

Fe and CO₂ at Loihi

Temporal and comparative variability of Iron and Carbon Dioxide of Loihi Seamount
hydrothermal systems

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Non-Technical Summary

Hydrothermal systems are visible representations of geological processes at work. Since their discovery, studies have shown them to be remarkable natural features with unique properties, venting fluids at extreme temperatures and supporting unusual biological communities. This study evaluates the effect of recent eruptions and seismicity on the hydrothermal systems of Loihi, a seamount 34 km south of the largest island of Hawaii, to determine whether the chemical makeup of the plume has changed since the last published measurements were taken in 2006. Determining the differences of the Loihi vent fields over time regarding iron (Fe) and carbon dioxide (CO₂) abundance, could give possible insight into certain geological and biological processes creating, sustaining, and continuously transforming these venting systems. Samples were taken of the neutrally buoyant plume at ~1180 m, sampling iron, pH and carbon dioxide. Research was conducted during the cruise on the *R/V Thomas G. Thompson* taking place between 27 December 2010 and 4 January 2011 . Four transects were conducted over Loihi resulting in a total of 33 samples within the plume. Samples were obtained using a CTD with a Niskin Rosette sampling in and near the neutrally-buoyant plume, as well as an open ocean control. Both Fe and CO₂ abundance measurements were lower than past values. The results of this study suggest smaller seismic swarms have little to no impact on the natural variability of hydrothermal activity.

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Abstract

A survey of the hydrothermal vent fields on Loihi Seamount, of the south eastern flank of Hawaii was conducted from Dec 27th to Jan 4th 2011. Water samples were collected from Niskin bottles fired within the apparent neutrally buoyant plume across four transects conducted over the summit of Loihi utilizing a CTD tow yo method. Samples were taken below the effective sill depth of 1165 m where anomalous values of both temperature and transmissivity were detected. Strong positive correlations between both Fe and CO₂ with temperature anomalies on the order of an R value of 0.91 and 0.79 respectively. Ranges of pH within the proximity of the plume spans from ~7.2 to ~7.4. Measurements of CO₂ as calculated from the carbonate equilibria of the system ranges from 170 ppm to 310 ppm. Iron concentrations range from ~1 nM/kg to ~800 nM/kg. These measurements are somewhat lower than their past measured values. This could signify that seismic swarms in 2001 and 2005 were not magmatic in nature and did not drastically affect vent fluid chemistry. Concentrations of Fe and CO₂ are both lower in the open ocean control than their Loihi counterparts at similar depths in the neutrally buoyant plume. Assuming a natural decay of activity, chemical ratios were not expected to increase due to eruptions and tremors instigated by seismic swarms.

The relatively new discipline regarding hydrothermal systems represents an exciting field. Sites of active venting are characterized by their hot temperatures and chemically unique effluent (Tivey et. al 2007). Hydrothermal vents often display high concentrations of CO₂, a magmatic volatile gas, and metallic particulates such as iron, an important macronutrient for

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oceanic biology. Studies examining these unique systems may enable an improved assessment of the role that intraplate fields contribute to the global carbon cycle via CO₂. Determination of iron abundance and flux may aid in the role of hydrothermal systems in the larger biological cycle since hydrothermal discharge adds more Mn and Fe to the oceans than any other source (Massoth et al 2006). Studies of metal input is imperative in understanding the nature of variability in the system and through that determine the ability of the effluent metals to affect their surroundings.

Hydrothermal systems are visible demonstrations of geological processes that take place in the earth's mantle, affecting other biological and geochemical processes, and providing habitats in extreme environments. Their discovery has led to shifts in the understanding of tectonic forces, and has lent credence to the theory of plate tectonics (Keith 2001). Research concerning hydrothermal systems is crucial to improve our understanding of what role they play in biological, chemical, and geological processes.

Seismic swarms, also known as earthquake swarms, are geological events caused either by the shifting and abrupt movement of tectonic plates, or the eruption of a magmatic chamber caused by pressurized gas (Waite and Smith 2002). Seismic swarms are a series of earthquakes that occur rapidly in a short period of time. Dike injections into the seafloor are the result of magmatic eruptions, often altering chemical ratios of vent fluids if hydrothermal systems are near to the eruption by increasing CO₂ outgassing and temperature and therefore Fe.

