Temporal changes in venting at Brothers volcano, as indicated by backscatter and oxidation-reduction potential

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Few measurements have been conducted into the temporal variability of venting along volcanic arcs. To characterise any temporal changes, two survey track lines were conducted over Brothers Volcano, Kermadec arc, on March 6 and 7, 2009 on board the *R/V Thompson*. Conductivity (salinity)-temperature-depth-optical (CTD-O) and oxidation-reduction (ORP) measurements were taken to map the spatial distribution of hydrothermal fluids in the water column. Previous surveys conducted in 2002 and 2007 show that levels of ΔNTU had decreased from 2002 to 2007, followed by a small increase in 2009. Previous ORP data are only available from the 2007 cruise, and reveals an increasing anomaly with time. Changes in the salinity of the plume waters, combined with ΔNTU trends, suggest that from 2002 to 2007 hydrothermal venting shifted to the emission of vapours with low ion concentrations. This shift may indicate that the system has heated up, perhaps due to a pulse of magmatic activity. From 2007 to 2009 a large increase in the salinity of plume waters and ΔNTU was documented. ORP data does not match this hypothesis, but cannot be reliably quantified due to the constant variability of plume ORP signals, and its short spatial extent from the centre of the plume. Two different background waters were also observed in the 2009 track lines, representing an anomalous patch of warmer waters transported into the area. This anomaly was not present in the 2002 or 2007 tows, and may have implications for plume dynamics.

Abstract: To investigate the temporal nature of hydrothermal venting, two tow-yo surveys were conducted over Brothers volcano, Kermadec Arc, New Zealand on the *R/V Thompson* on March 6 and 7 2009. Light-scattering (ΔNTU - nephelometric turbidity units) and oxidation-reduction potential (ORP) measurements were recorded and extrapolated to indicate the extent and intensity of hydrothermal venting. Existing data from 2002 and 2007 were extrapolated and plotted in the same manner with colours normalised between the three time periods to allow for easier comparisons. The salinity of fluids venting from both the Cone and NW Caldera had decreased from 2002 to 2007 with an associated decrease in ΔNTU. This suggests that there was a pulse of magmatic activity leading to increased venting of low salinity vapours. Between 2007 and 2009, Cone and NW Caldera hydrothermal activity shifted towards venting of high salinity brines, with an associated increase of ΔNTU. ORP trends do not match those of salinity and ΔNTU, most likely due to the lack of equilibrium in the plume and the localized nature of the signal. Two water masses over Brothers volcano were identified in the 2009 survey from temperature and salinity plots. A southern water mass is believed to be background water at the venting sites, and dominant during the 2002 and 2007 sampling. During the 2009 field program, a cold core eddy present of Antarctic Intermediate Waters which had experienced more mixing with Pacific water was documented. This can influence plume advection by shifting currents, and adds to the complexity of calculating temperature anomalies.

Only recently have mid-ocean ridge systems have been well studied regarding their temporal and spatial evolution (Von Damm et al. 1997; Sudarikov and Roumiantsev 2000) and even fewer investigations have been conducted at volcanic arcs. Venting from volcanic arc systems differs greatly from that of mid-ocean ridges (MORs). For example, arc fluids are often 5 – 10 times enriched in chemical species compared to the average MOR system (Massoth et al. 2003). Volcanic arc venting also has a wider depth range than that of vents on MORs, increasing the volume of the world's oceans over which they influence. Due to this significant range in depth, high frequency of venting and the 2,500km length of the Kermadec (de Ronde et al. 2005), volcanic arc hydrothermal discharge is believed to be a major source of chemicals to the ocean (Massoth et al. 2003). Variability which affects chemical supplies to the ocean is of clear importance to ocean dynamics, and so warrants further study.

Major variations in the composition of hydrothermal fluids relative to the ambient seawater are believed to be caused by phase separation processes (Von Damm et al. 1997). During phase separation (condensation), hydrothermal fluids separate into a low density low salinity vapour, and high density brine droplets (Coumou et al. 2009). Salt content differences allow phase separation to occur at temperature-pressure conditions both above and below the phase separation point (3,000 m water depth and a temperature of ~400^{o}C, Figure 2). If the in situ pressure is lower than the critical pressure, boiling occurs generating highly gas rich vapours with very low salinities. However, pressures above the critical pressure results in low salinity vapours and brine production (Coumou *et al*. 2009). Because of the importance of phase separation and hydrothermal venting on ocean dynamics, this study examines temporal aspect of these features at three venting sites located on a single volcano.

The Kermadec Arc, located off the northeast coast of New Zealand's North Island (Figure 1), is formed by the subduction of the Pacific oceanic plate under the continental Australian plate (de Ronde et al. 2001; Massoth et al. 2007). Previous studies have highlighted the fact that hydrothermal venting varies spatially both along and across the Kermadec arc. This is due to differences in the subduction of sediments along the arc, and the influence of continental rocks and fluids which impact the magma supply and rock chemical composition (de Ronde et al. 2003; Gamble and Wright. 1995). Few studies have investigated temporal changes in the chemistry of hydrothermal fluids at a single volcano. Many of the vent systems on the Kermadec arc volcanoes are at a shallower depth than those of MORs. Therefore fluids of these systems are subjected to lower pressures than those at MORs, resulting in lower maximum fluid temperatures. A consequence of which is that phase separation and boiling are more common along the arc, with increased emission variability (Coumou et al. 2009). These processes are important because they enhance mineral deposition at the venting site.

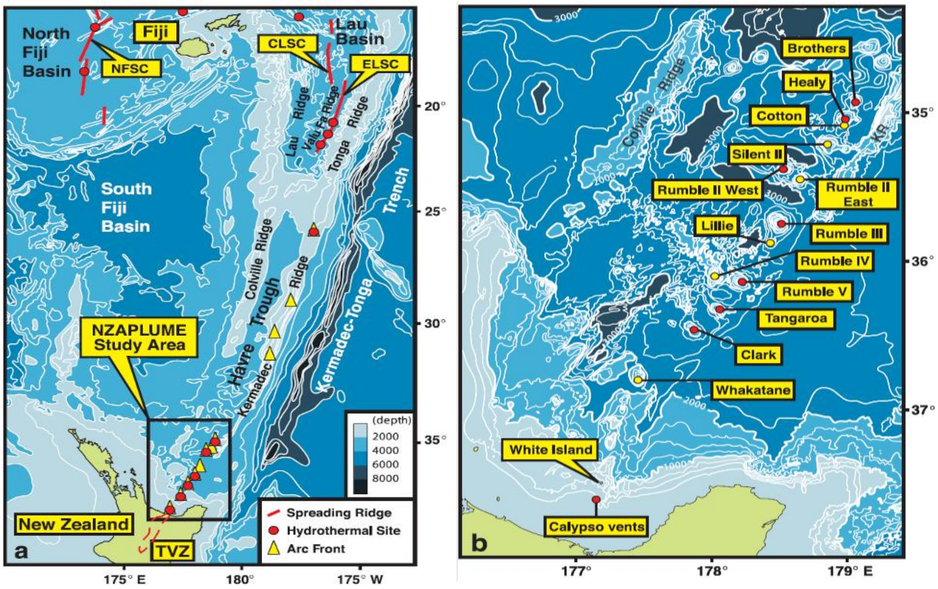


Figure 1: a) The location of the Kermadec-Tonga arc off the North Island of New Zealand. b) The location of Brothers volcano within the arc system (image from de Ronde et al. 2001).

