Diffuse Degassing and the Hydrothermal System at Masaya volcano, Nicaragua

by

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DEDICATION

To my parents, John and Su,

and my sisters, Alexa and Cassie.

In memory of my grandfather, Wilfred, who would have loved to see this.
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Diffuse Degassing and the Hydrothermal System at Masaya volcano, Nicaragua

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ABSTRACT

Hydrothermal systems change in response to volcanic activity, and in turn may be sensitive indicators of volcanic activity. Fumaroles are a surface manifestation of this interaction. We use time series of soil temperature data and numerical models of the hydrothermal system to investigate volcanic, hydrologic and geologic controls on this diffuse degassing.

Soil temperatures were measured in a low-temperature fumarole field located 3.5 km from the summit of Masaya volcano, Nicaragua. They respond rapidly, on a time scale of minutes, to changes in volcanic activity also manifested at the summit vent. The soil temperature response is repetitive and complex, and is characterized by a broad frequency signal allowing it to be distinguished from meteorologic trends.

Geophysical data reveal subsurface faults that affect the transport of fumarole gases. Numerical modeling shows that these relatively impermeable faults enhance flow through the footwall. On a larger scale, modeling suggests that uniform injection of fluid at depth causes groundwater convection in a permeable 3-4 km radial fracture zone transecting the entire flank of the volcano. This focuses heat and fluid flux and can explain the three distinct fumarole zones located along the fracture.
We hypothesize that the rapid response of fumarole temperature to volcanic activity is due to increased flow of gas through the vadose zone, possibly caused by changes in the subsurface pressure distribution. Numerical models show that an abrupt injection of hot gas, at approximately 100 times background rates, can cause the rapid increase in temperature observed at the fumaroles during volcanic activity. A decrease in hot fluid injection rate can explain the gradual decrease in temperature afterwards. Mixing with surrounding vadose-zone fluids can result in the consistent and abrupt decreases in temperature to background level following hot gas injection.

Fumaroles result from complex interaction of the volcanic-hydrologic-geologic systems, and can therefore provide insight into these systems. Increases in fumarole temperature correspond to increased gas flux related to changes in volcanic activity, suggesting that monitoring of distal fumaroles has potential as a volcano monitoring tool, and that fumarole temperatures can provide insight into the response of shallow gas systems to volcanic activity.
CHAPTER 1

INTRODUCTION

A comprehensive understanding of volcanic systems is critical for reliable forecasting of eruptive activity, a major goal of volcanology (Sparks, 2003). Development of this understanding depends in part on understanding the relationship between groundwater and magma at active volcanoes in terms of heat and mass transfer. This understanding is needed because groundwater interaction on short timescales can increase the explosivity of eruptions (e.g., Mastin, 1991). On longer timescales, hydrothermal systems may cause significant alteration of volcanic edifices, leading to weakening and collapse (e.g., Reid, M. E., 2004; Scott et al., 2005). Conversely, changes in the groundwater system may, in some circumstances, result from changes in volcanic activity (Tanguy, 1994; Newhall et al., 2001; Shibata and Akita, 2001).

At many volcanoes, groundwater-magma interaction is manifested at the surface by low-temperature fumaroles and diffuse degassing, which occur where magmatic gases and water vapor reach the surface by porous flow over a relatively broad area. The spatial and temporal variations of low-temperature fumaroles and diffuse degassing on volcanoes reflect the interaction between magmatic, hydrothermal, and meteorological systems. These interactions, however, are complex. Through a series of works I address the physical controls on diffuse degassing on the flanks of Masaya volcano, an active volcano located in Nicaragua. I explore the timescales of variation in flank fumarole
temperature, and model these variations with the aid of geophysical measurements and spatially and temporally varying simulations of the hydrothermal system. Cumulatively, these studies provide insight into the causes of temperature variations in the flank fumaroles, and processes that give rise to diffuse degassing at Masaya. Most importantly, these models seek to explain how fumaroles located some distance from the summit crater at Masaya can respond rapidly, apparently on a time scale of minutes, to changes in the magmatic system.

An extensive literature describes previous studies of fumaroles at active volcanoes, and what they have suggested about the primary controls on diffuse degassing (see Section 1.1). To be able to interpret fumarole temperature variations in light of volcanic activity the hydrologic system must be constrained, which a number of studies have attempted to do at Masaya volcano (see Section 1.2). The volcanic activity must also be well described (see Section 1.3). Numerical modeling of the hydrothermal system can then be attempted using the multicomponent, multiphase fluid flow simulation program TOUGH2 (Transport of unsaturated groundwater and heat), a code based on the physics of fluid flow as described in Section 1.3.

The relationship between measured fumarole temperatures and atmospheric and volcanic effects is explored at Masaya volcano in Chapter 2. I find a correlation between fumarole temperatures and volcanic activity in the crater 3.5 km away, primarily identified from analysis in the frequency domain. However, rainfall also appears to have a significant effect. I propose that fumarole temperatures increase due to elevated levels of gas flux from a pressure wave originating in the volcanic system. The rainfall may increase pore pressure to also enhance this effect.
A good conceptual model of the hydro-volcanic system is vital to interpret fumarole temperature measurements. I use geophysical constraints to create a hydrothermal model of the subsurface, including local and regional geology (see Chapter 3). These models show that fumaroles can result from steady convection of groundwater within the saturated zone, and that relatively impermeable faults can redirect gas and heat flow locally.

During volcanic activity the fumarole temperature signals gain distinct characteristics, which can be partially explained with numerical models. Geophysical constraints combined with information from a previous groundwater model allow a temporally-varying model of the local hydrothermal system to be created (see Chapter 4). Model results show that the fumarole temperatures can be described by variations in gas flux, but could not be explained by any other single known mechanism. This highlights the usefulness of fumarole temperatures as a potential volcano monitoring tool and as a proxy for total gas flux in some circumstances.

All three of the later chapters are written to stand alone; Chapter 2 was published in *Geology* in December 2008, Chapter 3 is under review with *Geophysics, Geochemistry, and Geosystems* and Chapter 4 will be submitted in the near future. The term 'we' is used to refer to the collaborative nature of this project, particularly in terms of the geophysical analysis of data in Chapter 3.

1.1 Previous fumarole studies

Diffuse degassing has been studied for decades as a potential method for monitoring volcanoes. Fumarole temperatures, in particular, have the advantage of being
relatively inexpensive to measure, and cost only a few thousand dollars to monitor continuously. Not all active volcanoes have fumaroles (Varley and Armienta, 2001), but most do. Often, fumaroles are located in the crater of a volcano, making them dangerous to monitor. In some cases volcanoes also have fumaroles distal to the active crater (Baubron et al., 1991). These allow easier and safer access, particularly during elevated volcanic activity when deducing the state of a volcano is vital for minimizing damage to people and property. However, the interpretation of the signals from these flank fumaroles is often problematic because their temperature and gas flow reflect a combination of both hydrologic and magmatic systems, and are strongly affected by variability in the hydraulic properties of the rocks through which they pass. Previous studies help to understand controls on fumarole temperatures, thereby improving understanding of the mechanics of diffuse degassing and interpretation of its variations.

A relatively early study of fumarole temperatures in the literature was done by Barquero (1988). He took regular measurements of fumarole temperatures at Volcan Poas, Costa Rica from 1980 to 1987. He detected increases in temperature prior to phreatic eruptions in both 1981 and 1987, although there were other small phreatic eruptions that occurred during a long-term cooling trend. Another early study by Stoiber et al. (1975) detected a long-term cooling in fumarole temperatures during waning activity following eruptions of Izalco Volcano, El Salvador. Neumann van Pedang (1963) looked at crater temperatures at a range of volcanoes in Indonesia but could not find any strong precursory signals related to volcanic activity.

Sudo and Hurst (1998) found variations in temperature associated with volcanic activity at Aso volcano, Japan, during a study lasting 9 years. They measured soil
temperatures in two drill holes 200 m from the active crater, down to 150 and 70 m respectively. These measurements were not in a fumarole area, and temperatures varied from 6°C at the surface to 30°C at depth. The large depths and high time-resolution (every 10 minutes) allowed detection of atmospheric effects on temperature that had an increasing lag with greater depth, until other signals were detectable at 100 m and the atmospheric effects were minimal at 150 m. At that depth they observed the maximum temperature in November-December 1989, just after the most vigorous volcanic activity from September to November 1989.

A study by Yamashina and Matsushima (1999) at Mt Unzen found similar results to those of Sudo and Hurst (1998). There, they measured ground temperature in a horizontal cave outside of the fumarole areas. They measured temperatures every 5-10 minutes between 1991 and 1997. No diurnal fluctuations in temperature were observed in the cave, although there were seasonal changes. A lava extrusion reached its peak in June-December 1991, and ground temperatures peaked in 1992, several months later.

Connor et al. (1993a; 1993b) continuously monitored high-temperature (300-550°C) fumaroles at Colima volcano, Mexico. They did two studies, firstly measuring fumarole temperatures at four locations at the summit of the volcano intermittently through 1990 (1993a). They observed formation of new fumaroles and daily temperature fluctuations of between 30°C and 60°C associated with barometric effects, but otherwise the fumarole temperatures remained consistently elevated. Modeling showed that the variation in wall rock temperature due to the fumaroles could explain demagnetization patterns observed in the area. A negative magnetic anomaly at the same location as the fumaroles became the site of a new lava dome in 1991, which Connor et al. (1993a)
suggested was due to a preexisting fracture at depth which had previously been the site of steady-state degassing and so formed an easier pathway for magma to rise.

Another study by Connor et al. (1993b) monitored high-temperature fumaroles in five locations near the summit of Colima volcano between May 1991 and May 1992. The lack of obvious changes in volcanic activity allowed them to do an in-depth study of the correlation between fumarole temperature and atmospheric variables, showing that rainfall only had an impact if it directly hit a thermocouple. Atmospheric pressure, however, had a strong correlation with fumarole temperature variations and clear diurnal variations in fumarole temperature were attributed to atmospheric forcing. There was also a cooling of the fumarole temperatures during winter. Connor et al. (1993b) then went on to create a steady-state model of flow in a narrow fracture, showing that fumarole temperature will increase with increased mass flow, fracture width, and gas flow, and will decrease with greater distance to the magma body.

Other, more recent studies have found different correlations. For example, at Merapi volcano, Indonesia, Richter et al. (2004) measured strong decreases in temperature immediately after rainfall, and found no significant correlation between atmospheric pressure and fumarole temperature. They recorded fumarole temperatures every minute in a high-temperature fumarole zone 150 m from the active crater, and found that an increase in temperature of a few degrees often correlated with a certain type of seismicity, termed Seismic Cluster Ultra-long Period Seismicity (SCULP). The fumarole temperatures had the same duration but varying magnitude responses to these events. Richter et al. suggested that both seismicity and temperature were due to a sudden release of pressurized gas from a crack 100 m below the active crater.
Zimmer and Erzinger (2003) looked in more detail at the hydrologic relationship with fumarole temperature at Merapi volcano. They found that with lower gas rates the ratio of magmatic gas to meteoric water decreased, causing cooler fumaroles. With a higher gas flux there was also a build-up in pressure, resulting in relatively less meteoric water input and so greater fumarole temperatures. Geochemical measurements showed that immediately after rainfall the fumaroles had a higher concentration of water vapor, and also suggested that the input of meteoric and magma-derived water may fluctuate regularly.