Loihi Seamount, the presumptive newest island of Hawaii, is currently being created underwater over the Hawaiian hotspot within the Pacific plate, beginning its formation as early

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as 400,000 years ago. Its discovery prompted continuing research concerning this unique system (Karl et al. 1988) as it was considered distinct from other previously studied sites. In 1996, Loihi Seamount experienced the largest seismic swarm on record since its discovery. Believed to be a magmatic event (Garcia et al. 2005) and not a tectonic one, this eruption caused noticeable changes in the geomorphology of the vents and vent fluid chemistry by increasing CO₂ and in turn decreasing the pH, while increasing temperatures (Massoth et al. 2006).

Differences in magnitude prompts the question as to how smaller seismic swarms have affected the vent chemistry over time. Predictions can be made from this assumption that since the seismic swarms in 2001 and 2005, the pH has increased as a result of decreased CO₂ outgassing. Assuming these predictions it is possible that a decrease in Fe occurred due to the drop in venting fluid temperature (Boyle et al. 2004) which will have dropped in the absence of any magmatic influence. However, a measured increase in Fe and temperature along with increased Mn, may indicate a pre-eruptive state. This paper intends to present results and discuss whether, and if so, how the vent fluids of Loihi Seamount have changed over time since the last comprehensive published measurements.

Utilizing data provided by the USGS Hawaiian Volcano Observatory (HVO), observing and analyzing the effects of periodic seismic swarms of lesser magnitude than the 1996 event could be significant in identifying key features that drive Loihi and perhaps other hydrothermal systems. Iron is often utilized as an indicator of hydrothermal fields, and relative abundance of vented Fe and Mn are characteristic of Loihi Seamount before, during, and after the 1996 eruption (Massoth et al. 2006). Measuring the abundance and relative abundance in relation to

other constituents may allow a prediction as to whether an eruptive state is imminent, or if it is returning to a less active state.

Hydrothermal vents provide environments for extremophiles which exist and thrive in high temperature, low pH, and no light conditions. Reports suggest that, in the past, the immediate area around the vents has been devoid of luxuriant macrobenthic communities (Karl et al. 1988). Microbenthic organisms such as bacterial mats, however, exist in great quantities and it has been postulated that they play a major role in Fe oxidation and that Fe oxidizing bacteria are common at Loihi Seamount (Emerson and Moyer et al. 2002). Therefore, biology around the vents may also have an effect on the chemical ratios of the neutrally buoyant plume. Another study examined several constituents of the neutrally buoyant plume including iron. In this previous study iron was determined to be abundant in the plume, almost 1 mMol/kg.

In order to establish the magnitude of the neutrally buoyant plume and the chemical constituents therein, a level of significance must be used. It will also offer a comparison of this research to previous studies to conclude whether the measured variables are statistically different from each other. An established significant difference would lend credence to the proposed hypothesis. This study attempts to observe the change of chemical constituent ratios in order to examine the effects of secondary seismic swarms and possible natural decay. Research may enforce previous studies regarding natural decay of hydrothermal systems. Observing and analyzing may inform future studies regarding mechanisms behind venting fields. If the hypothesized results are indeed measured, insight may be gained regarding the

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relationship between magmatic and tectonic seismicity, and their effects on hydrothermal systems.

The analysis of the measured abundance of Fe and CO₂ and the range of pH will allow a comparison of current data to past data both before and after the seismic swarms. If there is a decrease in temperature CO₂ and Fe, it could tentatively be concluded that Loihi has returned to a less active state, and that the seismic swarms were not magmatic in nature. Assuming a decay of activity (Baker et al, 2004), measured amounts of perturbation of chemical ratios were expected (Lilley et al. 2003) over time due to eruptions and tremors.

Principal findings include an overall range of iron abundance between 1.4 and 792 nM/kg. CO₂ concentration ranges from 155 to 310 mMol/kg. pH ranges were determined to vary within the range of 7.2 to 7.4 within the neutrally buoyant plume, and 7.4 to 8 outside it. These findings and the corresponding temperature anomalies suggest that the seismic swarms occurring in 2001 and 2006 have not significantly changed the chemical ratios of the effluent in Pele's pit on Loihi. This leads to the conclusion that tectonic swarms, as opposed to magmatically induced seismic swarms have little to no effect on the chemical constituents of the vent fluids.