Brothers Volcano, located at 34.86^{o}S, 179.06^{o}E, strikes northwest to southeast with a length and width of 13 and 8 km respectively. Volcanic rocks at Brothers are silicic (de Ronde et al. 2005), in contrast to the basaltic composition of MORs. The caldera floor is 1.85 km below sea level with a base diameter of 3 km and walls up to 530 m high (de Ronde 2005). Within the caldera there is also a diacite cone with a summit at 1.2 km deep, which is partially joined to the southern caldera wall. Previous studies have shown vent sites at the Northwest Caldera (NW Caldera) wall, Southeast Caldera wall and Cone (Figure 2), with plumes reaching heights of 750 m (de Ronde et al. 2005). This high density of hydrothermal vent sites, monitored since their discovery in September 1998, suggests that Brothers has the strongest and most extensive array of hydrothermal vents in the Kermadec Arc (de Ronde et al. 2005). Variability existing between the Cone, North West and South East caldera sites represents different elements of a hydrothermal system. The Cone site is dominated by diffuse venting, the northwest caldera site contains 2 m tall black smoker chimneys, while the southeast caldera site hosts extinct sulphide rich chimneys (de Ronde et al. 2005). These differences within the caldera, combined with the high venting intensity, makes Brothers volcano a site of particular scientific interest.

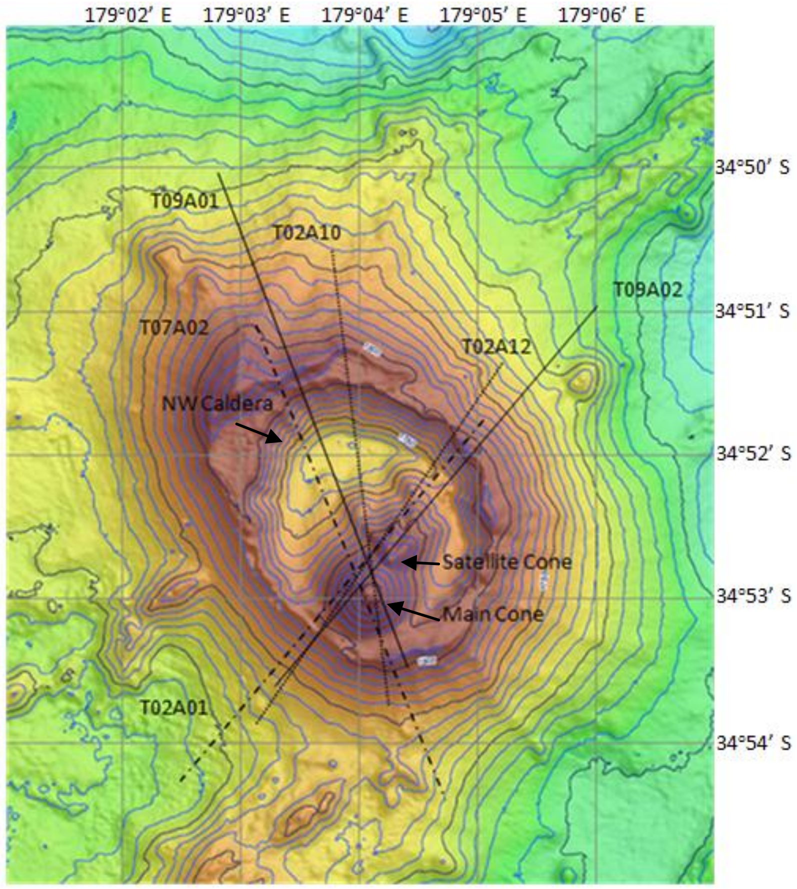


Figure 2: Active venting sites with tow-yo track lines for the 2002 (T02), 2007 (T07) and 2009 (T09) investigations over Brothers.

Projected end member concentrations of carbon dioxide (CO_2) and hydrogen sulphide (H_2S) gases in hydrothermal fluids released at Brothers require a magmatic vapour source. In addition, high iron concentrations of 4,720 nM in 1999 suggest the incorporation of an iron rich magmatic brine into the hydrothermal venting system (de Ronde et al. 2005; Massoth et al. 2003). Adding to the complexity of the Brothers hydrothermal system, significant temporal variability in fluid chemistry (Table 1) and in the location of predominant venting at the Cone has been revealed from previous time series studies (de Ronde et al. 2001, 2003).

Previous measurements conducted at Brothers reveal some of the highest hydrothermal iron concentrations measured for a submarine hydrothermal system, up to 27 times higher than typical mid-ocean ridge plume emissions (de Ronde et al. 2005). This indicates that rising plume fluids may act as a natural ocean iron fertilisation mechanism. Recent studies (Feely et al. 1990) have implicated the release of hydrothermal iron in scavenging of phosphate from the surface waters. The oxidation of vented Fe^{2+} creates iron oxyhydroxides which can potentially remove 10-30% of riverine phosphate additions. The removal efficiency of phosphate, a nutrient required for phytoplankton growth, via this scavenging has recently been shown to be less efficient with decreasing depths (Massoth et al. 2003). Discharges of hydrogen sulphide (H_2S) have been identified along the Kermadec arc, but could not be detected during the TELVE cruise along the Southern Tonga arc. Hydrogen sulphide discharge indicates a magmatic origin of the fluid (Massoth et al. 2003), and has shown to be variable along the length of the Kermadec – Tonga arc (de Ronde et al. 2001). Measurements taken from Brothers volcano in 1999 and 2002 also reveal that the concentrations of both Fe and H_2S vary over time at the Cone venting site. This variability in the composition of hydrothermal discharge must be characterised to fully appreciate volcanic arc effects on marine processes. This spatial and temporal variability in venting makes the Kermadec arc an interesting system for scientific investigation.

Table 1: Changes in the Cone vent site plume composition from 1999 -2002.

	1999	**2002**
Hydrothermal iron concentration.	4,720nM	175nM
Hydrothermal hydrogen sulphide concentration.	4,250nM	7,000nM
pH anomaly (CO_2 proxy).	-0.27	-0.22

The Cone vent site iron concentrations recorded in 1999 suggest the presence of a magmatic fluid component and the emission of a brine solution produced by phase separation (de Ronde et al. 2005). In contrast, vent fluid compositions in 2002 indicate reduced brine emissions, suggesting recovery of the hydrothermal system after volcanic activity (Figure 3) (Butterfield 1997; Von Damm et al. 1997). The site of predominate venting on the Cone had also changed between the investigations. In 1999, venting was predominately at the summit of the cone, with some side venting located along its flanks and from the northeast flank satellite cone. By 2002, the main venting had shifted to the northeast flank satellite cone as indicated by increased discharge creating a larger volume of high light-backscatter. Despite the changes at the satellite cone, there was still significant discharge from the cone summit (de Ronde et al. 2005).

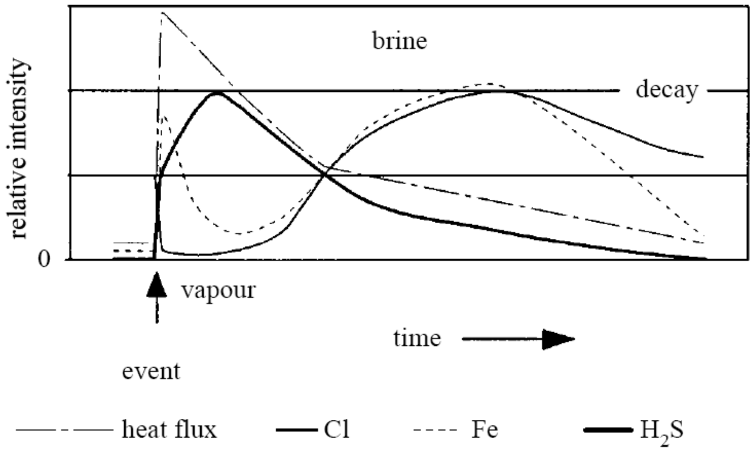


Figure 3: Changes in hydrothermal emissions following a volcanic event. (Butterfield et al. 1997)

This investigation on the nature of hydrothermal plumes at Brothers in 2009 was designed to build on that of de Ronde (2005), by increasing the temporal range of these studies. Remotely controlled vehicles were not available during the investigation, so measurements were made by towing a conductivity-temperature-depth-optical (CTD-O) unit through the plumes created by the discharge of hydrothermal fluids. Changes in venting are derived from light scattering and ORP readings in the hydrothermal plume waters taken along two tow-yo track lines similar to those used in previous temporal studies (Figure 2).