Tedesco et al. (1991) also looked at hydrothermal inputs, at Vulcano, Italy. After some recorded seismicity they noted an increase in fumarole temperature from 200 to 330°C, as well as aerial extensions of the fumarole field and new fractures across the crater rim associated with increased gas flow. However, during their continuous monitoring study the seasonal variations dominated and there was no new seismic activity. From chemical variations they were able to deduce that the fumaroles contained a mixture of hot crater fluids and cooler hydrothermal fluids from residual magma degassing near the coast, and that variations in fumarole temperature were therefore due to variations in mixing between the two.

At Stromboli volcano De Gregorio et al. (2007) continuously monitored soil temperature in a low-temperature fumarole on the southern rim of the crater, but only recorded measurements every hour. They measured temperatures anomalies in 70°C and 55°C fumaroles, mainly involving a decrease in temperature of up to 30°C followed by an increase of a few degrees. On one occasion however they observed a rapid and long-term increase in temperature, and a loss of diurnal variations. This occurred again several
months later but with a smaller change in temperature. They found that these anomalies corresponded well with measured variations in total dissolved gas pressure. As total dissolved gas pressure variations result from variations in the carbon dioxide present in the aquifer, De Gregorio et al. attributed the anomalies to changes in the degassing regime. They also noted a cooling effect of rainfall and a drop in temperature associated with volcano-tectonic events, which they attributed to degassing switching to the main conduit. In contrast, Chiodini et al. (2007) noted an increase in soil temperature surrounding a high-temperature fumarole following seismic swarms at Vulcano, although this did not occur at the fumarole itself. They attributed this to an influx of hot fluids from a deeper part of the hydrothermal system, with a time lag for the fluids to reach the surface.

Other studies have found similarly variable correlations between fumarole temperatures, volcanic activity, seismicity and/or surface features. Okada (1990) noted an increase in geothermal and fuming activity before an eruption at Mt Tokachi, Japan. Ingebritsen et al. (2001) found that fumarole temperatures were relatively stable around 90°C at a variety of quiescent volcanoes in the western USA and were controlled primarily by snow melting. They were not directly related to mass flow, which did show some relationship with volcanic activity. My own measurements at Masaya volcano, Nicaragua show a good correlation with volcanic activity (Pearson et al., 2008) but at Telica and Cerro Negro volcanoes, Nicaragua the strongest correlation is with soil moisture content, and therefore by extension with rainfall (Figure 1.1).

Although there is considerable disparity between these systems, with study areas ranging from high-temperature fumaroles in the crater to low-temperature fumaroles far
from the crater to sites with no diffuse degassing, there is still commonality between the results that suggests that they can be useful for our study. In both high-temperature fumaroles and non-degassing areas, correlations with volcanic activity were found (Barquero, 1988; Sudo and Hurst, 1998; Yamashina and Matsushima, 1999). In both high- and low-temperature fumaroles, rainfall, seasonal affects, barometric pressure and changes in gas flux were found to have an effect on temperature (Tedesco et al., 1991; Connor et al., 1993b; Richter et al., 1994; Zimmer and Erzinger, 2003; De Gregorio et al., 2007). Therefore it is necessary to understand the hydrothermal system, both the thermal and hydrologic components, and to consider atmospheric effects on this system, in order to understand the response of fumarole temperatures to volcanic activity.

Figure 1.1. Fumarole temperature measurements recorded at a) Telica volcano and b) Cerro Negro volcano, Nicaragua in 2007. The strongest correlation is with soil water potential (SWP), a measure of soil moisture content. No known volcanic activity occurred at either volcano during this measurement period. There were considerable problems with instrumentation, which may explain the difference in magnitude between the SWP measurements at the two volcanoes.
There are also several other ways to monitor fumaroles that can provide insight into the hydrothermal system and help us to understand fumarole temperature variations. Self-potential (SP) is one such method, as it provides a way to track changes in movement of hydrothermal and meteoric fluid. For example, Hashimoto and Tanaka (1995) noted an increase in SP before a lava extrusion at Mt Unzen, and a change in the SP signal afterward which they attributed to changes in hydrothermal convection. Friedel et al. (2004) measured noticeable changes in SP that correlated to rainfall at Mt Merapi; there was no volcanic activity during their study. Zlotnicki et al. (2008) measured changes in SP, total magnetic field and ground temperature on the flank of Taal volcano, Philippines, associated with a seismic crisis which prompted self-evacuation of hundreds of people. Although this was not followed by a volcanic eruption, it suggested shallow magma and a possible new site of activity along a fissure in the northern part of the volcano.

At Masaya volcano, a consistent positive SP anomaly was attributed to upwelling of hydrothermal fluids (Lewicki et al., 2003; Lehto, 2007). However, there was no change in the anomaly during observed changes in volcanic activity. Instead, the SP signal was dominated by atmospheric effects, with diurnal signals that correlated with barometric pressure. During rainfall the SP decreased and took a minimum of several hours to return to average levels. The lack of a correlation between volcanic activity and SP could be due to the suppressing effect of rainfall, or because any new fluids have the same ionic charge as surrounding fluids (Lehto et al., 2007). SP at Masaya shows that hydrothermal fluids are constantly circulating, but that atmospheric effects must be included when studying diffuse degassing at this volcano.
CO$_2$ flux is another, more expensive, method to track changes in fumaroles, and is often done concurrently with soil temperatures (e.g. Chiodini et al., 1998; Rogie et al., 2001; Aiuppa et al., 2004). For example, at the Phlegrean fields, Italy, soil CO$_2$ and temperature were measured once or twice per month (Granieri et al., 2003). Some correlation was observed between soil CO$_2$ flux and ground deformation, but environmental effects dominated. Approximately 58% of CO$_2$ flux variance could be explained by soil humidity, and therefore there was also a significant relationship with rainfall. They attributed this to the fact that the monitoring station was on high ground, and so rainfall flowed into the surrounding area and diverted gas flow toward the CO$_2$ monitoring station.

At Masaya volcano previous studies have shown a good spatial correlation between elevated SP, CO$_2$ and temperature (Lewicki et al., 2003; Lehto, 2007). The subsurface geology is therefore likely to be an important factor in controlling subsurface fluid flux. Continuous CO$_2$ flux measurements collected at a fumarole zone near Comalito cinder cone, 3.5 km from the active crater, varied between 300 and 11000 g/m$^2$d (Figure 1.2). This is well within the range measured by Lewicki et al. (2003). There were no clear long-term trends, other than the increase between 2007 and 2008 which may due to instrument error as the fluxmeter stopped working in August 2007 and/or possibly a change from the rainy season to the dry season. There is a diurnal signal which suggests atmospheric forcing, and the consistently elevated flux shows that the hydrothermal system is constantly active.
Figure 1.2. CO$_2$ flux measured at Comalito cinder cone during this study. It is constantly elevated, with predominantly diurnal variations. The large increase in temperature between 2007 and 2008 may be due to instrument error or the change from the rainy season to the dry season.

Todesco et al. (2003) did a study of gas fluxes at the Phlegrean Fields, focusing on numerical simulations. They modeled the shallowest 1500 m of the system using geophysical, geochemical, petrological and well log data as constraints. With a fully saturated model they discovered that injection of hot water and CO$_2$ could reproduce the distribution of heat observed at the surface at the Phlegrean Fields, and also the single-phase gas region at the crater inferred from geochemistry. The results were dependent on the temperature of injected gas, the rate, its source depth, and host rock properties. High permeability or a deeper source resulted in distal areas remaining cold, and no dry gas zone. Increasing permeability at shallow depths caused a decrease in pressure and temperature in the single-phase gas region. Enhanced permeability near the single-phase region, however, changed the pressure and temperature conditions to enhance boiling and change both gas composition and flux rate. Even with injection of hot fluids from a steady source, the surface discharge composition and rate could be highly variable both in time and space and was more limited by rock properties. Changes in the source fluid took longer to be recognized than changes in permeability (on the order of years to decades).
although periods of intense magma degassing could still induce important changes in the reservoir that fed the surface fumaroles (Todesco et al., 2004).

To understand the impact of variations in the hydrothermal system, Todesco et al. (2004) modeled deformation associated with it. Using the temperature and pressure from the numerical model as input in a FLAC3D model, Todesco et al. found that periods with higher injection rates caused heating and build-up of pore pressure that could trigger significant rock deformation. The models suggested that periods of intense degassing resulted in fast uplift followed by slower subsidence and large changes in gas composition. The deformation would be focused at the end of these periods while the gas composition would change several months after the injection rate was reduced again, as observed at the Phlegrean Fields.

The hydrothermal model of the Phlegrean Fields (Todesco et al., 2003) was also compared to time-varying gravity signals to further validate the model. The distribution of fluid density is affected by ascent of hot fluids, phase changes and variable gas composition (Todesco and Berrino, 2005). Although the gravity signals associated with this are small compared to injection of new magma, they are also very shallow so may still be detected. Residual gravity signals increase when the fluid injection rate increases because mass injection increases, water vapor condenses due to increased pore pressure, and liquid water is displaced upwards. Gravity changes computed as a function of volume, depth, distance from the observation point and average fluid density were summed over the numerical model from Todesco et al. (2003), who showed that by varying the injection rate, composition and duration of volcanic crises, both the distinct gravity trend and variable gas composition recorded at the Phlegrean Fields could be
recreated. The volcanic crises were attributed to a pulsating source of hot fluids which discharged large amounts of CO$_2$-rich fluids, also affecting hydrothermal circulation. However, in 2005 the rate of subsidence declined and new uplift began, with gradual gas enrichment over 5 years and a significant drop in the gravity residual. This could not be recreated with the previous model (Todesco et al., 2006). Todesco et al. suggested that the mechanism feeding the fumaroles had probably changed, as had the magma composition and subsurface permeability distribution. A wider source region over the previous few years and more frequent and shorter unrest crises suggested that the rate of fluid injection, timing and duration needed to be reassessed to explain more recent signals, and that variable magmatic degassing and emplacement of deep source fluids was probably occurring (Todesco et al., 2006).

Although the system at the Phlegrean Fields is not analogous to the one at Masaya, the numerical models are useful for our study. At Masaya volcano a lava lake occasionally forms in the crater, showing that the system is open (Rymer et al., 1998; Williams-Jones et al., 2003; Stix 2007), unlike that at the Phlegrean Fields. This makes it unlikely that increased injection would result in the same degree of deformation. The fumaroles at the Phlegrean Fields are also much hotter, but the dominant controls are still likely to be similar. Therefore that we need to particularly consider gas injection rate, rock permeability, and to a lesser extent source depth and gas injection temperature in our models.

Previous studies suggest that the relationship between diffuse degassing and fumarole temperature is complex, but that variations in the temperature are often attributable to changes in gas flux through the system. Despite being unable to explain
and/or recreate all of the signals observed at fumaroles on active volcanoes, these studies have provided important insight into factors controlling diffuse degassing, and its link with volcanic activity.

1.2 The hydrologic system at Masaya

The hydrologic system at the Phlegrean Fields is well constrained, and modeling has shown the importance of incorporating it into models of diffuse degassing. However, the hydrologic system at many active volcanoes is poorly known (Hurwitz et al., 2003) and hydrologic properties are rarely characterized. At Masaya volcano most of the numerous studies have focused on the geological structure (e.g., Williams, 1983a; McBirney, 1956; Rymer et al., 1998) or the gas composition (e.g., Duffell et al., 2003; Lewicki et al., 2003), which are described in the relevant chapters of this dissertation. However, the hydrologic system has been previously assessed and will be described here.