Materials and Methods

Samples for this study were collected on board the R/V Thompson during the Hawaii cruise using equipment such as the Conductivity Temperature Depth (CTD) and Niskin Rosette. The preferred technique employed in the effort to locate the neutrally buoyant plume of

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feasible sites was the tow yo of a CTD, lowering the CTD at ever decreasing rates as it neared the bottom while the R/V Thompson traveled at ~1-1.5 knots and raising it to a set minimum depth in a repeating manner (Boyle et al 2004). Although a minimum depth of ~ 950m was discussed, the CTD never rose above 1100m while in tow-yo. A horizontal profile of the water column at depth was obtained by raising and lowering the CTD over a 10m range, yielding a small vertical swath over each of four transects conducted in and around Pele's Pit. The sampling method employed deviated from standard sampling methods which attempt to measure over a greater vertical scale, on the order of 250m, as opposed to 10m, although acceptable results were nonetheless acquired.

To correctly and successfully locate one or more actively venting hydrothermal vents the cast was observed real time in an attempt to see simultaneous anomalies in the temperature and transmissivity via the transmissometer to pinpoint the plume. Upon observing anomalous activity in the temperature on the order of 1/10th of a degree and a decrease in transmissivity occurring at the same depth in the water column, bottles were fired two at a time within the apparent "plume" to ensure the validity of the measurement. In the open ocean water samples were obtained using the CTD in order to acquire a control or reference point for the samples retrieved from the neutrally buoyant plumes on Loihi (Petersen 2011).

Four variables were measured: Fe, temperature, and CO₂ through measured pH. pH was measured continuously throughout the water column via the pH sensor, located directly on the CTD. Water samples to be evaluated for iron content and pH were collected from the CTD's Niskin Rosette. Upon retrieval of the CTD, sub-samples of the neutrally buoyant plume fluids were collected in 50 mL containers for pH determination and 125 mL bottles for iron, using

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trace metal gloves and trace metal equipment, adhering to the methodology of trace metal sampling to reduce or eliminate contamination (Measures et. al 1995). Samples were recorded at several locations during the four transects although because of the nature of the pit, it was difficult to sample at specific locations.

Iron samples were stored until the Thompson returned to the University of Washington where their contents were determined through acid filtration and flow injection analysis using a Tecator FIAStar 5010 (Measures et al 1995). Fe samples were filtered through 0.2 um pore diameter filters, and acidified. Dissolved iron content was determined in the NOAA lab by comparison to preconcentrations of iron, with precision around 1 standard deviation, or 5% (Massoth et al 2006). Calibrations were verified and abundance of iron was found via comparison of voltage over time to the calibrated regression line.

Due to the fact that the pH meter attached to the CTD operated only to 1200m, the depth profile was limited. pH samples were titrated with acid directly after acquisition to enable the determination of CO₂ concentrations via the carbonate equilibria (Andersen 2002). Using a titrator, pH samples were measured and recorded for future use in calculating the alkalinity to discover the CO₂ concentration in the plume. Each sample was measured for pH and then titrated down to a pH around 3. Alkalinity r values were determined after pH and using the gran titration calculation, alkalinity was solved for. Calculating the carbonate equilibria using the alkalinity allowed CO₂ concentrations to be obtained.

Results

Irregularities in both temperature and transmissivity were measured for while conducting the tow yos over Pele’s Pit. Samples were collected when it was observed that transmissivity decreased and temperature increased simultaneously (Figure 1). Anomalous temperature behavior at depths of around 1200 m range from 3.7 C to 4.25 C across all four transects conducted. Transmissivity at depth had little variability being nearly binary in nature, shifting between two values for a majority of the time.

