and Mn associated with magmatic-hydrothermal emissions from Lō'īhi volcano was conducted. Measurement of vent fluid and proximal and distal plume samples collected by submersible and from surface ships was accomplished over a time period that bracketed the first documented magmatic-tectonic event at an intraplate volcano: Lō'īhi summit.

[53] 2. Preevent observations revealed distributed venting sources along the south flank of Lō'īhi with most concentrated venting located at Pele's Vents. A weak but discernible hydrothermal plume was mapped dispersing predominantly at the depth of Pele's Vents and to the southwest of the summit area. Our results are consistent with historical data for Lō'īhi and add to our knowledge of distal plumes in this area.

[54] 3. Sampling conducted coincident with the seismic swarm on Lō'īhi summit and soon after magmatic collapse formed Pele's Pit (RRC) revealed plume concentrations of Fe and Mn that are unprecedented in chemical intensity. Plumes at East Pit had an Fe/Mn value of ~ 4 , typical of source fluids whose chemistry is moderated by water-rock reaction, and were in striking contrast with plumes at Pele's Pit, where a high Fe/Mn value (42 ± 7) implied a CO₂-moderated fluid source. Within six weeks, Fe/Mn values at the two pits had reversed, with East Pit Fe/Mn values well within the CO₂-moderated range and Pele's Pit Fe/Mn values approaching water-rock moderated values. We interpret these results as charac-

teristic of a pulsed release of reservoir fluids and/or solubilization-resuspension of iron-rich sediments at Pele's Pit. Following this release, a remnant thermal mass most likely resulting from a local dike injection continued to drive hydrothermal circulation resulting in a predominant influence on plume chemistry at this site. At East Pit, where no seafloor collapse occurred, we surmise that hydrothermal circulation resulting from a relatively small dike intrusion controlled plume chemistry during the immediate aftermath of the event, but soon was volumetrically overridden by the effects of pervasive leakage of CO₂-moderated fluids in this area, possibly channeling through fractures recently opened as a consequence of recent tectonic activity. Plumes dispersing from Lō'īhi at this time had unprecedented high concentrations of Fe and Mn 9 km distant. Approximately 1.5 months after the 1996 event, distal plume (>10 km from source area) maxima were fourfold to tenfold elevated in Fe and Mn concentration compared to the precollapse plume.

[55] 4. Trends in vent fluid and plume Fe/Mn values following the 1996 event suggest the heat source driving hydrothermal flow beneath Pele's Pit persisted as a significant contributor to discharge from Lō'īhi until at least 2001 (a duration of 5 years) and that a return to a "chronic" state, like that observed at Pele's Vents during the decade preceding the 1996 event, was immanent.

[56] 5. Time series monitoring of the concentrations and relative abundances of Fe and Mn at Lō'īhi has demonstrated a utility for gauging changes in fluxes of these (and associated) elements from an intraplate submarine volcano to the ocean and for providing insight regarding the magmatic-hydrothermal seafloor processes controlling their genesis. Observations of appreciable hydrothermal plumes at Lō'īhi and other intraplate volcanoes suggest these sites may constitute an important source of Fe and Mn to the ocean.

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