In 1993, Instituto Nicaraguense de Acueductos y Alcantarillados and Japan International Cooperation Agency used well soundings outside of the caldera at Masaya volcano to infer a water table elevation of 190 meters above sea level (masl) to the south of the caldera and 130 masl to the north of the caldera. They assumed fairly consistent gradients across the caldera. Transient electromagnetic soundings (TEM) showed that this was an oversimplification and that a more detailed study was necessary to approximate groundwater flow within Masaya caldera (MacNeil et al., 2007).

TEM soundings at 30 sites throughout Masaya caldera detected a highly resistive layer overlying one or more conductive layers (MacNeil et al., 2007). This was interpreted as dry basaltic rocks overlying porous, saturated lava flows. Therefore the
boundary between the two layers corresponded to the water table. A simple two-layer model suggested that the water table was a subdued reflection of topography (Figure 1.3), although the near-vent area was possibly vapor-dominated and was too complex for the caldera-scale model to recreate. One important feature of the geology that was included in the hydrologic model is that caldera-bounding faults form walls that are up to 400 m in height and have bounded lava flows in the past (Williams, 1983b). Dikes have possibly been injected along these faults (Williams, 1983b). This has created a strong lithologic and hydrologic boundary that minimizes flow of groundwater between the caldera and the surroundings, causing the caldera to be relatively isolated hydrologically. Therefore evapotranspiration, degassing and rainfall can all be assumed to be contained within the caldera.

MacNeil et al. (2007) used the TEM soundings to create a 3D groundwater flow model with MODFLOW2000. The average measured rainfall of 1.6 m/year, degassing rate of 400 kg/s (Burton et al., 2000), and estimated evapotranspiration rate of 1.1 m/yr were used as constraints in the model. They found that, as with the two-layer model, the water table was at its shallowest depth close to Laguna Masaya, which has the lowest elevation in the caldera (Figure 1.4a). Close to the active vent, which has the highest elevation, dramatic gradients occurred and the water table followed topographic gradients. The modeling study concluded that a high permeability zone beneath the volcanic edifice must exist at depth (Figure 1.4b) that transmits groundwater toward the active vent.
Figure 1.3. a) Topographic map of Masaya volcano. b) Elevation of the water table as estimated from TEM soundings. Reproduced from MacNeil et al., 2007 (with permission from Elsevier).
Figure 1.4. Groundwater distribution at Masaya in meters above sea level, according to MODFLOW2000 results. Arrows indicate direction of groundwater flow. a) At the surface. b) At depth, where a high-permeability zone results in groundwater flowing toward the active crater (Reproduced from MacNeil et al., 2007 with permission from Elsevier).

A study of self-potential wavelet tomography by Mauri et al. (2010) is in good agreement with the model of MacNeil et al. (2007), although their estimated depths to the water table are consistently less (Figure 1.5). This supports the model of a water table that approximately follows topographical contours, with a lower hydraulic head further...
from the vent (Figure 1.5a), but with groundwater flowing toward the active crater at depth (Figure 1.5b).

![Graph showing estimated water table depths](image)

Figure 1.5. Estimated water table depths. Brown line represents land surface, points represent water table estimated from SP wavelet tomography, and gray profile represents water table estimated by MacNeil et al. (2007). (Reproduced from Mauri et al., 2010 with permission from Elsevier).

1.3 Volcanic activity at Masaya volcano (adapted from Tenorio et al., 2010)

Although the volcano-hydrologic system at Masaya volcano is relatively stable and the volcano has been consistently degassing for over a decade, both the magnitude and the style of degassing is constantly fluctuating. The last major explosion was in 2001, when a number of people were injured by ash and rocks that were ejected from a new vent that formed in the crater. From 2001 until 2005 occasional ash explosions and incandescence were observed. In 2005 a landslide blocked the active vent and degassing dropped to low levels. From 2006 until 2009, my study period, activity varied between low-level degassing, ash explosions, incandescence, and the formation of a new lava lake (Figure 1.6). This provides an excellent opportunity to observe any changes in fumarole temperature related to changes in volcanic activity.
At the beginning of the study period, from October 2005 until May 2006, gas emanations from the crater were strong and consistent. On May 25 2006 at 11:30 am the Volcan Masaya National Park staff reported a rockfall in the crater, and on May 30 incandescence was visible in the active vent. The park staff also described ‘tongues of flame’ and some incandescence in the old crater vent. There was no corresponding change in seismicity or fumarole temperature (Figure 1.7, 1.8). In June 2006 the crater vent widened by 5 m and the incandescence and ‘tongues of flame’ were still visible, although only at night. The incandescence was visible at night for the next year, until May 2007.
Figure 1.7. Real-time Seismic Amplitude (RSAM) and total number of earthquakes recorded per month during the study period. There was no clear correlation with volcanic activity.

Figure 1.8. Fumarole temperature recorded about once a month by INETER scientists. There are no obvious correlations with volcanic activity.

Crater degassing remained consistent from June until October 2006, when surface features changed in the crater. Mini-DOAS measurements and visual observations showed a marked increase in both degassing and magmatic activity in October (Figure 21.
A fracture formed in the crater floor during the first two weeks of October, and National Park staff noted unusual incandescence on October 21. On October 22, National Park staff observed that a new vent had formed in the North-East part of the crater, with an estimated diameter of more than 5 m. Strong degassing and light were visible from a new lava lake at the vent (Figure 1.10). The vent formed from the larger explosion in 2001 still hosted more degassing than this new vent however. Intense rain from 20-22 October hindered observations of the new vent formation, and also resulted in acid rain that damaged vegetation and trees to the east of the crater.

Figure 1.9. Sulfur dioxide flux from the active crater during the study period. There was a marked increase corresponding to the formation of the lava lake in October 2006.
Figure 1.10. Images of the new lava lake that developed in the crater in October 2006.

For the next 7 months gas emissions from the new crater remained strong, and incandescence was still visible at night. Seismicity changed slightly, with an increase in RSAM units (Figure 1.7) and a change in dominant frequency from 1.5 Hz to 5 Hz in February 2007. In May 2007 emissions decreased slightly, enough that the temperature in the new vent could be measured (Figure 1.11, 1.12). It was discovered that neither the new mini-DOAS installation nor the broadband seismic station were working.

Figure 1.11. On average temperatures decreased slowly at the 2006 vent, even after a rockfall blocked it in early 2008.
From July 2007 activity changed as the plume became more ash-rich and reached higher elevations, resulting in a number of reports from the Washington VAAC (Global Volcanism Program, 2010). In July 2007 seismicity, fumarole temperature and gas emissions remained consistent with the month before (Figures 1.7-1.9). However, on 15 July National Park staff reported ash deposits on both the road and the lookout station to the southeast of the crater. On 16 July they observed that the plume was a darker color than the usual white, water-vapor-dominated plume. INETER scientists attributed this to either an increase in ash or sulfur content. A large, ash-rich plume was visible from July 2007 until May 2008, drifting in a variety of directions. The degassing was primarily from the 2001 vent, particularly after a rockfall closed the 2006 vent in January 2008. In September there were some rockfalls in the crater, and in October acid rain affected vegetation and new fumarole activity was observed in the east part of the crater (Figure 1.13).
On 18 June 2008 2 ash explosions were felt seismically, and emitted medium amounts of ash and gas to 1 km. There were no visible rockfalls or ash deposits afterwards. From June 2008 until July 2009 the volcano was the site of some low-level tremor and persistent, strong degassing, although with reduced ash content (Figure 1.14). In August 2009 the crater gas emissions visibly decreased, and activity remained low (Figure 1.15) until late November 2009, when abundant gas emissions were visible from the SE of the crater (Figure 1.16).
Figure 1.14. Strong, consistent degassing in September 2008.

Figure 1.15. Degassing levels dropped in late 2009.

Figure 1.16. By the end of 2009 activity had returned to similar levels to early 2006.
1.4 Numerical modeling

Improvements in computational power have revolutionized volcanology, allowing increasingly sophisticated numerical simulations to approximate a volcanic system or certain aspects of it. We began by creating simple models of heat and mass transfer using a finite difference, implicit code we wrote in MATLAB (see Appendix), and with the COMSOL Multiphysics program, a finite element code to solve partial differential equations. We then used COMSOL multiphysics to create a 2-dimensional heat flow model of a fracture and its adjacent rock at Comalito cinder cone (Figure 1.6), which was observed to be the site of considerable degassing. we used the 2D convection and conduction mode of COMSOL. The interior of the model was only subject to heat conduction, given by Fourier’s Law:

\[ q = -k \nabla T \]

where \( q \) is the heat flux, \( k \) is the thermal conductivity, and \( \nabla T \) is the local temperature gradient. The top and bottom boundaries were at fixed temperature to represent the heat source and the surface, respectively. The right boundary was no-flow. The left boundary of the simulation was given by forced convection to simulate heat flow through the fracture:

\[ n \cdot k \nabla T = q_o + h(T_{\text{inf}} - T) \]

where \( q_o \) is the heat flux across the boundary into the model (in this case 0), \( h \) is the heat transfer coefficient and \( T_{\text{inf}} \) is the temperature outside of the model. This resulted in a simple conductive profile, with temperature decreasing moving through the wall rock away from the convective boundary (Figure 1.17).
To create more sophisticated models we used the TOUGH2 numerical code. This is a numerical simulator of multicomponent, multiphase fluids in porous rock (Pruess, 1991). It can simulate high temperatures and pressures, flow of gases and liquids, and flow through porous and fractured media, making it ideal for models of heat and mass transfer around and within a fracture on the flank of an active volcano.

Originally developed by Lawrence Berkeley National Laboratory as a research code called MULKOM, TOUGH (Transport Of Unsaturated Groundwater and Heat) was first released to the public in 1987 (Pruess, 2004). It was designed for geothermal reservoir simulation primarily, particularly for the Yucca Mountain project, and took into
account the nonisothermal nature of flow, the importance of both boiling and condensation, and the highly nonlinear nature of two phase, water-steam flow (Pruess, 2004). It was gradually expanded to include more applications and modules (TOUGH2), non-aqueous phase liquids in contamination problems (T2VOC and TMVOC), coupling with geochemical reactions (TOUGHREACT) and coupling with rock mechanics (TOUGH-FLAC; Pruess, 2004). My study focuses on flow of groundwater and gases through porous rock and their affect on surface temperature and gas distributions, and therefore we worked exclusively with TOUGH2.

1.4.1 Governing equations (adapted from Pruess et al., 1999; Pruess, 2004)

TOUGH2 solves energy and mass balance equations for flow of multicomponent, multiphase fluids through porous and permeable material. These can be written as:

mass accumulation = mass flux + sinks and sources, or;

\[
\frac{d}{dt} \int_{V_n} M^k \, dV_n = \int_{\Gamma_n} F^k \cdot n \, d\Gamma_n + \int_{V_n} q^k \, dV_n \quad [1]
\]

where \( k \) is the component \( 1 \ldots nk \) (air, water etc.), \( V_n \) is an arbitrary subdomain of the flow system, \( \Gamma_n \) is the closed surface bounding it, and \( n \) is a normal vector on surface element \( \Gamma_n \) pointing inward into \( V_n \) (Figure 1.18). Essentially, the rate of change of fluid mass \( (M) \) in \( V_n \) is equal to the net inflow across \( V_n \) \((F)\) plus the net flux from other sources \((q)\).
Looking at the mass accumulation term first, $M^K$ is the total mass of component $k$ obtained by summing over fluid phases $\beta$:

$$M^K = \phi \sum_\beta S_\beta \rho_\beta X^K_\beta$$ \hspace{1cm} [2]

where $\Phi$ is the porosity, $S$ is the saturation of the phase (the fraction of the pore volume occupied by that phase), $\rho$ is the density of the phase, and $X$ is the mass fraction of component $k$ present in phase $\beta$. Similarly, the heat accumulation term of a multiphase system is given by:

$$M^{NK+1} = (1 - \phi)\rho_r c_r T + \phi \sum_\beta S_\beta \rho_\beta u_\beta$$ \hspace{1cm} [3]

where $\rho_r$ is the density of the rock, $c_r$ is its specific heat capacity, $T$ is temperature and $u_\beta$ is the specific internal energy in phase $\beta$. In this case heat accumulation is not dependent on the component, and so there is only one term per cell.