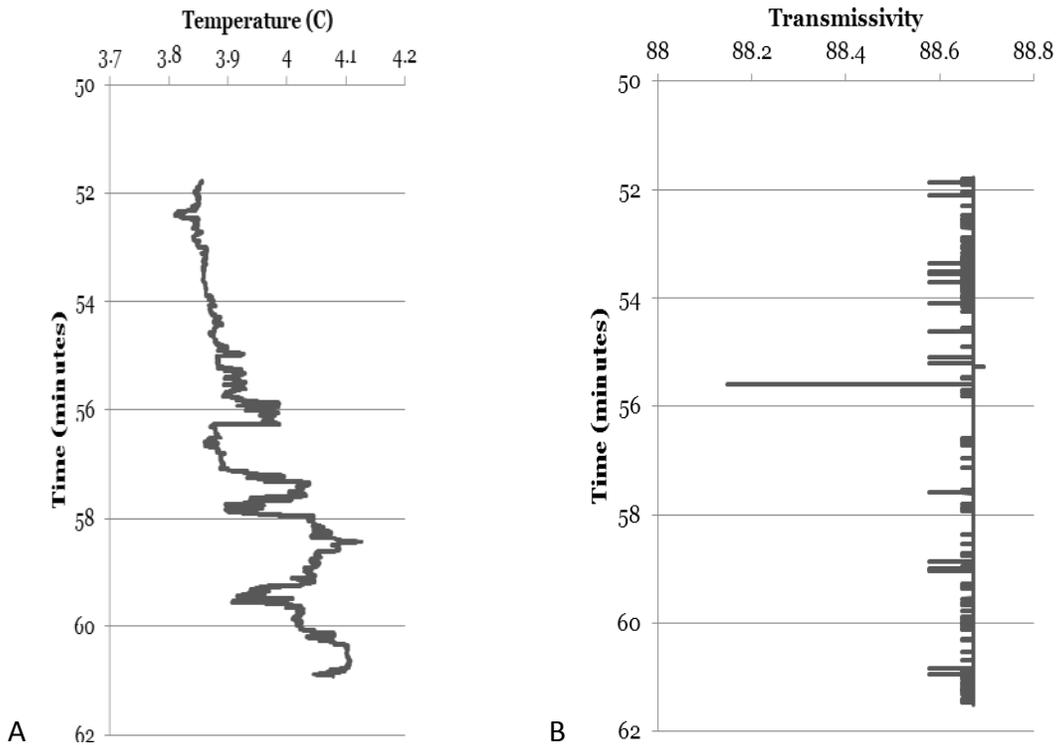


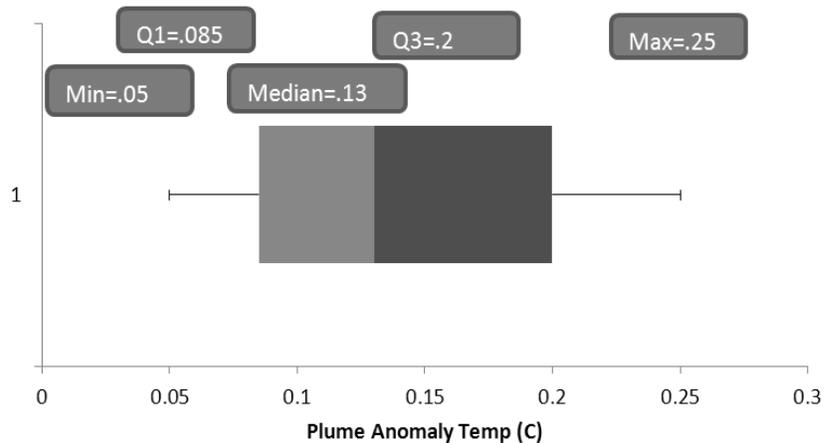
Figure 1. Anomalies in temperature vs time and transmissivity vs time represent possible plume signal. Bottles were fired at each selective location based upon the magnitude of the anomaly

Significance of the plume before the determination of Fe and CO₂ levels was established by the magnitude of the anomalous behavior of the temperature in the apparent neutrally

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buoyant plume (Figure 2). Temperature anomalies were assessed by observing deviations from the vertical profile of the water column on the flank of the seamount.

This enabled a baseline from which measurements of both iron and CO₂ as well as pH to be measured and compared to. Using the distribution of temperature, which ranged from 3.7 C to 4.35 C,



correlations between the variables and temperature were found (Figure 3). Iron had

Figure 2. Distribution of data based upon temperature anomalies which warranted sampling within the apparent plume. Fifty percent of data resides between .085 and .2 degrees C.

a strong positive correlation of .91 and CO₂ a strong positive correlation of 0.79.