Methods

Light backscatter and oxidation-reduction potential readings

Plume data were collected using the *R/V Thompson* on March 6 and 7, 2009. Conductivity-temperature-depth and optical (CTD-O) tow-yo's were conducted with advisors from both the National Ocean and Atmospheric Administration (NOAA) and the Institute of Geological and Nuclear Sciences (GNS) along two transects of Brothers volcano (Figure 2) at a speed of 1.5 knots. Readings were taken by extra sensors attached to the CTD-O rosette for light backscatter (ΔNTU) and oxidation-reduction potential (ORP), with anomalies from background levels calculated to identify the location of hydrothermal plumes. Niskin bottles were tripped for H_2S sampling at depths with either a high ΔNTU or low ORP anomaly, indicating the presence of a hydrothermal plume. CTD-O data were logged using Seabird 5.39 software and gridded in Surfer using the inverse distance to a power algorithm. X-direction and y-direction grid spacing were set at 1 m and 10 m respectively. The resultant data were then plotted in MATLAB with bathymetry data overlain to provide better visualization of spatial-depth relationships of the data. The same analytical procedures were conducted for previous ΔNTU and ORP data from the 2002 (NZAPLUME II) and 2007

(ROVARK) cruises (acquired from Walker, S. pers.comm). Both ΔNTU and ORP readings are plotted on a log scale to provide optimal visualisation of hydrothermal plume variability.

Hydrogen sulphide analysis

Samples of plume water were collected for H_2S analysis to indicate the magmatic origin of vent fluid (Massoth et al. 2003). Samples were collected using the CTD-O Rosette's 21 Niskin bottles, at sites with either a low ORP or high ΔNTU reading. Sub sampling was conducted via plastic tubing into plastic bottles with a small invert in the lid to ensure that no air was collected with the water sample. Analysis was conducted immediately to reduce the risk of hydrogen sulphide oxidation. The initial analysis was modified from Cline (1969), with scaling to the 120 ml glass oxygen bottles used in this study. The reagent yielded too intense a blue colour for analysis in the available spectrophotometer. As an alternative, a HACH DR/850 data logging portable colorimeter with an advertised estimated detection limit of 0.01 – 0.70 mg/l S^{-2} was provided by Matt Leybourne (GNS). The programmed methylene blue method (method 8131) was used with the reagents provided with the HACH unit. Twenty five ml of each sample were reacted with 1 ml of each of the two reagents, and the reaction was allowed to proceed for 5 minutes before a reading was taken in the HACH unit.

Calibration of the HACH unit was conducted after completion of the cruise at the University of Washington, Seattle. Attempts to create standards according to Cline (1969) were unsuccessful, so calibration followed the data available in Fogo and Popowsky (1949). A solution of methylene blue was created by dissolving 4.33 mg methylene blue into 1 litre of water. This was then run in a spectrophotometer and HACH unit at several dilutions, with the equivalent concentration of sulphide calculated using the calibration curve in Fogo and Popowsky (1949) (Figure 3). The calibration resulted in a calculated HACH minimum detection limit of 0.20mg/l. Because of this, all the data collected on hydrogen sulphide on the cruise is below the calculated HACH detection limit, and cannot be used further in this investigation.

Temperature and salinity profiles

Potential changes in the background water masses were evaluated by plotting the collected data in a temperature and salinity diagram. This also allowed the conduction of inter-annual calibration of the CTD-O data by comparing the salinity values of the deep water which is known to be fairly constant with time. The data from 2002 and 2007 appeared to show little change in salinity, with 2009 data offset by 0.04. This offset was then included in future plots of salinity data. Temperature and salinity anomaly plots were also created to emphasise the differences between the background waters in the 2009 surveys.

Results

Light backscatter variability

Track line T02A10 (Figure 4) follows a predominately N-S direction, and contains the highest backscatter reading (1.76 nephels) recorded throughout the time series investigation. Three maxima plumes of ΔNTU are clearly displayed in the extrapolated data for track T02A10 (Figure 3), indicating discharge from the Cone, Satellite Cone and NW Caldera vent sites. Tow-yo line T07A02 has a similar location to that of T02A10 and a similar plume distribution. The satellite cone plume is also shown to be much smaller in both horizontal and vertical extent. In 2002 the highest ΔNTU satellite cone plume signal extended around 2,000 m north and had a vertical width of around 150 metres. By 2007, this horizontal extent had been reduced to only 665 m with a vertical extent of only 10 m – the smallest resolution of the extrapolation. Venting at the NW caldera site also appears to have decreased. In 2002, the caldera was filled with high backscatter water, with readings ~0.1 nephels. The tows of 2007 reveal that turbidity in the Caldera has decreased by around 0.08 nephels. Despite the reduction in the deeper caldera plume values, plumes from the venting sites of the NW caldera appear to have maintained high particulate concentrations, in a similar distribution to that of 2002.

Tow-yo backscatter data from 2009 reveal another change in the distribution of hydrothermal plumes. Track T09A01 (Figure 4) follows a similar course to that of T07A02, and reveals that the intensity of the Cone plume is reduced in both areal distribution and intensity. From 2007 to 2009, the dominant Cone ΔNTU reading dropped to around 0.032 nephels, with a 550 m horizontal extension of ΔNTU values over 0.1 nephels, compared to the 2,550 m extent in 2007. Plume emissions in 2009 at the satellite cone site are slightly stronger than in 2007, and there is a significantly noticeable increase in the extent of the Caldera plume as indicated by ΔNTU readings of over 0.1 nephels across the caldera. Despite an increase in the southward penetration of the plume by 500 m, there appears to be no further penetration of the NW Caldera plume down into the caldera. There is also a continuation of two bands of higher ΔNTU values in the NW Caldera plume at 1.5 and 1.55 km deep.