Next the advective mass flux term is calculated by summing over the phases:

$$F^K = \sum_\beta X^K_\beta F_\beta$$ \hspace{1cm} [4]
where $F_\beta$ is the multiphase version of Darcy's Law:

$$F_\beta = \rho_\beta u_\beta = -\frac{k \kappa_\beta}{\mu_\beta} \rho_\beta (\nabla P_\beta - \rho_\beta g)$$

Here, $u_\beta$ is the Darcy velocity, $\kappa$ is absolute permeability, $\kappa_\beta$ is relative permeability of the phase, $\mu_\beta$ is the viscosity of the phase, and $g$ is gravity. $P_\beta$ is the fluid pressure, given by the sum of the pressure of the reference phase (generally a gas) and the capillary pressure. The heat flux has a similar form and is calculated to include both conduction and convection:

$$F^{NK+1} = -\lambda \nabla T + \sum_\beta h_\beta F_\beta$$

where $\lambda$ is the thermal conductivity and $h_\beta$ is the specific enthalpy in each phase.

The diffusive fluxes of all phases are also included by summing the fluxes of each component $k$ in phase $\beta$:

$$f_\beta^k = -\phi \tau_\theta \tau_\beta P_\beta^k d_\beta^k \nabla X_\beta^k$$

where $\tau_\theta \tau_\beta$ is the tortuosity (the former depends on the porous medium, the latter on the phase saturation), $d$ is the diffusion coefficient and $X$ is the mass fraction as above.

Other complexities can also be included that are not relevant to this study and so are not described, for example hydrodynamic dispersion and the gas phase permeability increase that occurs at low pressures.

To transform these equations into a partial differential equation from which a numerical solution is generally derived, Gauss' theorem can be applied to equation [1]:

$$\frac{\partial M^k}{\partial t} = -\nabla F^k + q^k$$
1.4.2 Solving the equations

To solve the equations above, a numerical approximation is made. The spatially and temporally continuous integrals that make up the mass accumulation and mass flux terms are discretized. This is done by averaging for each cell and then summing all cells, the mass accumulation over volume and the mass flux over area. To discretize the mass flux term, the change in pressure between nodal grid blocks is divided by the distance between the blocks to give the $\nabla P$ term in Darcy’s Law (Equation 5). The gravity is the net value in the appropriate direction between the two blocks, and all other values are averaged over adjoining cells. This is then substituted back into equation 1 to give a first order differential equation. The flux and source and sink terms are calculated for each new time step to give a fully implicit, first order backward finite difference scheme. This results in a series of coupled, non-linear algebraic equations in each cell, with one for each mass component and one extra for the energy balance. These are solved simultaneously and then Equation 1 is rearranged to give a residual on the left and all the original terms on the right. Newton-Raphson iteration is used to get the residual below a preset convergence tolerance, with automatic time step adjustment. There is 100% upstream weighting of flux terms at interfaces for unconditional stability, and time steps that are not too small.

Solving these equations is dependent on the fluid properties (pressure, volume, temperature), and the interaction between the fluids and permeable medium. TOUGH2 includes a number of equations of state (EOS) that describe these. We used EOS3, air and water, for all of our modeling as this allows us to model the vadose zone. We therefore assume that air is representative of the volcanic gases, although at Comalito cinder cone
the fumarole gases were measured to be around 50% air (Chiodini et al., 2005). However, compared to the uncertainties in our models and the relatively small range of temperatures and pressures of the fluid, this is unlikely to be a major source of error.

A number of assumptions are included in EOS3, including the fact that air is an ideal gas, air and vapor partial pressures are additive in the gas phase, and that the solubility of air in water is a constant, although the latter's small magnitude and slowly-varying dependence on temperature make this unlikely to be a large source of error.

Complications arise from the multiphase nature of TOUGH2 that have to be addressed. For a single phase model, temperature and pressure are the inputs. However, for a multiphase model pressure is not independent of temperature and so another variable must be used in place of one of these. A particular quirk of EOS3 is the fact that air mass fraction is input with pressure and temperature for the single-phase case, while gas saturation is the input for the two-phase case. As both of these fall between 0 and 1, the input representing the gas saturation is actually $S_g + 10$ so that the single- and two-phase simulations are numerically distinguishable. To determine if the model changes phase, the pressure is the determining factor. For a single phase liquid model, the saturated pressure must be less than the fluid pressure. For a two-component (air + water) model, the sum of the saturated vapor pressure and the air pressure must be less than the fluid pressure, otherwise a gas phase will evolve. The models can switch between the two, with the input of air mass fraction being replaced by very small gas saturation.

To actually implement these models, the permeability, porosity, capillary pressure relations, thermophysical properties of the fluid, initial and boundary conditions of the flow system and sinks and sources must be estimated and assigned. These are user inputs,
except for most of the thermophysical properties of the fluid, which are calculated within TOUGH2. The model geometry, program options, computation parameters and time-stepping information are also specified by the user. In this project we used fairly simple, regular grids and therefore were able to use the Petrasim interface to TOUGH2, a more graphical approach. This allows the user to specify values in tables and on images of the model domain rather than using the text file format utilized by TOUGH2. It also outputs images of the model results and time cell history plots.

Probably the most critical part of TOUGH2 modeling is determining the boundary conditions. For Neumann conditions the fixed heat and/or mass flux is simply prescribed as a source or sink. This can vary with time. For no-flux conditions the connections across the boundary are simply removed. Dirichlet conditions, with fixed temperature and/or pressure, are more difficult to implement. For a fixed Dirichlet condition which does not vary with time, a cell can be set as inactive in TOUGH2 (fixed state in Petrasim). Inactive cells appear in flow connections and initial conditions but are ignored otherwise. Another way to set a Dirichlet condition is to specify very large volumes for the boundary cells so that the thermodynamic conditions do not change from fluid or heat exchange. For time-dependent Dirichlet conditions, a sink or source has to be introduced into the cell at the correct rate to get the desired variations. For a simple temperature boundary the porosity and permeability are set to negligible values to limit mass flow into and out of the cell, and the heat flow is specified to give the desired temperature. A similar approach is taken for fixed pressure conditions, but with zero thermal conductivity and mass flow into or out of the cell specified instead.
For more information on code architecture, implementation and applications, see Pruess et al. (1999), Pruess (2004) and the Petrasim users manual.

1.4.3 TOUGH2 validation (adapted from Oldenburg and Pruess, 1994)

To assess the validity of the numerical approximations created by TOUGH2, a number of comparisons were made with models established in the literature. Of particular relevance for the advective-diffusive part of TOUGH2 as utilized in our models, the seawater intrusion problem of Henry (1964) and the free convection problem of Elder (1967) were modeled and compared with previous results.

In the Henry problem, injection of fresh water into the left-hand side of a two-dimensional model results in constant flow of fresh water toward the right, where the boundary is set to be that of seawater and the pressure is set at hydrostatic pressure. This results in density variations of 2.5%, with seawater along the right boundary and the base of the model near this boundary, and fresh water throughout the rest of the model domain. Comparisons with results from Voss and Souza (1987), which are representative of the literature, show good agreement. Results are found to be relatively insensitive to grid dimensions.

In the Elder problem, heat is injected from below, resulting in free convection. A common adaptation of this problem is for solutal convection, where there is a salt source at the top rather than a heat source at the base. Oldenburg and Pruess (1994) simulated the solutal convection problem with TOUGH2. They found similar results to those calculated by Elder (1967) and Voss and Souza (1987) for similar grid dimensions. However, Elder (1967) also did a laboratory experiment with a Hele-Shaw cell, and
observed a number of convection cells forming compared to the two of the numerical simulations. The center of the apparatus was also the site of upwelling fluid, compared to downwelling fluid in the numerical simulations. By reducing the grid spacing in the TOUGH2 simulations, much better approximations of the laboratory results could be computed.

Comparisons of TOUGH2 with previous experimental and numerical simulations show that it can adequately represent the systems we are trying to describe. Grid dimensions are found to be important in the Elder problem, and therefore in other models involving free convection. For each of my models in this study, I tested a variety of grid resolutions to ensure that the heat and mass flow was not being aliased.
CHAPTER 2

RAPID RESPONSE OF A HYDROLOGIC SYSTEM TO VOLCANIC ACTIVITY

2.1 Introduction

Time series of fumarole soil temperature variations are of interest both in monitoring active volcanoes (De Gregorio et al., 2007; Yamashina and Matsushima, 1999), and for studying the nature of heat and mass transfer in volcanic systems (Tedesco et al., 1991; Connor et al., 1993b; Sudo and Hurst, 1998). High-temperature fumaroles located in the craters of volcanoes have been observed to increase before eruptions (Barquero, 1988). Temperature responses of lower-temperature flank fumaroles are often less clearly correlated with changes in volcanic activity (Richter et al., 2004; Sudo and Hurst, 1998; Yamashina and Matsushima, 1999), in part due to interaction between volcanic and hydrologic systems. Yet this interaction can play an important role in the nature and timing of volcanic eruptions (e.g., Nakada et al., 2005). Here we present time series showing very rapid and significant temperature changes in low-temperature fumaroles in response to volcanic activity during two episodes at Masaya volcano, Nicaragua. Rapid and multi-channel data acquisition allows us to identify cyclic variations in temperature in both of these volcanic episodes, revealing new details about the response of the hydrologic system to changes in volcanic activity.
2.2 Masaya Volcano

Masaya volcano, Nicaragua (Figure 2.1), is one of the most persistently active volcanoes in central America (McBirney, 1956; Williams, 1983a; Stoiber et al., 1986). It has been constantly degassing from Santiago crater (Figure 2.1) since 1993 (Duffell et al., 2003; Mather et al., 2006) and has one of the largest reported noneruptive gas fluxes at any volcano, with intermittent lava lake development associated with an extensive magma plumbing system (Stoiber et al., 1986; Rymer et al., 1998; Williams-Jones et al., 2003). Low-temperature (~65°C) fumaroles zones are located along a northeast-trending fracture system that extends down the edifice of the volcano for ~4 km (Figure 2.1). Near Comalito cinder cone, located along the fracture 3.5 km from and 200 m below Santiago crater, some of the highest known diffuse carbon dioxide fluxes from low-temperature fumaroles worldwide have been identified and mapped. The presence of magmatic gases in the fracture system (Lewicki et al., 2003; Shaw et al., 2003) increases the likelihood that Comalito fumaroles might respond to changes in volcanic activity.

Figure 2.1. Aerial photograph showing location of studied fumaroles adjacent to Comalito cinder cone on flanks of Masaya volcano (Instituto Nicaraguense de Estudios Territoriales (INETER); W. Strauch, 2006, personal commun.). Dashed line represents fracture zone inferred from the distribution of thermal areas measured by Lewicki et al. (2003). Active degassing is occurring in Santiago crater, where vent widened noticeably in June 2006 and small lava extrusion was observed from new vent onto crater floor on 23 October 2006. Location of Masaya is shown in inset map.
Throughout the 9-month study period, seismic tremors were recorded and incandescence was visible at night in Santiago crater. Two periods of increased volcanic activity were noted by Instituto Nicaragüense de Estudios Territoriales (INETER), in June and October 2006 (W. Strauch, 2006, personal commun.). In June, vent widening with increased incandescence followed a rockfall on 25 May 2006. During 21-23 October 2006, a small lava lake formed in the crater, following a peak in seismicity and an increase in SO₂ flux (W. Strauch, 2006, personal commun.).