Correlations between temperature and the measured variables were established, allowing an assumption that the samples and observations were indeed representative of a hydrothermal plume. The

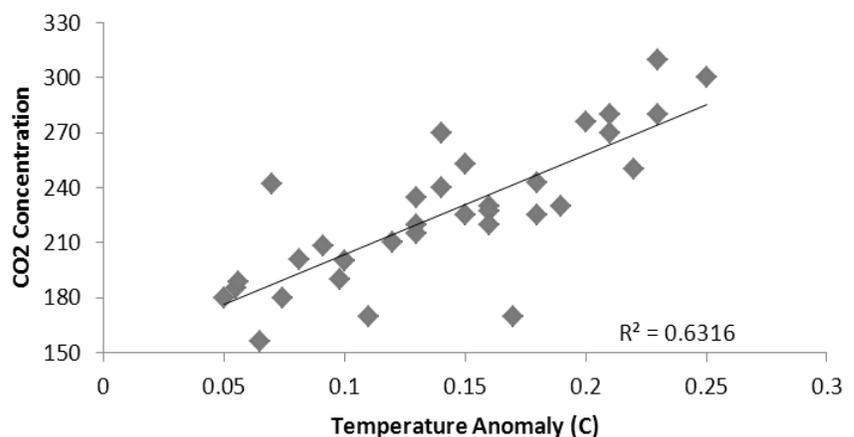


Figure 3. As the magnitude of the temperature anomalies increase, CO₂ increases as well. A positive correlation of .79 exists between the two variables. Plume signals of greater magnitude results an increased quantity of CO₂ being outgassed.

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correlation represents where the greater the temperature, the greater the concentration of CO₂ or iron. CO₂ concentration varied within the neutrally buoyant plume with a range of 155 to 310 ppm. pH had little variation at depths around 1200 m, ranging from 7.2 to 7.4, whereas the open ocean control ranged from 7.4 to >8.

Iron abundance was measured in 4 distinct areas, as were the other variables (Figure 4). On the North Eastern flank of the seamount, the highest concentration of iron observed was 2.65 nM/kg at 100 m while the remainder of the cast displayed an insignificant amount which could not, in fact, be reliably quantified due to the detection limits of calculated Fe content. The open ocean had an increase in Fe at the surface and a high at a depth of 1000 m. The summit was

increased in iron at the surface and at 1200 m, a 3 fold increase over the control value at similar depths, although this does not represent the maximum measured iron concentration. In

comparison to the average abundance overall, the maximum at the summit is quite low (Table 1). The two measured variables differ somewhat over the locations. The transects have averages ranging from 148 to 301 nM/kg iron and CO₂ ranges from 279 to 307 ppm.

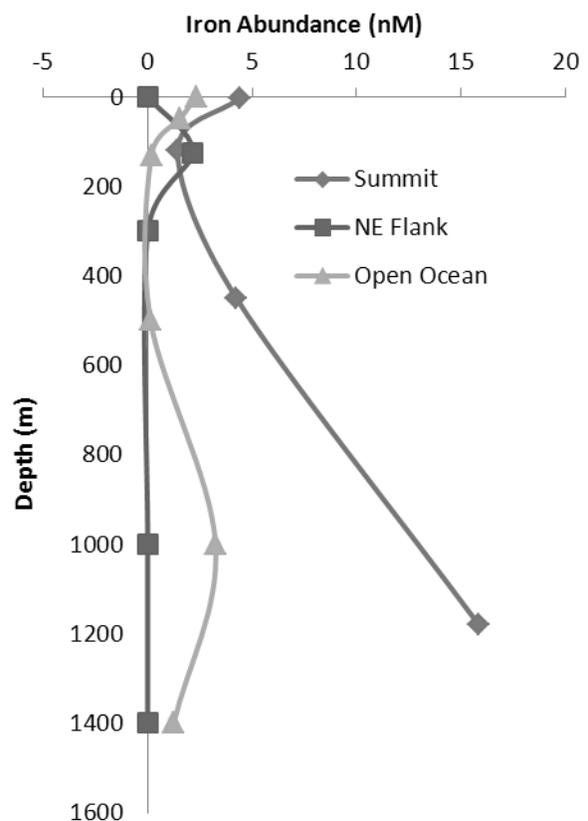


Figure 4. Abundance of iron at 3 locations including verticle profiles of the North eastern flank, the summit of Loihi, and the open ocean control. NE flank values below 200m assumed to be zero.