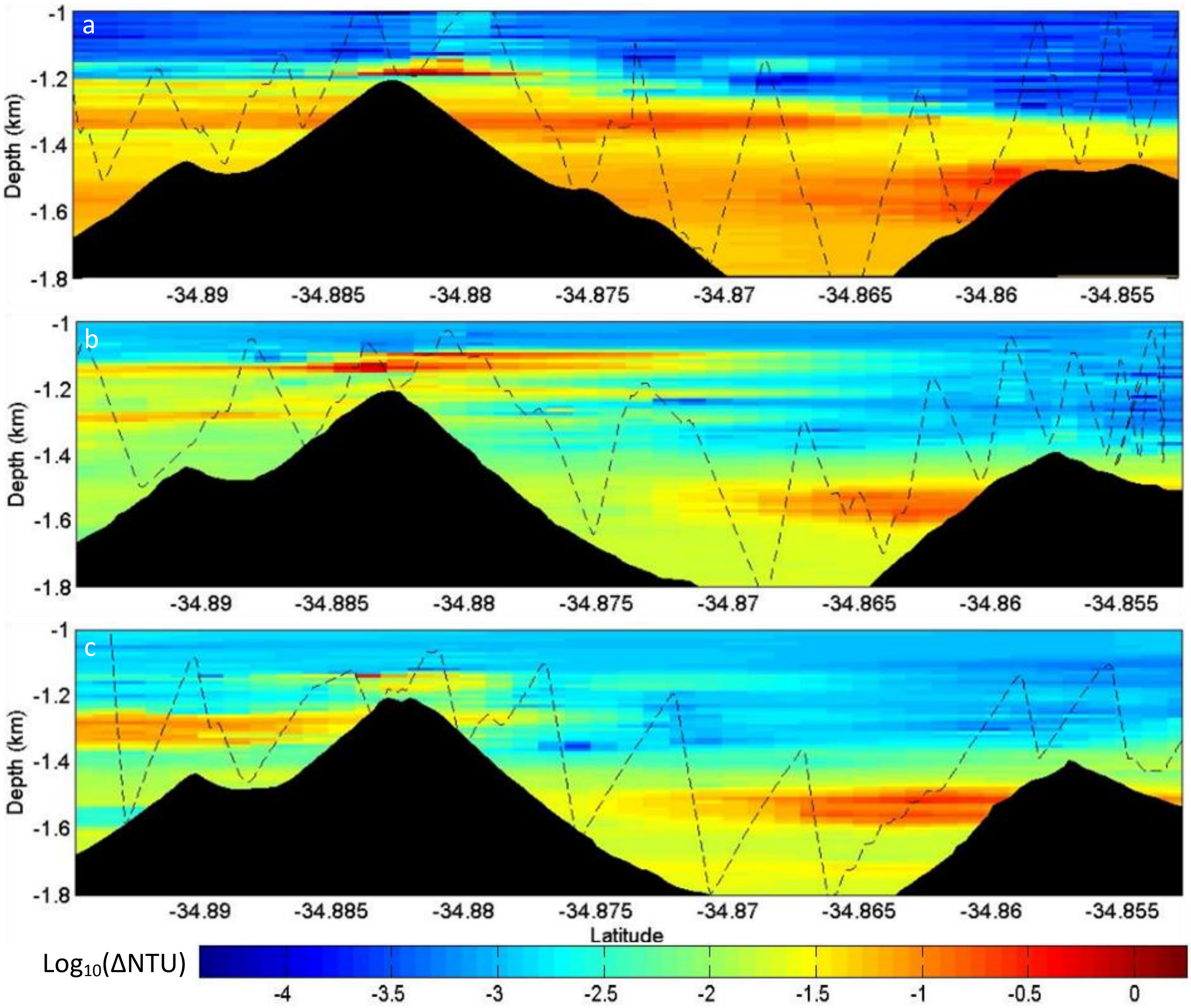


Figure 4: Light scattering data (ΔNTU) for NW-SE oriented tows conducted over Brothers. Note values are in a log scale. a) 2002 tow-yo T02A10. b) 2007 tow-yo T07A02. c) 2009 tow-yo T09A01.

Track T02A12 follows a more NE – SW direction than T02A10, with the cone venting site more apparent in the bathymetry data (Figure 5). The plumes measured in this direction appear to be weaker with respect to ΔNTU values, and the distinct plume rising from the satellite cone is no longer apparent. The rise height of the plume to the south of the volcano is also around 100 m deeper than observed in T02A10. The 2007 track line T07A01, (Figure 5) follows a similar path as T02A12. In a similar manner to T02A12, the readings of ΔNTU are low, with plume signatures only reaching around 0.016 nephels. A generally similar distribution of plume signature to that of 2002 results from the extrapolation, with increased horizontal extent of the cone plume so that it covers most of the volcano summit.

This tow also provides evidence for an increase in rise height of the cone plume by about 50 metres.

Tow-yo T09A02 (Figure 5) follows a similar route to that of T07A01 and T02A12, and continues the trend of a weaker ΔNTU signal than T09A01. The strength of the signal flowing south of the volcano has increased again to similar values as is in 2002. There is also a general increase in the ΔNTU readings of the background waters to 0.01 nephels. ΔNTU readings of around 0.04 nephels appear to follow the slopes of the cone and satellite cone down into the caldera, which may disguise any weak venting signal produced by the satellite cone.

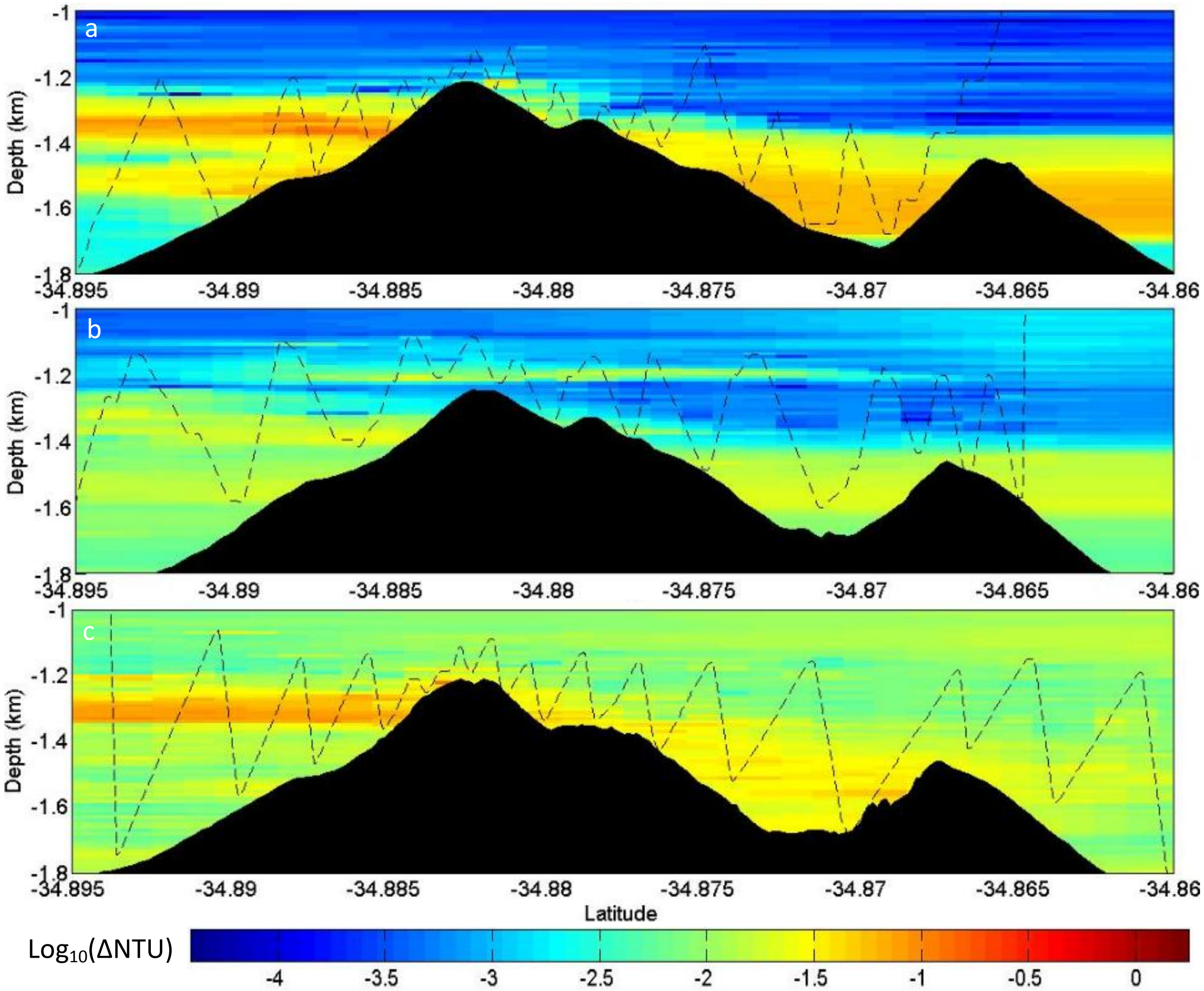


Figure 5: Light scatterance data (ΔNTU) for NE-SW oriented tows conducted over Brothers. Note values are in a log scale. a) 2002 tow-yo T02A12. b) 2007 tow-yo T07A01. c) 2009 tow-yo T09A02.