2.3 Method

Monitoring equipment was installed in May 2006 near Comalito cinder cone (Figure 2.1). Four tubes were driven into the ground within a 1 m² area in a fumarole zone, to depths of 33 cm, 63 cm, 95 cm and 150 cm, and a fifth was driven to 150 cm in a different fumarole area, located 7 m away. An ungrounded chromel-alumel (type-K) thermocouple with a resolution of 0.1 °C was inserted in each tube, which was then sealed with putty. Rainfall, barometric pressure, and atmospheric temperature were also recorded adjacent to the thermocouples. Each sensor was sampled every ten seconds. Temperatures and atmospheric pressure were averaged every five minutes and rain measurements were cumulative over each five minute period. Real-time seismic amplitude measurements (RSAM) were calculated by INETER from seismic data recorded at a broadband seismometer near Santiago crater (Figure 2.1).

2.4 Results

Fumarole soil-temperature time series for the sampling period are shown in
Figure 2.2a. The coolest temperatures were consistently recorded by the deepest thermocouples, and the highest temperatures were recorded by the shallowest thermocouples (Figure 2.2a). This is due to the presence of a thin (~5–20 cm) low-permeability clay-rich layer at the surface, causing accumulation and convection of hot gases in the shallow subsurface.

Distinctive signals occurred during the two periods of anomalous crater activity in June and October. During these periods, temperature increased to a peak value over ~20 minutes, followed by an exponential decrease asymptotically approaching a threshold temperature for as long as one day, and then a sudden drop to background temperature occurred (Figures 2.2b-d). In individual fumaroles, the threshold temperatures were remarkably consistent across the numerous heating cycles. For example, the shallowest thermocouple (33 cm) recorded a background temperature of 72 °C, a peak temperature of ~80 °C, and a threshold temperature of ~74 °C.

Analysis of the frequency spectrum of the soil-temperature time series reveals unique characteristics during volcanic activity. At background state the time series were dominated by diurnal and semidiurnal variations. These periodicities disappeared during the two periods of volcanic activity, when series included a broad range of frequencies (Figures 2.3a and 2.3b). Thus, while the magnitudes of these anomalies were less than 5 °C and their signatures were complex, the anomalous behaviors were easily identified on spectrograms.
Figure 2.2. (a) Temperatures recorded at different depths in a fumarole zone. Note the increases in temperature in early June and late October, highlighted in gray, corresponding to periods of increased volcanic activity. (b) Heating cycles recorded in the temperature signal during the first period of volcanic activity in June 2006. In several instances, sharp increases in temperature appear to correspond to rainfall events shown along the bottom of the graph. (c) The distinctive signal formed by a sharp increase in temperature followed by an exponential decrease and then a sudden drop recorded at 33 cm depth. (d) One of these cycles recorded at 95 cm depth consists of (i) sudden increase in temperature due to an increase in pressure; (ii) exponential decrease in temperature while the system is stabilizing during higher gas flow; and (iii) rapid decrease in temperature to background (see Section 2.5).
Individual rainfall events often coincided with rapid increases in the soil temperatures of as much as 3 °C. Of these temperature spikes, ~30% occurred during rainfall, although it was raining during only 1.35% of the sampling period (Figure 2.4d); thus temperature spikes have a positive correlation with rainfall with >99% confidence (binomial interval estimate). During volcanic activity the sudden increase in soil temperature at the onset of cycles was often accompanied by rainfall (Figure 2.2b).

In non-eruptive periods, soil temperatures were characterized by a slight increase in average temperature (0.0010 °C/day - 0.0094 °C/day), diurnal and semi-diurnal variations (inverse to barometric pressure), and seasonal variations associated with rainfall (Figures 2.2a, 2.4a, and 2.4b). There was a peak in RSAM during the temperature excursion prior to the formation of the new lava lake in October 2006, but many larger RSAM spikes were observed when there were no changes in temperature or reported volcanic activity (Figure 2.4c).
Figure 2.3. (a) Spectrograms showing dominant frequencies in the fumarole soil-temperature time series. Each spectrogram corresponds to a different thermocouple buried to the depth indicated. During the anomalies in June and October 2006, marked by red arrows, the fumarole temperature signals contained a much greater range of frequencies than during background activity, revealed by greater intensity of high frequencies during these periods. Changes in frequency content in late August and mid-November occurred when the datalogger was opened for maintenance. (b) Fourier transforms of the temperature record from 95 cm depth during each of the anomalies, in June and October 2006, and during background state, in December 2006. The dotted red lines highlight diurnal and semi-diurnal frequency variations, which are only observed at the thermocouples during background conditions.
Figure 2.4. Time series of monitored data, with anomalous episodes highlighted in gray. (a) Average fumarole temperature and daily temperature fluctuations increased from the rainy season to the dry season. (b) Ground fumarole temperature was recorded at 95cm depth but is representative of changes at all depths. (c) Peaks in RSAM sometimes corresponded to increases in temperature, particularly at the onset of the June and October anomalies. (d) Differential of temperature at 95cm depth highlights rapid increases in fumarole temperature that show some correlation with rainfall. No decrease in temperature was noticeable after individual rainfall events.
2.5 Discussion and Conclusion

Changes in magmatic activity at Masaya during October and June 2006 appear to be reflected in both temperature variations in the Comalito fumaroles and mild volcanic activity within Santiago Crater. Widening of the active vent in June 2006 and a new lava extrusion on the floor of Santiago crater in October 2006 both corresponded to rapid fluctuations in soil temperatures near Comalito cinder cone. Anomalous temperatures during volcanic activity are particularly clear on spectrograms (Figure 2.3a) and suggest that fumarole temperature time series can be a sensitive monitoring tool in some circumstances.

The nature of temperature anomalies during the episodes of crater activity provide clues about the mechanisms causing these anomalies. The temperature variations were rapid, with initial increases of up to 5 °C in less than 20 minutes. As bulk hydraulic conductivity is meters per day at Masaya volcano (MacNeil et al., 2007), transfer of heat by advection of hot fluids from Santiago crater, or even from a closer source, to fumaroles near Comalito is not a plausible source of these temperature anomalies. The flow of groundwater toward the active vent, rather than away (MacNeil et al., 2007), makes direct advection of hot fluids from Santiago crater even less tenable.

Instead, we suggest that rapid increases in temperature may be a response to pore pressure increase in the fracture zone. A relevant observation is the durations of temperature anomalies during volcanic activity, which are consistently ~1500 min. The hydraulic conductivity ($K$) of fractured basaltic lavas in the edifice is $\sim 1 \times 10^{-3}$ m s$^{-1}$ (MacNeil et al., 2007). Assuming specific storage ($S_s$) of this aquifer is typical of fractured rock, $\sim 1 \times 10^{-5}$ m$^{-1}$, the hydraulic diffusivity ($D = K/S_s$) would be $100$ m$^2$ s$^{-1}$.
The dimensionless response time ($\alpha$) of a hydraulic pressure wave through an aquifer is equal to the ratio $Dt/L^2$, where $t$ is time and $L$ is the distance from the pressure pulse source (perhaps beneath the volcanic vent) to the Comalito fumaroles. A full response occurs at a value of $\alpha = \sim 1$. If $D = 100 \text{ m}^2 \text{s}^{-1}$ and $L = 3500 \text{ m}$, a full response time is $\sim 2000 \text{ min}$. Given that the duration times of the events were always very close to this, $\sim 1500 \text{ min}$ (Figures 2.2b-d), we think this duration time may reflect the hydraulics of the pressure pulse that is traveling along the fracture zone from the source.

We emphasize that all five fumarole soil-temperature time series responded in the same way and the air temperature did not, although the magnitudes of soil temperature responses varied among the fumaroles. These temperature variations contained distinctive, repetitive cycles (Figures 2.2b-d) that are similar to those observed in pressure time series related to hydraulic fracturing (Enever et al., 1992). In light of this similarity we propose a similar mechanism. Volcanic activity causes an increase in pore pressure throughout the nearby groundwater system. Along the fracture zone (Figure 2.1), this pore pressure increase dilates fractures or perhaps opens new fractures, enhancing permeability and resulting in increased fluid transport to the surface. Rainfall also increases pore pressure (Wang and Sassa, 2003) and appears to sometimes trigger the temperature response, perhaps by creating fractures (Husen et al., 2007) and/or increasing pore pressure in the fracture zone past some threshold value. Initially this change in pore pressure causes spikes in fumarole soil temperatures as water vapor is transported rapidly to the surface, but afterwards the temperature in the fumarole decreases exponentially as ascending fluids reach a new equilibrium and lose heat to the surrounding rock. At the end of the cycle, pore pressure drops due to a change in the volcanic system, fractures
close, and fluid flow rapidly returns to background conditions. In addition, pore pressure
decrease at the end of the cycle could facilitate mixing between ascending fluids and
cooler, shallow meteoric waters, as proposed at Merapi Volcano (Zimmer and Erzinger,
2003).

In this model, each cycle of rapid temperature rise, flow at a new higher rate, and
rapid decrease corresponds to pressure changes in the magmatic system. The distal
fumarole soil-temperature data suggest that the June activity was characterized by 13
cycles of pressure changes and the October activity by 11 cycles. Such cyclic
pressurization of the magmatic system during episodes of volcanic activity may be
characteristic of Masaya volcano.
CHAPTER 3
INTEGRATED GEOPHYSICAL AND HYDROTHERMAL MODELS OF FLANK DEGASSING AND FLUID FLOW AT MASAYA VOLCANO, NICARAGUA

3.1 Introduction

Surface diffuse degassing is a direct result of magma decompression, and therefore changes in diffuse degassing can be related to changes in volcanic activity (Chiodini et al., 1998). However, the connection between surface degassing and the magmatic source region often involves groundwater, which can strongly affect the location and magnitude of surface emanations that we can detect (Todesco, 2008). Volcanic terrains in particular are characterized by faults, fractures and permeability variations that strongly affect fluid flow paths and rates (Todesco, 1997; Caine et al., 1996; Evans et al., 2001; Manzocchi et al., 2008). These features can also change over time. Geophysical investigations can help constrain these subsurface variations. Numerical simulations allow us to explore how these structures can affect fluid flow, and aid in relating surface diffuse degassing variations directly to their volcanic source.

Volcanic activity perturbs groundwater flow by adding heat and gases to groundwater systems, manifest at the surface by flank degassing, development of springs, and flank fumaroles. Observation of diffuse degassing has been applied as a volcano monitoring tool with varying degrees of success at Mt. Merapi, Indonesia (Toutain et al.,
2009); Mt. Fuji, Japan (Notsu et al., 2006); Mt. Etna, Italy (Badalamenti et al., 2004); Phlegraean Fields, Italy (Granieri et al., 2003); Stromboli volcano, Italy (Finizola et al., 2002); Taal volcano, Philippines (Zlotnicki et al., 2008); Ruapehu volcano, New Zealand (Werner et al., 2006); Nisyros, Greece (Brombach et al., 2001); Mammoth Mountain, USA (Rogie et al., 2001); and San Vicente volcano, El Salvador (Salazar et al., 2002). These studies all indicate that a good geological model of the subsurface is a vital prerequisite to interpreting changes in diffuse degassing in light of volcanic activity. In this study, therefore, we performed detailed geophysical investigations of flank degassing at Masaya volcano, Nicaragua, to constrain numerical models of fluid transport.