Location	Fe nM/kg	CO ₂ ppm
North East Flank	2.5	180.9
Loihi Summit	15.2	238.3
Transect 1	213.7	280.5
Transect 2	206.9	279.3
Transect 3	148.5	290.1
Transect 4	301.1	307.6
Open Ocean	1.44	162.9

Table 1. Tabulation of the variables Fe and CO₂ at 7 locations. Transect values are averaged over similar depths. North East Flank, Summit, and Open Ocean values are discrete and correspond to depths similar to those of the transects for comparison.

Discussion

Data from this cruise and previous studies have been compiled in order to assess the temporal changes of the Loihi hydrothermal systems. Over the 15 year time span since the 1996 eruption event, it is evident that the plume signal is decreasing and experiencing either natural decay or a period of quiescence. The aspect of greatest importance regarding this research is not the measured variables, but the determination of the presence of a hydrothermal plume. Without a reasonable assumed presence, the samples would not be viable in any study addressing hydrothermally active sites. Therefore the observation of a decrease in transmissivity and an increase in temperature on the order of 1/100th/ to 1/10th of a degree C indicating the possible presence of a plume was the first milestone. Temperature

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rises near the sea floor relative to the ambient water but anomalous activity where temperature rises due to the venting heat was observed (Figure 1). These anomalies often occurred simultaneously with a decrease in transmissivity, presumably due to the increased particulates in the water column. These two criteria satisfied, it is reasonable to assume that said anomalies indicate the existence of a neutrally buoyant plume.

In this study, iron abundance was found in a large range, although it remained fairly consistent within the 4 transects. The overall average of iron, while not entirely accurate of the distribution of iron within Pele's Pit, offers the best solution to the integrated nature of the pit. Pele's Pit houses many actively venting sites, and the effluent from these sites tend to pool within the crater as hydrothermal plumes integrate and reflect the respective volumetric contributions of the local seafloor sources (Massoth et al 2006). Due to the integrated nature of the neutrally buoyant plume, it is difficult to determine the exact nature of any single sites that are currently venting.

The limitation of the CTD did not allow a more thorough observation, thus an average of iron abundance is the most prudent choice. The average Fe within Pele's Pit was found to be approximately 160 nM/kg. In 1996, following the seismic swarm, total dissolvable iron in Pele's Pit, was measured at 400000 nM/kg . In 2006, average iron abundance at the effective sill depth in Pele's pit was about 400 nM/kg (Garcia et al 2005). Levels of significance were solved for using this study's average iron content and the Garcia et. al (2005) value. Calculated using a p value of .05, it was found that there is a statistically significant difference between the measurements taken from similar locations at the same depth in the past and the present.

The statistical difference of the measurements implies that the seismic swarm of 2005 had no impact on Pele's Pit hydrothermal systems. Decreases in both CO₂ and Fe indicate that these past smaller seismic swarms were not induced by magmatic intrusions. A magmatically induced seismic swarm would have led to increased CO₂ outgassing and an increase in temperature resulting in more iron outflow. As this increase was not observed but a decrease instead, this signifies that the smaller seismic swarms of 2001 and 2005 were not magmatic in nature and had little to no effect on the system.

Iron varied greatly between the samples within the pit and outside it. The north east flank was measured to have the lowest relative quantity of iron, most samples below detection limits. This lack may be due to the predominant south west current, preventing the neutrally buoyant plume to form at the northern flank. The East and West Pits have few actively venting sites which may account for the distinct absence of larger concentrations of iron at the effective sill depth. Abundances of iron were higher at the summit than at the open ocean control and the north eastern flank although still low in comparison to the values of iron within the transects.

The significantly different value of iron indicates effluent output in Pele's Pit has decreased as a result of natural decay in respect to its last measured abundance. However, it is possible that the interval over which the chemical ratios are perturbed were over a shorter time period than this study's proposed interval (Sedwick et al 1992). Therefore, the conclusion of this study may not truly represent the effect that smaller seismic swarms have on hydrothermal systems as a whole. The system in Pele's Pit may have changed the chemical effluent over a brief time period before it reverted back to its normal rate of decay.