Oxidation-reduction potential variability

Previous ORP data were only available from 2007 (Figure 6), and shows strong negative anomalies indicating the presence of hydrothermal plumes. Significant sensor variability was noted between background waters in the 2007 and 2009 tows due to the sensors lack of steady background value (Walker, S. pers. comm.). This error source was removed by calculating the anomaly of ORP in a similar manner to that of ΔNTU. Consistent with the backscatter results, there is no evidence of a negative ORP anomaly in the NE-SW T07A01 tow-yo. There is also less variability in the ORP readings than in that of backscatter. The second track line, T07A02 reveals a much stronger ORP signal, with a higher vertical spread than the associated backscatter readings. The strongest negative anomaly measured is 1.25 mv, and is also shaped more like a typical plume, showing an initial rise of the fluid, followed by levelling off at the density equilibrium (Speer and Rona 1989). A weaker signal of around 1.15 mv is also located at the NW Caldera, but 100 m below the peak in the ΔNTU readings.

A much higher negative ORP anomaly appears in the 2009 tow-yo's conducted over Brothers volcano (Figure 6). The maximum recorded anomaly is 93 mv, and appears to be emitted from the Satellite Cone vent site. Once again the rise height of the ORP anomaly is higher than that of the ΔNTU, but the horizontal extent cannot be accurately determined due to the lack of sampling conducted at that depth. The NW Caldera plume ORP signal is weaker than in 2007, and also at a shallower depth (1,500 m deep) coinciding with the ΔNTU maxima.

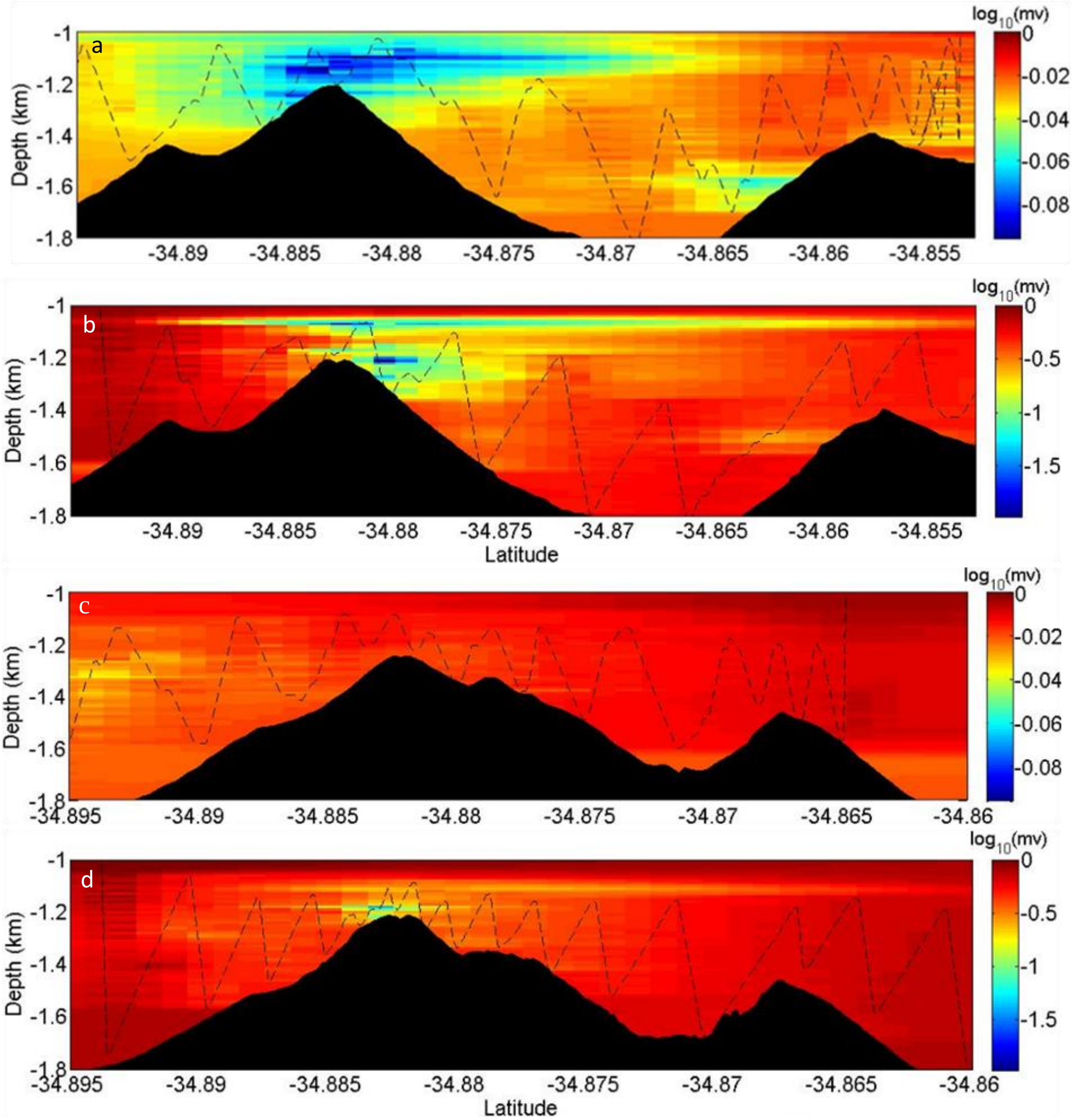
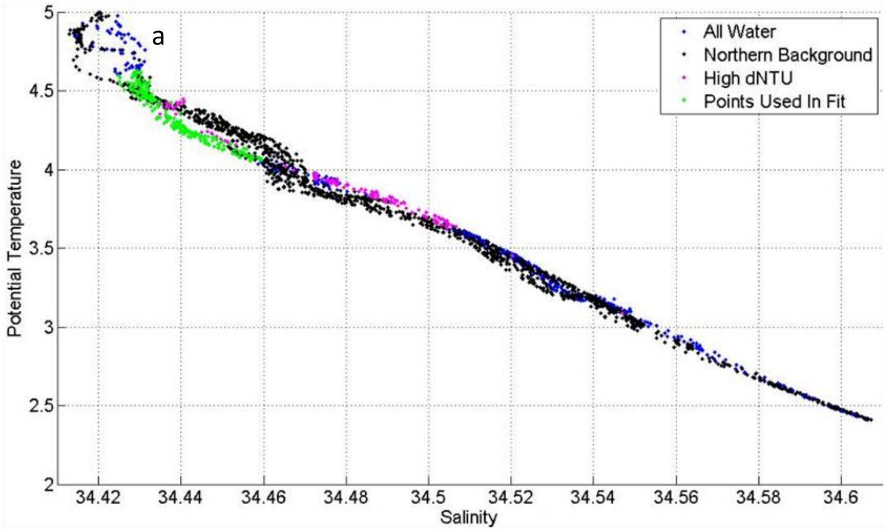


Figure 6: Oxidation-reduction potential (ORP) readings taken over Brothers volcano. a) 2007 tow-yo T07A02. b) 2009 tow-yo T09A01. c) 2007 tow-yo T07A01. d) 2009 tow-yo T09A02.

Temperature and Salinity Anomalies

The relationship between potential temperature and salinity for the 2009 tows show that there appears to be two different water masses present in the study area. Evidence for this is shown in Figure 7, which reveals space in the distribution of points in the plot between salinities of 34.43 and 34.46. Separation of the water masses at a latitude of 34.882^{o}S resulted in a cooler southern water mass and a warmer northern water mass.

Temperature and salinity anomaly plots were created (Figure 7) to emphasise this change. Background waters were selected using points from the southern water mass with low ΔNTU readings and a density range that resulted in a straight line. A second order polynomial of potential temperature and a function of potential density (referenced to 1500 dbars) was fitted to the data points, allowing an expected temperature to be calculated, and the temperature anomaly evaluated. These plots revealed that around the plumes, the northern background water had higher temperature and salinity anomalies than the high ΔNTU and southern background water. Above and below the plume depth, the northern background water returned to its cooler, fresher state (Figure 6). There was no evidence for two water masses in the 2002 or 2007 data sets (not shown).