We collected magnetic data in a 133 m x 125 m low-temperature fumarole zone on the flank of Masaya volcano, and used these data to infer local geological structures and permeability variations. These structures, and information about the hydrologic system gained from transient electromagnetic soundings (MacNeil et al., 2007), are used to constrain a TOUGH2 numerical simulation. Fluid flux output from the TOUGH2 model is compared with CO₂ flux and self-potential (SP) measurements to create and refine a structural and hydrothermal model of the flank fumarole zone. The consistent spatial distribution of diffuse degassing is then used to constrain a TOUGH2 hydrothermal model of the entire fracture zone along the flank of the volcano.

### 3.2 Methods for Delineating Flow Paths

The geophysical techniques that we employ in this paper are each sensitive to a different rock or fluid property, and each technique provides unique information about the system. Magnetic data are particularly useful for detecting structures in volcanic
terrains, due to the high contrast in magnetic properties between basaltic lava, scoria, and alluvium (Stamatakos et al., 1997). Magnetic profiles and maps have been used successfully to infer geological features such as faults at a number of sites (e.g., Jones-Cecil, 1995; Connor et al., 1997; La Femina et al., 2002), even in granitic areas where the magnetic contrast is relatively small (McPhee et al., 2004). On basaltic volcanoes, magnetic anomalies associated with faults are often on the order of 100-1000 nT, two to three orders of magnitude larger than the magnetic anomalies induced through electrokinetic effects associated with fluid flow (Zlotnicki and Mouel, 1990; Adler et al., 1999).

SP variations result primarily from fluid flow, and therefore provide information about fluid flow paths and rates. Three different relevant mechanisms generate SP anomalies (Bedrosian et al., 2007): thermoelectric, electrokinetic and fluid-disruption effects. Although each can play a part, electrokinetic effects are theoretically larger (Corwin and Hoover, 1979) and most likely to dominate in a low-temperature system like the flank fumaroles at Masaya. Electrokinetic interaction between moving pore fluid and the electric double layer at the fluid-solid interface generates an electric potential gradient that is detectable with SP electrodes (Overbeek, 1952). In extensional tectonic environments volcanic gas and vapor often rise buoyantly along faults (Goff and Janik, 2000), resulting in positive SP anomalies (Zablocki, 1976; Nishida et al., 1996; Michel and Zlotnicki, 1998). Negative SP anomalies around fissures and craters are interpreted as meteoric water recharge (e.g. Sasai et al., 1997).

After water, CO₂ is the most abundant magmatic gas (Finizola et al., 2002), and variations in CO₂ flux can therefore be used to deduce variations in total gas flux
(Chiodini et al., 2005). In low-temperature hydrothermal systems (≤100°C), CO$_2$ emissions likely reflect exsolution from groundwater or a hydrothermal aquifer (Evans et al., 2001). The permeability and porosity of the medium through which the gases travel significantly affect the location and magnitude of surface outflux (Evans et al., 2001; Lewicki et al., 2004). Thus spatial variations in surface CO$_2$ flux can be used to infer fractures and other variations in the subsurface (e.g., Azzaro et al., 1998; Etiope et al., 1999; Finizola et al., 2002).

### 3.3 Geologic Setting

Masaya is a basaltic shield volcano located 20 km south of Managua, Nicaragua (Figure 3.1), and is one of the most persistently active volcanoes in Central America (McBirney, 1956; Stoiber et al., 1986; Rymer et al., 1998). It is bounded by a 12 x 5 km caldera that has been the site of Plinian basaltic eruptions during the last ~6ka (Williams, 1983a; van Wyk de Vries, 1993; Walker et al., 1993; Wehrmann et al., 2006; Kutterolf et al., 2007).
Figure 3.1. (a) Topographic image of Masaya volcano, showing the active crater, Santiago. White dots represent fumaroles zones (Lewicki et al., 2003). The volcano is bounded by Masaya caldera. The inset map shows the location of Masaya volcano within Nicaragua. (b) Digital elevation map of the NE flank of Masaya volcano, highlighted by the black box in (a). The geophysical surveys were carried out at the central fumaroles zone. The fracture zone that we modeled (dashed line) links all three fumaroles zones to the summit craters.

Current activity is limited to an area of small pit craters within the caldera, including Masaya, Santiago, and Nindiri craters (Figure 3.1). Santiago crater is the most active of these and has been the site of very large noneruptive gas flux in recent decades (Stoiber et al., 1986; Horrocks et al., 1999; Burton et al., 2000; Delmelle et al., 2002; Duffell et al., 2003). Crater gas flux and composition are consistent over time (Horrocks et al., 1999) and imply a magma body of approximately 10 km$^3$ (Walker et al., 1993), fed by gas-rich magma that ascends from depth, degasses, and sinks, producing an open, relatively stable system (Stix, 2007). Post-caldera eruptions have also been widespread.
elsewhere within the caldera (Walker et al., 1993; Rymer et al., 1998; Williams-Jones et al., 2003).

On the northeast flank of the volcano, outside of the pit crater network, there is a fault and fracture zone extending some kilometers where water vapor and CO$_2$ are emitted at moderate temperatures (40-80°C; Lewicki et al., 2003; Pearson et al., 2008). This radial fracture zone on the northeast flank of Masaya volcano extends past Comalito cinder cone (Figure 3.1), which apparently formed during the 1772 eruption. The fracture zone is approximately 100 m wide, as suggested by ground penetrating radar (GPR) and magnetic profiles, positive SP anomalies, and elevated CO$_2$ flux and temperature. In some areas along its length it also forms a topographic offset at the surface. There are three fumarole zones along the fracture in the 3-4 km between the summit area and Comalito (Figure 1; Lewicki et al., 2003; Pearson et al., 2008). The third fumarole zone, closest to Comalito cinder cone, hosts some of the highest known CO$_2$ fluxes from low-temperature fumaroles (Lewicki et al., 2003). Carbon isotopes indicate that gases emitted by these fumaroles retain a magmatic component (St-Amand et al., 1998; Lewicki et al., 2003). Changes in temperature at these flank fumaroles correspond to increased volcanic activity at the summit vent (Pearson et al., 2008).

Within the caldera, the groundwater budget is controlled by the balance between meteoric recharge, evapotranspiration, and degassing, which occurs primarily in Santiago crater. This budget, supported by numerical models of groundwater transport, indicates that groundwater flow in the area of Comalito and the radial fracture zone is toward Santiago crater, which acts as a groundwater sink due to vaporization (MacNeil et al., 2007). Thus, it appears unlikely that the source of heat or magmatic gases emitted from
flank fumarole zones is directly beneath Santiago crater. Rather, flank degassing 3-4 km from the active vent suggests the presence of a deeper, more widespread source of heat and gas within the caldera. Our study is primarily concerned with modeling the thermohydrologic conditions that give rise to flank fumarole zones.

3.4 Data Collection and Results

Geophysical studies of the flank fumarole area were completed over several years of field work. During this time there were no discernible changes in the location or nature of flank degassing, and volcanic unrest was limited to lava lake activity and crater collapse in Santiago crater. A total of 4508 ground magnetic measurements were gathered at the middle fumarole zone on the flank of the volcano in August 2007 (Figures 3.1 and 3.2a). They were recorded along approximately parallel transects covering an area of 133 m x 125 m. The readings were taken with a Geometrics, Inc. Portable Cesium Magnetometer G858, which has a sensitivity of 0.01 nT. Measurement locations were recorded using a GPS (Leica Geosystems Inc. GS20 Professional Data Mapper) with an accuracy of approximately 40 cm, using a GPS base station to improve accuracy (baseline < 1 km).

Three SP and CO₂ flux profiles were completed in May 2006. The profiles were approximately parallel and between 95 and 105 m long (Figure 3.2a), depending on topography and dimensions of the fumarole zone. SP measurements were referenced to an electrode at the end of the line outside of the fumarole area and were recorded every 1 m using non-polarizing Pb-PbCl₂ electrodes and a high impedance voltmeter. CO₂ flux measurements were made every 2 m using a LI-COR, Inc. Li-800 portable gas fluxmeter,
which has an error of ±6% and a range of 0-20000 ppm. An SP map was also made from data collected in 2003 and used to interpolate five transects covering the same area as the magnetic measurements.

Magnetic measurements ranged between 32000 and 41000 nT, with an average of 35900 nT (Figure 3.2b; Table 3.1), consistent with the International Geomagnetic Reference Field (35400 nT, 37° inclination, 0.5° declination). There is a NE-SW trending magnetic anomaly of 2300 nT in the eastern portion of the map area. This anomaly corresponds remarkably well to the location and trend of the topographic offset, and is interpreted as a fault. The topographic offset and magnitude of the magnetic anomaly become significantly larger downslope within the fumarole zone. The magnetic anomaly amplitude ranges from 1000 nT along profile d-d' to 2300 nT at profile a-a' (Figure 3.2b; Table 3.1).

SP measurements ranged between -151 and 160 mV, with peak-to-peak amplitudes of 135 to 210 mV along a single profile. There is a NE-SW-trending, 30-m-wide positive anomaly of up to 140 mV along the center of the map (Figure 3.2c). The anomaly decreases gradually to the west, more abruptly to the east. The eastern boundary reaches a minimum of -150 mV, and coincides with the topographic offset. The relative size of the anomalies remained approximately 200 mV between the map measurements in 2003 and the profile measurements in 2006. However, the absolute values were consistently smaller in 2006, with an average measurement of 31 mV in 2003 and -21 mV in 2006, possibly due to seasonal fluctuations in pore water content. Several SP profiles (Figures 3.3 and 3.4) show a gradual increase and then a more rapid decrease.
Figure 3.2. (a) Topographic map of the central fumarole zone, showing offset extending to the NE, and locations of GPS and magnetic measurements (gray dots) and SP and CO$_2$ flux measurements (dashed lines 0-2). (b) Map of magnetic results overlain on topographic contours. The NE-trending positive magnetic anomaly corresponds to the topographic offset. Dashed lines (a-e) show locations of magnetic profiles in Figure 3. (c) SP map overlain on topographic contours. A positive SP anomaly occurs NW of the topographic offset. Dashed lines (A-E) show the locations of SP profiles in Figure 3. (d) Map of magnetic data plotted with SP contour lines.
from NW to SE (Lines 0, 1, 2 and B). The changes are concordant with fault locations estimated from topography and magnetic data.

CO₂ flux measurements varied between 0 and 2200 gm⁻²d⁻¹ (Figure 3.4). Although Line 2 showed some agreement with SP data, CO₂-flux variations were generally more abrupt and less consistent than changes in SP. Elevated CO₂ flux was detected only NW of the topographic offset; there was a complete absence of CO₂ to the SE.

Table 3.1. Statistical results from magnetic, CO₂ and SP surveys

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<th>Observed Mag (nT)</th>
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<th>Min</th>
<th>Ave</th>
<th>SD</th>
<th>Anomaly</th>
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<td>35843.3</td>
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Figure 3.3. Magnetic and SP profiles. Red dots correspond to observed magnetism and black lines to calculated magnetism. The solid green lines are SP profiles captured from the map in Figure 3.2c. Shaded areas represent the structures estimated from magnetic data. The darker shaded unit corresponds to lava with a magnetic susceptibility of of $2 \times 10^{-2}$ (cgs units). The lighter shaded unit corresponds to an overlying veneer of scoria with a magnetic susceptibility of $1 \times 10^{-6}$. Arrows suggest estimated normal faults. Broad (30 m) SP anomalies are observed to the NW side of the estimated faults, with much smaller-amplitude anomalies to the SE.
Figure 3.4. Profiles of SP (solid green lines) and CO$_2$ flux (blue dashes). Measurements were recorded along lines 0-2 in Figure 2a, and show positive anomalies in the NW part of the study area.