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In the past the neutrally buoyant plume over Pele's Pit was predicted to be around 100 m above the actively venting areas (Garcia et al 2005). Samples in this study were taken at no more than 30 m above the seafloor which would suggest that the plume height has decreased in height over time as a result of natural decay. Reduction in the height of the plume lends evidence to the hypothesis that the seismic swarms in 2001 and 2005 did not, in fact, temporarily affect the system over the ten year time period.

These findings may inform future studies as to the nature of seismic swarms at intraplate hydrothermal systems and their resulting impact. Hydrothermal systems play an important role in the global iron flux. This study may allow future studies to take into account the lack of impact that smaller seismic swarms have on hydrothermal systems. It may enable a more accurate flow rate to be calculated.

Correlations between temperature and Fe and CO₂ are needed to establish the significance of the plume. CO₂ levels were increased in water samples that were taken in areas that had higher relative temperatures (Figure 2). The existence of a positive correlation between CO₂ and temperature anomaly significance leads to the conclusion that the greater the amount of effluent, the greater the temperature at that location.

Concentrations of CO₂ at Pele's Pit have always been relatively high in comparison with other MOR type systems, a result of the unique magmatic activity. Garcia et al (2005) reported concentrations of CO₂ as 310 ppm while also pointing out the decreasing trend in alkalinities from 1993 to 1997 was interpreted to correspond to decreasing magmatic CO₂. This decrease in magmatic CO₂ is also an indicator that Loihi hydrothermal systems may be returning to a chronic state. Unfortunately, water samples from depths greater than 1200 m were not

measured for CO₂ concentration due to the depth limitation on the pH meter which prevented it from going any deeper than 1200 m. Allowing the CTD to travel deeper than 1200 could have enabled a closer observation yielding more accurate measurements, rather than the neutrally buoyant plume. Although a setback, this did not drastically influence the results.

The sampling method employed, while differing from the standard swath width of around 200 m, did yield interesting results. Pele's Pit, represented an area where a small vertical swath width may be more beneficial to the utilized sampling method. Due to the relatively small area, a profile of a more vertical nature may have resulted in fewer samples but may have also been beneficial. Following standard procedure would be more prudent if the transect had been over a larger horizontal range. While the chemical ratios of vent fluids differ between sites, this study may inform future studies as to the benign nature of smaller, non-magmatically induced seismic swarms on the nature of hydrothermal circulation at actively venting sites.

The conducted study of Loihi's hydrothermal systems is not without its faults. The proposed methodology of sampling was not used, limiting the range of observation. Tow yos conducted in this study only measured a vertical extent of less than 30m as opposed to the proposed 150 m extent, thus restricting the area of observation. A greater vertical extent may have given more insight into the nature of the plume. The integrated quality of the pool may prevent anomalous activity from being seen. Some vents may have been subject to change in chemical composition of its effluent after the 2005 seismological event although the plume structure may have prevented observation of these changes. Vertical casts may have been more prudent, using a pogo method to box in an apparent plume. This method would have

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allowed specific vents to be sampled with much greater accuracy in the measurements. Comparison of measurements required past studies to have acquired samples from the neutrally buoyant plume as well.

Conclusion

In conclusion the survey of Loihi Seamount and Pele's Pit yielded promising results regarding hydrothermal activity on Loihi. As predicted, both CO₂ and Fe have decreased in concentration over the last 5 years. Iron has seen a decrease from an average of 400 nMol kg⁻¹ to 160 nMol kg⁻¹ while CO₂ has decreased from 310 to 240 ppm. Iron has been shown to be significantly different than in the past. These results may be indicative that the tectonically induced seismic swarms of 2001 and 2005 had little to no effect on the chemical ratios of the hydrothermal effluent. This conclusion may help in understanding the natural variability and role that intraplate fields play in the global iron flux, as well as tectonic processes.

However, the conclusions of this study may be skewed as a result of sampling method, which deviated from CTD tow yo standard procedure which measures over a greater vertical extent. An approach which covered the water column with greater verticality may be a more prudent method of sampling and yield more pertinent results.

In the future, studies may benefit from multiple vertical casts rather than continuous tow yos as several locations which may offer comparison on a broader scale, perhaps useful in determining variability between separate venting fields.

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