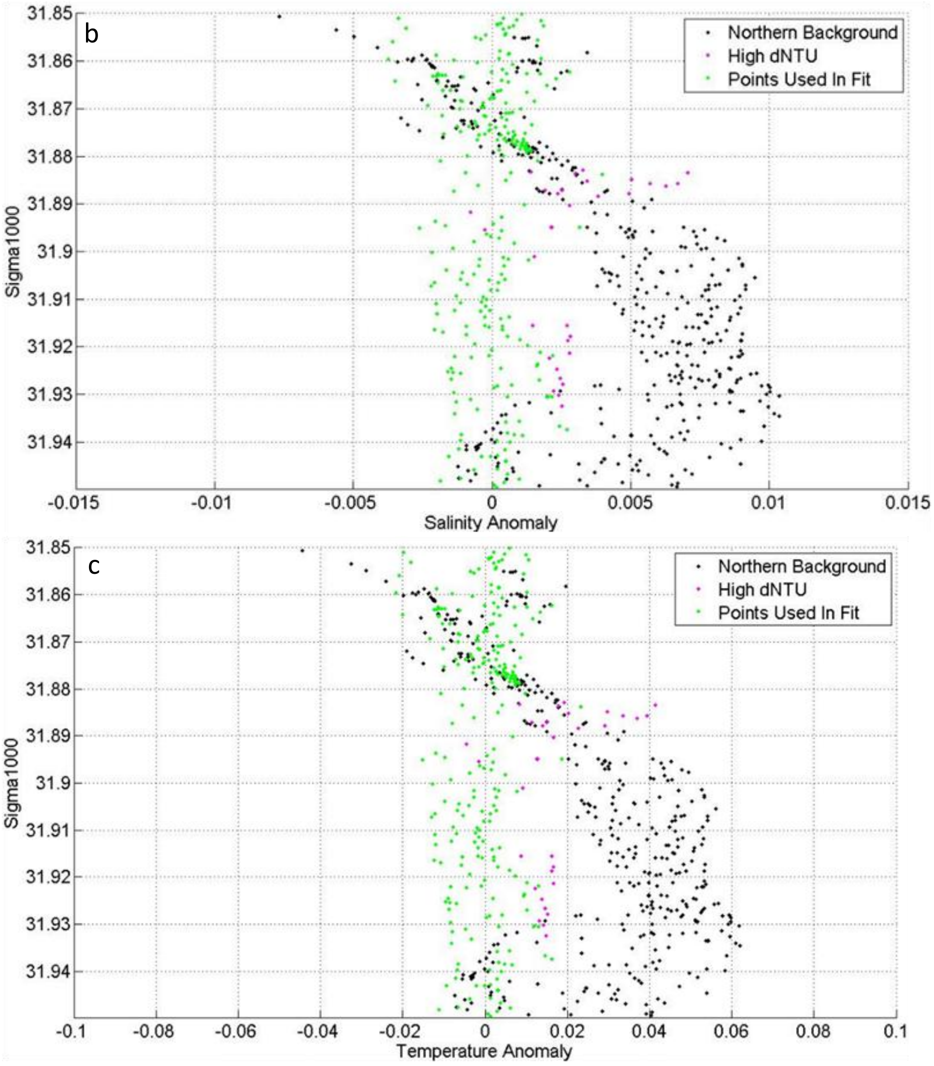


Figure 7: a) Identification of the two water masses as evidenced by the T09A02 tow-yo. b) salinity anomaly from the T09A02 tow-yo. c) temperature anomaly from the T09A02 tow-yo. Note that the fit of background water is local to plumes at a depth of 1,200 m, and does not represent the whole water column.

Discussion:

Data collected from the 2002, 2007 and 2009 cruises at Brothers volcano were complied in order to evaluate temporal changes in hydrothermal venting. Across the seven year time-span of plume studies at Brothers, results from tow-yo investigations consistently indicate a weaker hydrothermal plume signal in the NE-SW direction. This indicates that the plumes are predominately being advected in a general westwards direction (Figure 2), giving rise to the higher ΔNTU and ORP values in the NW-SE tows. This is supported by the surface current data gathered by the acoustic Doppler current profiler (ADCP) and is consistent with the results of Lavelle et al. (2008). It should also be noted that the northern extent of the main cone plume of T07A02 has been extrapolated by Surfer with no boundary limitations by the presence of actual tow-yo data. Because the plume extent is similar to that documented by tow T07A01, it is believed that the data is accurate. However, the apparent reduction of vertical extent in 2009 may just be due to the availability of actual data to restrict the extrapolation.

Changes in the plume rise height can result from changes in the plume water composition, density, and current variability (Middleton 1986). Slower current velocities allow a buoyant plume to reach equilibrium density, and the maximum rise height possible whereas stronger currents result in reduced plume rise height (Middleton 1986). Despite deployment of the towed camera device throughout the cruise, no vent site locations were discovered at Brothers volcano. Because the dimensions of vents could not be defined, it is not possible to model the plume rise height based on currents and density using the Environmental Protection Agency's 'Visual Plume' software. However, major changes in the plume chemical composition can be inferred using the collected ΔNTU and ORP data.

Previous temporal investigations at a hydrothermal black smoker in the East Pacific Rise by Von Damm et al (1997) revealed the evolution of emissions of a single vent from vapour to brine. They hypothesised that after a volcanic eruption, vapours are initially released, while liquid phase brine is locked away in the oceanic crust and vented at a later time. The depth of the Brothers vent sites (1200 m at the cone, 1600 m at the caldera) most likely places the hydrothermal system at low pressures, which would promote phase separation of the fluids from the base of the hydrothermal cell to the seafloor (Coumou *et al*. 2009). Variability of hydrothermal venting is known to highest at low pressure systems due to the increased area in which phase separation can occur (Coumou *et al*. 2009).

Temperatures of Brothers vent fluids calculated using sulphur isotopes indicate emission at temperatures of ~290^{o}C (de Ronde et al. 2005). This is too low for phase separation to occur at the base of the hydrothermal cell (Figure 8). High concentrations of iron (Table 1) and helium in vent fluids, especially located at the Cone, combined with strong negative pH anomalies suggest a magmatic component of the vent fluids released at Brothers (de Ronde et al. 2005). A similar evolution to that described in Von Damm et al. (1997) may therefore have occurred at Brothers except with a pulse of magmatic activity causing changes in the magmatic fluid components of vent fluids over the 2002-2009 time-series (Figure 9). This hypothesis is consistent with the conclusions of de Ronde et al. (2005). .

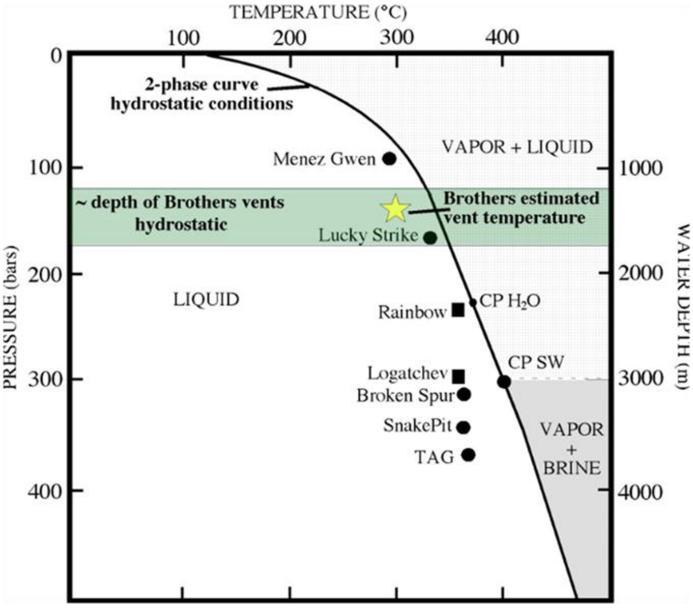


Figure 8: The location of Brothers on a phase separation curve. CP = Critical Point (Kelley, D. pers. comm.)