3.5 Modeling and Interpretation

3.5.1 Magnetic data

The distribution and dip of faults in the study area was estimated from ground-magnetic data using Geosoft Inc. Oasis Montaj software. The total intensity of magnetization is the sum of the intensity of induced and remnant magnetization (Plouff 1975), and these two magnetization values can be estimated separately. As we are only interested in the total vector of magnetization, we created a model using bulk magnetizations. We assumed constant remnant magnetization because all of the potential magnetic sources at Masaya are much younger than the last reversal of the Earth’s magnetic field (~0.78 Ma; Cande and Kent, 1995), and tectonic rotations are thought to be minimal during this time.

A peak-to-peak amplitude of over 1000 nT is consistent with vertical separation of basalt that has a strong magnetization (e.g., La Femina et al., 2002). We consider the
magnetic source to be a lava flow unit of high bulk magnetization beneath scoria of low bulk magnetization (Figure 3.3b). Modeling is used to estimate depth to the top of lava beneath a veneer of scoria. We used vectors of magnetization of magnitude $2 \times 10^{-2}$ for the lava flow and $1 \times 10^{-6}$ for the scoria. This produces a plausible lava flow structure with a depth < 20 m and a variable depth to the top of the lava of +/- 10 m (Figure 3.3). This structural model and the observed topographic offset indicate the presence of SE-dipping normal faults in the map area.

3.5.2 Hydrothermal models

Numerical modeling of the hydrothermal system was done using the Petrasim interface to the TOUGH2 code. TOUGH2 is a sophisticated program to model multiphase and multicomponent fluid flow, evolved from the MULKOM code (Pruess, 2004). TOUGH2 numerically simulates coupled non-isothermal heat and fluid transport through porous media. Thermodynamic conditions according to the steam-table equation (International Formation Committee, 1967) are used to calculate phase transitions, so that gases and liquids can be included. The effects of capillary pressure and relative permeability of each phase are calculated as a function of phase volumetric fraction. Full details of the model can be found in Pruess (1991).

3.5.2.1 Vadose zone

Our various geophysical data and models provide constraints on the shallow hydrothermal system. Transient electromagnetic soundings throughout the caldera indicate that the groundwater table is approximately 250 m beneath the surface in the study area (MacNeil et al., 2007). Magnetic data and models are consistent with a faulted
terrain, dominated in this area by steeply dipping (60°) normal faults. SP and CO₂-flux data indicate that these faults serve as barriers to flow, rather than enhancing flow along the fault plane. Shallow temperature measurements recorded over a period of years at five different depths at Comalito cinder cone show average temperatures of between 46 and 74°C, and maximum temperatures of between 61 and 82°C (Figure 3.5). The average near-surface maximum temperature over all the depths is 73°C. Thus the hydrothermal system should be locally dominated by upward flow of fluids through the footwalls of these faults, with near-surface temperatures of ~70°C.

![Figure 3.5. Example time series of fumarole temperature recorded at Comalito cinder cone. The average near-surface temperature is 70°C, used as a constraint in the numerical modeling. Temperature anomalies correspond to episodes of minor volcanic activity in Santiago crater (see Pearson et al. 2008).](image)

We created a 30 by 30 rectangular grid 500 m wide and 250 m deep (Figure 3.6c). These dimensions correspond to the width of the fracture zone (and slightly beyond), and to the approximately 250-m-deep water table (MacNeil et al., 2007). Within the grid, impermeable faults dip at approximately 60° (Figure 3.6c). The entire model was initially at atmospheric pressure and contained moist air (99% air, 1% water vapor). The upper
Figure 3.6. (a) SP measurements recorded along profile C-C’ (Figure 4.3b) in 2006. (b) Modeled vertical fluid flux along a profile just below the surface, using the geometry in (c). (c) Geometry used in a TOUGH2 model to represent vadose-zone conditions. Other parameters used in the model can be seen in Table 2. (d) Output of the TOUGH2 model after injecting heat at 3 W/m$^2$ for 250 years. Black arrows represent gas flow, and colored contours show temperature. Heat and fluid flux increase toward the footwall of each fault. (e) Output of TOUGH2 model after injecting heat at 4.5 W/m$^2$ and moist air at $1 \times 10^{-4}$ kg/s for 250 years. Fluid flow and temperature increase significantly toward the footwall of each fault.
boundary of the model domain was fixed at atmospheric pressure, 20°C, 99% air, and 99% porosity (to represent the atmosphere). Both of the vertical boundaries were impermeable to represent the limit of the fractured/faulted zone. The interior of the model was initially 20°C. The bottom boundary, corresponding to just above the water table, was at 100°C. Heat and/or fluid were injected uniformly along the base of the model, with the rate of injection determined by comparison of model outputs with observed surface temperatures. Bulk permeability was similarly determined. Other parameters (Table 3.2) were measured by Chiodini et al. (2005), MacNeil et al. (2007), or are typical of fractured basalt. The model was run for 250 years, the length of time since this area last saw surface volcanic activity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock density</td>
<td>kg/m³</td>
<td>2000</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>Permeability of vadose zone rock</td>
<td>m²</td>
<td>1 x 10⁻⁸</td>
</tr>
<tr>
<td>Permeability of fault</td>
<td>m²</td>
<td>1 x 10⁻²⁰</td>
</tr>
<tr>
<td>Permeability of saturated zone rock</td>
<td>m²</td>
<td>1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Wet heat conductivity</td>
<td>W/m°C</td>
<td>1.43</td>
</tr>
<tr>
<td>Specific heat</td>
<td>J/kg°C</td>
<td>850</td>
</tr>
<tr>
<td>Enthalpy of water</td>
<td>J/kg</td>
<td>4.19 x 10⁵</td>
</tr>
<tr>
<td>Enthalpy of steam</td>
<td>J/kg</td>
<td>1.27 x 10⁵</td>
</tr>
</tbody>
</table>

After 250 years of heat injection moist air is circulating steadily, primarily controlled by the geometry of faults (Figure 3.6d). Convection cells develop on each side of both faults, with the largest gas fluxes occurring between the two faults (Figure 3.6b). Upward flow of gas increases towards the footwall of each fault, and becomes negligible over the faults. This effect is particularly distinct near the surface. Close to both vertical
boundaries gas flows downward. Temperatures correlate with gas flux, increasing near the footwall of each fault. The maximum near-surface temperature is 70°C and the maximum temperature over the entire model domain is 175°C. The maximum temperature occurs where hot gases are trapped between the two faults.

When fluid is injected in addition to heat, fluid flow is enhanced across the entire model. There is a more even surface-temperature distribution, with a maximum near-surface temperature of 70°C and a maximum temperature of 99°C overall. Gas flux and heat flow are enhanced in the footwall of the left-hand fault compared to the model without mass injection (compare Figures 3.6d and e). The hanging wall of the right-hand fault is isolated from fluid injection, and fluid circulation there is the same in both models.

Permeability and heat-injection rate are both unknown, but can be partially constrained by the known surface temperature. The measured surface temperature of 70°C can be modeled with a permeability between $3.5 \times 10^{-9}$ and $3 \times 10^{-8}$ m$^2$ and heat-injection rates of 2.4 to 9 W/m$^2$ for the heat-injection-only case (Figure 3.7a). Within this range there is a threshold permeability for convection. Below this permeability value the relationship between heat injection and temperature is approximately linear. For convection-dominated systems ($k > \sim 3.5 \times 10^{-9}$ m$^2$) higher permeabilities require higher heat injection rates to attain temperatures of >70°C. In Figure 3.6, we used an intermediate permeability of $1 \times 10^{-8}$ m$^2$ and a heat-injection rate of 3 W/m$^2$ to show representative gas flux within the system. These values are within the fully convective regime.
When both heat and fluid are injected, fluid flow is enhanced. Much lower permeabilities, and a wider range of permeabilities, can support a surface temperature of 70°C (Figure 3.7b). To obtain the results shown in Figures 3.6e and 3.7b, moist air (99% air, 1% water) was injected along the base of the model at a rate of $1 \times 10^{-4}$ kg/s. Above a high-permeability threshold of about $10^{-8}$ m$^2$, temperature decreases with increasing permeability. For a model permeability of $1 \times 10^{-8}$ m$^2$, a larger heat injection rate (4.5 W/m$^2$) is required for the near-surface temperature to reach 70°C, compared to the heat injection rate required without fluid injection (3 W/m$^2$).

Figure 3.7. Near-surface temperature as a function of permeability. Numbers labeling the curves are heat-injection rates in W/m$^2$. a) Heat injection only; b) Injection of both heat and moist air. The observed temperature of 70°C (grey line) can be matched with a range of conditions.
The magnetic models suggest a shallow scoria layer underlain by lava. However, a uniform permeability distribution appears to give the best fit to the data. Adding a more permeable shallow layer causes the heat and gas flux to become more focused. Adding a less permeable layer results in more even temperature and gas-flow-rate distributions (Figure 3.8). We infer that although fractured lava and scoria have very different magnetic properties, they have similar permeabilities.

Permeability and heat input affect fluid velocities as well as the temperature and gas distribution at the surface. Maximum gas velocities vary from $5 \times 10^{-4}$ m/s in the low-permeability models to $2 \times 10^{-1}$ m/s in a system with a high permeability of $10^{-7}$ m$^2$ and a heat input of 35.5 W/m$^2$. This implies travel times ranging from 20 minutes to 5 days between the water table (250 m depth) and the surface. The velocity for our average model (permeability $1 \times 10^{-8}$ m$^2$, heat injection 3 W/m$^2$) was $5.5 \times 10^{-3}$ m/s, resulting in a minimum travel time of 13 hours. The maximum surface gas flux from our average model was $1.4 \times 10^{-2}$ kg/s and the maximum surface heat output was 105 W/m$^2$, comparable to the 91 W/m$^2$ measured at Comalito (Chiodini et al., 2005). Injecting fluid as well as heat did not appear to significantly affect these values.
Figure 3.8. Fluid flow and heat transfer when there is a strong permeability contrast between the scoria and lava layers. Top: Overlying scoria is two orders of magnitude more permeable than lava. Bottom: Scoria layer is two orders of magnitude less permeable.

3.5.3.2 Saturated zone

The degassing system at Masaya volcano is unusually stable and open, and the consistent spatial distribution of diffuse degassing can be used to infer spatial variations in fluid flux at depth. The three distinct fumarole zones along the fracture zone on the flank of Masaya volcano (Figure 3.1) are all characterized by stable and consistently
elevated temperature and CO₂ flux. Soil temperatures at the Comalito cinder cone fumarole range between 55 and 80°C (Pearson et al., 2008), and are similar to those measured at the fumarole closest to the crater (38 to 83°C). Measured CO₂ fluxes are similar at all three fumarole zones, varying between 2000 and 2255 g/m²/d. At Comalito cinder cone, measured gas fluxes are stable over remarkably long periods of time, varying by less than 10% from average over 5 months. The uniformity in temperature and CO₂ flux across the three fumarole zones suggests that they share a common source. Gases at Comalito cinder cone, 3.5 km from the active crater, retain a magmatic component (Lewicki et al., 2003), but as groundwater flow is from Comalito toward the active crater (MacNeil et al., 2007) there must either be separate magmatic sources, or one extensive source at depth. Lava lake formation in the active crater in 2006 corresponded to changes in temperature at the Comalito cinder cone fumaroles (Pearson et al., 2008), suggesting that there may in fact be an areally extensive magmatic source at depth beneath the caldera.