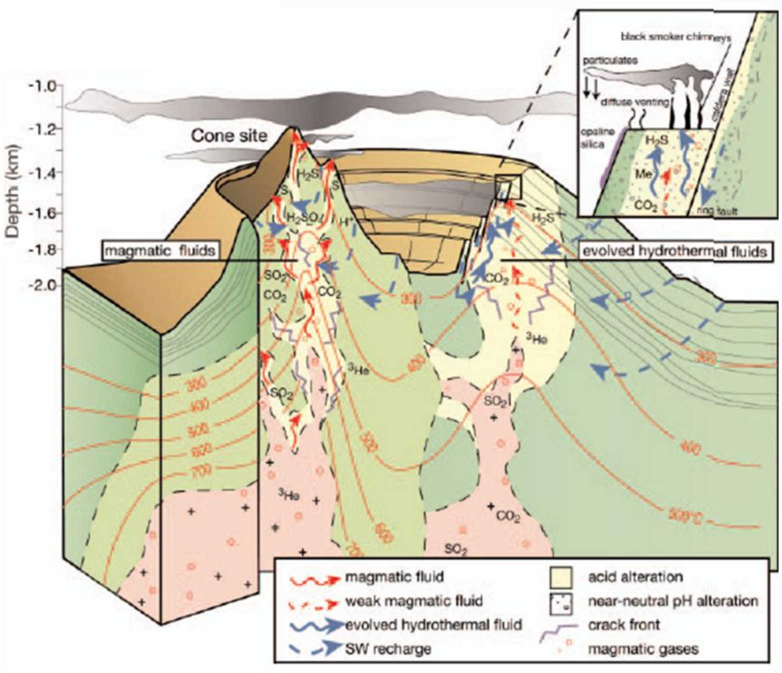


Figure 9: The influx of magmatic fluids into the hydrothermal system. (image from de Ronde et al. 2005)

A comparison of salinity data collected from a maximum of 50 m above bottom indicates the temporal and spatial variability in hydrothermal plume salinity from 2002 to 2009 (Figure 10). Cone and Caldera vent sites were separated using latitude ranges of -34.885^{o}S to -34.88^{o}S for Cone venting, and -34.87^{o}S to -34.865^{o}S for the Caldera. This prevents salinity changes being affected by the different vent types found within Brothers. Between 2002 and 2007, salinity at the cone decreased by 0.054 with a corresponding 0.03 decrease at the Caldera. This decrease matches the reduction of ΔNTU at both venting sites in 2007. Changes in the salinity and ΔNTU all suggest that there was an increase in the venting of low salinity vapour, known to be discharged after a volcanic event (Butterfield et al. 1997; Von Damm et al. 1997). The 2009 tow-yo's reveal that salinity has increased by 0.08 at the Cone and 0.07 at the Caldera, with associated increases in ΔNTU. This data is consistent with a change in venting from low salinity vapour back to brine emissions. This trend is expected to lead to a reduction of hydrogen sulphide evolved as vapours are no longer being dominantly discharged (Figure 3). The ORP data collected in 2007 and 2009 does not, however, match this trend. Emissions of low salinity vapours are believed to result in a stronger ORP reading due to the increased presence of H_2S (Sudarikov and Roumaintsev 2000). The collected data shows that the highest ORP anomaly was measured in 2009, at a time when salinity readings suggest that the emissions are becoming more brine dominated. This deviation from the salinity and ΔNTU trends may be due to several issues with measuring ORP. Firstly, the system is not in equilibrium, and the sensor is moving in the water column so a single value is rarely reached. Secondly there is a lag time involved with the sensor. Changes in ORP are quickly identified, but the sensor has a memory effect which causes low ORP measurements to be recorded out of the hydrothermal plume. Finally, hydrothermal plumes are not fixed features and therefore measurements taken may not be representative of the maximum plume values (Walker, S. pers. comm.). This will be especially true for the ORP data, which is the most localized signal due to the rapid oxidation of H_2S (Sudarikov and Roumiantsev 2000).

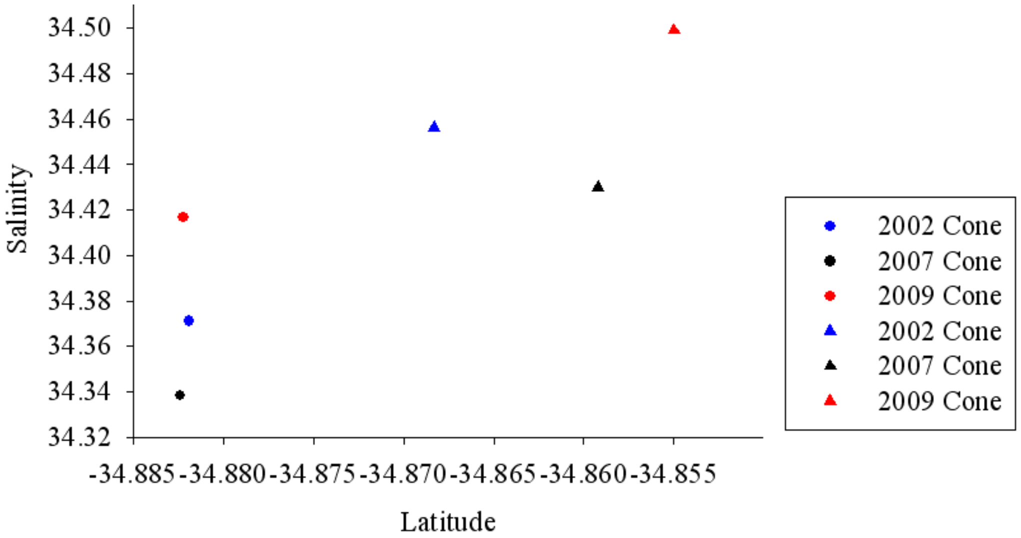


Figure 10: Changes in the salinities of plume waters from 2002 to 2009. The largest salinity error is 0.0023, and is too small to be shown on the plot.

In the base of the Brothers caldera, there is a remarkable decrease in turbidity from 2002 levels through 2009. This change is unlikely to be an artifact of different track lines, as they are spatially very similar. Because of the consistency of ΔNTU maxima depth between 2007 and 2009, it is also unlikely that the direct affects of tidal flushing in the caldera plume caused this difference. Instead, a reduction in the intensity of highly saline hydrothermal fluids released is more likely to have caused the observed changes. The NW caldera trends indicate that high salinity brines were released in 2002 with a switch to low salinity, low particulate vapours in 2007. Tidal flushing would have cleared the caldera, and then the release of vapours containing low ion concentrations would not be able to replace the particles lost, decreasing light-scattering.

Comparisons of the ΔNTU and ORP plots for T07A01 suggest the ORP signal is a much more localised indicator of hydrothermal activity than backscatter. The fact that the ΔNTU and ORP signals appear to correlate well in the T07A02 track plot suggests that the track line was probably further into the main plume, with stronger hydrothermal signals. Another key feature of the T07A02 plot is that the maximum ΔNTU signal is about 50 metres above the maximum ORP signal. Sudarikov and Roumiantsev (2000) noted a similar structure in the hydrothermal plumes at the Logatchev vent field on the Mid Atlantic Ridge. They attributed this to particulate iron sulphide falling out of the plume shortly after emission, while the remaining iron rapidly precipitates as iron oxides and hydroxides. This results in a dominance of iron sulphides (creating low ORP) at the plume base, and iron oxides (creating high levels of ORP) at top of the plume (Sudarikov and Roumiantsev 2000). The depth of the NW caldera ORP maximum has decreased over the two years by approximately 50 metres (Figure 6). Because the rise height of the ΔNTU maxima appears to have remained constant over with time, this ORP change is believed to be due to changes in the chemistry of the plume waters being emitted - specifically a reduction in the release of iron sulphide.

Plots of potential temperature measured during the 2009 cruise against salinity (Figure 7) resulted in the identification of two water masses along the tow track line. Lavelle et al. (2008) also identified two distinct water masses around Brothers during their deployment of current meters. They identified the northern water mass as a cold core eddy which was temporarily overlying Brothers. Observations of satellite dynamic topography of the area (Figure 11) confirm the presence of a cold core eddy situated over Brothers during the tow-yo's. ADCP current data also indicates a south westerly flow during both 2009 tow-yo's (Figure 11), consistent with a cyclonic upwelling eddy. There was no evidence of two water masses present during the cruises of 2002 and 2007, from both satellite and in situ data (not shown). In the calculations for temperature and salinity anomaly, the boundary of the northern water mass was estimated to be at 34.882^{o}S, thus this water mass affects the Satellite Cone and NW Caldera venting sites. The presence of this different water type may have some implications with the higher backscatter and ORP background readings of these tow-yo's compared to those of 2002 and 2007. However, due to the strong difference in ΔNTU readings for the ambient background water between the 2009 tow-yo's, it is believed that the sensor was fouled on the track T09A02. ORP changes are believed to be due to inter-annual sensor drift.

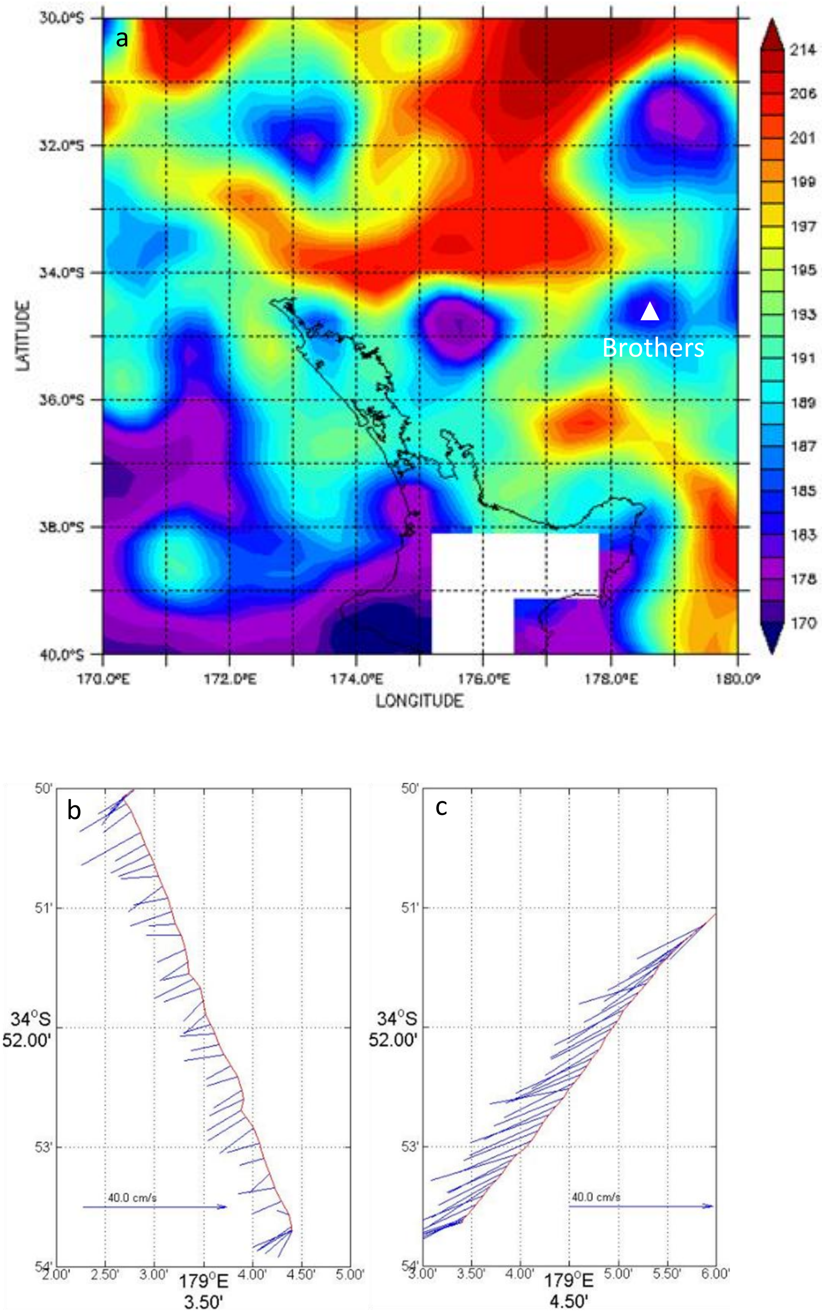


Figure 11: a) Satellite dynamic height (image from http://las.aviso.oceanobs.com). b) T09A01 and c) T09A02 current data averaged over 374 – 394 metres every five minutes.

Temperature and salinity anomaly plots (Figure 7), indicate that the southern water mass is warmer and saltier on the isopycnals than the plume waters. This believed to be Antarctic Intermediate Water (AAIW) which has been subject to more mixing with Pacific waters, sourced from the cold core eddy. The potential temperature and salinity plots (Figure

7) also indicate that there are fresher and cooler waters present, which may be a second mass of (AAIW) which has retained more of it's original properties. This water may be sourced from an area of stronger AAIW influence. Antarctic Intermediate Waters south of Chatham Rise are known to be fresher than around Brothers (Piola and Georgi. 1982), but the general circulation patterns suggest that this water mass cannot be the source of the northern background water. Alternatively the northern background water may be an indication of a short-circuiting of the AAIW circulation between South America and New Zealand (Tomczak and Godfrey 1994).

Conclusion

A time series of measurements of hydrothermal venting from Brothers volcano were taken in 2002, 2007 and 2009 and extrapolated in Surfer to create contour plots of both backscatter (ΔNTU) and oxidation-reduction potential (ORP). Due to the lack of visual identification of venting sites with the towed camera device and the deep depth at which the volcano summit is situated, modelling to predict the effects of current variability could not be conducted. However, changes in the chemical composition leading to changes in the plume distribution could be estimated.

The plume distribution is constantly indicated to be in a south westerly direction, consistent with the surface current data collected by the ADCP during 2009 and geostrophic flows calculated by Lavelle et al. (2008). Reduced salinity over both the Cone and NW Caldera vent sites was observed between the 2002 and 2007 tow-yo investigations, suggesting a pulse of magmatic activity shifting venting from brines to low salinity vapours (Butterfield 1997; Von Damm et al. 1997). This hypothesis is supported by lower ΔNTU values in 2007 suggesting a vapour discharge. It is expected that hydrogen sulphide concentrations would also be at their highest during this time (Von Damm et al. 1997).

Salinities then increased in 2009, with a corresponding increase in ΔNTU as brines with high particulate concentrations are released. ORP data does not support this hypothesis but can be explained by the sensor variability and short range of the ORP signal from the main plume. Iron concentrations are believed to be decreasing from 2007 to 2009, as shown by a decrease in the depth maxima of ORP.

2009 revealed the presence of two background water types, with a cold core eddy recorded by satellite dynamic height during the time of sampling. This resulted in the anomalous warmer and fresher water mass along the isopycnals of the high backscatter plume waters. There are also cooler and fresher waters present which may be due to interleaving of Antarctic intermediate waters. In future studies of temporal venting changes, the properties of ambient water masses present also need to be monitored. The presence of eddies can result in variations in currents with time, affecting plume locations and increasing the complexity of calculating the plume temperature anomaly

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