We created a TOUGH2 model of the saturated zone, to determine whether variations in fluid flux at depth could result in the three distinct fumarole zones observed at the surface. A square 30 by 30 grid extended over 3500 m was used to represent the entire length of the fracture zone (Figure 3.9a). A depth of 3500 m was assumed for simplicity, as there is no information to constrain depth to the heat source. Heat and/or fluid was injected at various rates along the bottom boundary, and the entire model was fully saturated and under hydrostatic pressure (Table 3.2; Figure 3.9a). Vertical boundaries were impermeable to reflect the limit of the fractured area. This model was also run for 250 years.
Figure 3.9. (a) Geometry used for numerical model, representing a cross-section of the flank fracture at Masaya (Figure 4.1b). The system is fully saturated. (b) Results show that convection of groundwater can create three zones of elevated fluid flux and temperature at the surface in a homogeneous fracture above a uniform heat source.
TOUGH2 modeling shows that injecting liquid evenly into the base of the model at 20 kg/s (2/3 kg/s into each cell) results in convection along the length of the fracture system (Figure 3.9b). With a permeability of $10^{-10}$ m$^2$, three distinct zones of elevated temperature and fluid flux result. The maximum temperature is 70°C near the surface and 91°C overall, with a near-surface fluid flux of 4 kg/s. Similar results are found for a heat injection rate of 600 W/m$^2$. Higher and lower injection rates result in hotter and cooler temperatures, respectively. The number of plumes can also vary. Permeability and model and dimensions similarly affect maximum temperature and the number of plumes created, for example a model that is twice as wide has twice as many plumes.

Constant heating at depth could potentially cause convection in both the vadose and saturated zones. Simple calculations can show whether convection is likely along the fracture, either within the saturated or unsaturated zone. The onset of convection depends on the porous-media Rayleigh number (Zhao et al., 2003):

$$Ra = \frac{(\rho_0)^2 c_p g \beta \Delta T k_0 H}{\mu \lambda_0}$$

Substituting values appropriate for the vadose zone at Masaya volcano (Table 4.3; Zhao et al., 2003; Chiodini et al., 2005; MacNeil et al., 2007) yields:

$$Ra = \frac{0.62 \times 2000 \times 1.1 \times 7 \times 10^{-4} \times 80 \times 1 \times 10^{-8} \times 250}{1.2 \times 10^{-5} \times 1.43} = 58$$

for gases within the vadose zone. The critical Rayleigh number is given by (Zhao et al., 2003):

$$Ra_{critical}^{2D} = \frac{[1 + (H_3/H_2)^2]^2 \pi^2}{(H_3/H_2)^2}$$

$$Ra_{critical}^{3D} = \frac{[1 + (H_3/H_1)^2 + (H_3/H_2)^2]^2 \pi^2}{(H_3/H_1)^2 + (H_3/H_2)^2}$$

70
where $H_1$ is the length of the fracture, $H_2$ is its thickness, and $H_3$ its height. For this two-dimensional approximation to be valid, $H_2 \ll H_3$, which is only the case for our models of the saturated zone. We find that convection readily occurs along the fracture within the saturated zone (Table 3.4). However, within the vadose zone natural convection is not expected to occur with a uniform heat source at the groundwater table. Thus, the spacing, temperatures and gas fluxes in the fumaroles areas distributed along the fracture are most consistent with groundwater convection. It is also noted that the shape of this convecting system is not significantly affected by lateral groundwater movement.

Table 3.3. Parameters used in Rayleigh number calculations. Where two values are listed, the first is for water in the saturated zone and the second for gas in the vadose zone

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value water/steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_0$</td>
<td>W/m°C</td>
<td>1.43</td>
</tr>
<tr>
<td>$H$</td>
<td>m</td>
<td>250</td>
</tr>
<tr>
<td>$k_0$</td>
<td>m²</td>
<td>$1 \times 10^{-10}$/$1 \times 10^{-8}$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>J/(kg°C)</td>
<td>4185 / 2000</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>kg/m³</td>
<td>1000 / 0.6</td>
</tr>
<tr>
<td>$\beta$</td>
<td>K⁻¹</td>
<td>$2 \times 10^{-4}$/$7 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Ns/m²</td>
<td>$1 \times 10^{-3}$/$1.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Table 3.4. Parameters used to determine whether convection will occur along the fracture at Masaya volcano

<table>
<thead>
<tr>
<th>Model</th>
<th>$H_1$</th>
<th>$H_2$</th>
<th>$H_3$</th>
<th>$Ra$</th>
<th>$Ra_{crit}$</th>
<th>Convekt?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vadose zone</td>
<td>3500</td>
<td>100</td>
<td>250</td>
<td>58</td>
<td>83</td>
<td>No</td>
</tr>
<tr>
<td>Saturated zone</td>
<td>3500</td>
<td>100</td>
<td>3500</td>
<td>$1.6 \times 10^5$</td>
<td>$1.1 \times 10^5$</td>
<td>Yes</td>
</tr>
</tbody>
</table>

3.6 Discussion

Interpretation of magnetic traverses on the flank of Masaya volcano suggest that SE-dipping normal faults redirect upward fluid movement (e.g., Figure 3.3b). This has a strong effect on mass flux, soil gas concentrations, and fumarole temperature. Numerical modeling shows that relatively impermeable faults dipping at 60° focus flow in the footwalls, and inhibit flow in the hanging walls (Figures 3.6b, 3.6d, 3.9). Positive SP and CO$_2$ anomalies to the NW, in the footwall of the main fault, are in excellent agreement with this model, as is a complete absence of CO$_2$ and a small SP anomaly to the SE (Figures 3.3, 3.4, 3.6). The small negative SP anomaly to the SE could result from circulation in the hanging wall, as seen in the model, or from near-surface permeable sediments and/or fractured bedrock channeling fluid away from the fault. However, the second possibility cannot explain the large positive SP anomaly observed in the footwall (Goff and Janik, 2000; Hochstein and Browne, 2000).

Normal faults dipping at 60° and extending to the water table can explain the distinct distribution of CO$_2$ and SP anomalies observed at the surface. More steeply dipping faults would result in sharper and more localized anomalies than we observe (Figures 3.4 and 3.5a; Goff and Janik, 2000; Hochstein and Browne, 2000). For a water table at 250 m depth, a 60° normal fault would channel fluids to the surface from an
approximately 150 m wide area. This is generally consistent with the dimensions of the top of a single convection cell in our saturated-zone modeling (Figure 3.8c).

Figure 3.10. Conceptual model of the hydrothermal system at Masaya volcano, as determined by geophysical observations and numerical models. On a km scale, groundwater convection is a dominant control on fluid flux. Uniform heat injection at depth creates three zones of elevated fluid flux and temperature. Within the vadose zone, relatively impermeable faults redirect shallow fluid flow. The line marked with an open triangle represents the water table.

Numerical models are influenced by system geometry, heat injection rate, and rock permeability. Although the fracture geometry at Masaya volcano is constrained by surface features and GPR and magnetic surveys, heat injection rate and permeability are unknown. Permeability of basalt is typically in the range of $10^{-14}$ to $10^{-9}$ m$^2$ (Freeze and Cherry, 1979; Ingebritsen and Scholl, 1993; Saar and Manga, 1999), with young, unaltered basalt in the range of $10^{-11}$ to $10^{-9}$ m$^2$ (Ingebritsen, 2009). Our inference of 3 x
$10^{-9}$ to $3 \times 10^{-8}$ m$^2$ within the vadose zone is reasonable for the highly fractured basalt of our study site. Our inferred saturated-zone permeability of around $10^{-10}$ m$^2$ is within the range of measured basalt permeabilities worldwide. It is orders of magnitude lower than our inferred vadose-zone values, consistent with the fact that the permeability of basalt decreases with depth (Ingebritsen and Scholl, 1993). The fracture zone is however still relatively permeable, possibly explaining why it hosts the only extensive hydrothermal feature observable outside of the crater at Masaya volcano (MacNeil et al., 2007). Such focused degassing has also been observed at other volcanoes (Chiodini et al., 2001).

Although faults are often assumed to be permeable conduits to flow (e.g., Evans et al., 2001), the faults in our vadose zone models are relatively impermeable. Previous studies have shown that permeability can vary by several orders of magnitude within a fault (Manzocchi et al., 2008), and/or can create a predominantly low-permeability zone with channels of high permeability (Marler and Ge, 2003; Fairley et al., 2003). Permeability is a function of fracture dilatancy, cementation, compaction, clay formation, deformation stress and temperature histories, micro-cracking of dense rock, chemical alteration, diagenesis, and mineral precipitation (Goff and Gardner, 1994; Goff and Janik, 2000; Fisher and Knipe, 2002; Wibberley and Shimamoto, 2003; Bernabe et al., 2003). Low-permeability fault gouge may be present, as at Elkhorn Fault Zone, South Park Colorado, USA (Marler and Ge, 2003). Fault geometry can also be important. Caine et al. (1996) showed that a fault zone can be divided into fault core, fractured damage zone, and undeformed protolith. The fault core may be clay-rich, brecciated and/or geochemically altered, resulting in a low permeability. If the fault core is large relative to the fault as a whole, the overall permeability will be low. In addition, Caine et al. showed
that small damage width of a fault (relative to its total width) will result in localized strain which inhibits flow, acting as a low-permeability zone. There are therefore a number of ways that the faults at Masaya volcano could behave as low-permeability zones that redirect fluid flow.

To recreate the surface temperatures observed at Masaya volcano we had to estimate both permeability and heat-injection rate. When heat alone is injected into the base of the vadose zone, vadose-zone permeabilities of $3 \times 10^{-9}$ to $3 \times 10^{-8}$ m$^2$ and heat-injection rates of 2.4 to 9 W/m$^2$ are required to match observed surface temperatures of ~70°C (Figure 3.7a). When both moist air and heat are injected into the base of the vadose zone, vadose-zone permeabilities of $<1 \times 10^{-8}$ m$^2$ and heat-injection rates of 4.5 to 6 W/m$^2$ are required to match observed surface temperatures (Figure 3.7b). Our preferred heat-injection rates of 2.4 to 9 W/m$^2$ are less than the measured heat output of 91 W/m$^2$ at Comalito cinder cone (Chiodini et al., 2005), but our model extends beyond the surficial-degassing area, and maximum values are comparable.

Gas velocities within the vadose zone suggest travel times on the order of hours to days. This is compatible with observations; fumaroles are known to respond to changes at depth, but there is generally a time lag. The maximum gas flux from our average model was $1.4 \times 10^{-2}$ kg/s, orders of magnitude less than the 400 kg/s measured in the active crater several kilometers away by Burton et al. (2000). The maximum heat output was 105 W/m$^2$, within 20% of that measured by Chiodini et al. (2005) at Comalito Cinder cone and representative of volcanoes worldwide (Harris and Stevenson, 1997).

Numerical modeling shows that even with totally uniform fluid injection, three distinct and stable fumarole zones can develop along a fracture zone (Figure 3.8c).
However, extremely high heat injection rates would be required for natural convection to take place. Injecting fluid results in forced convection with a simulated surface gas flux of 4 kg/s, two orders of magnitude smaller than that measured by Burton et al. (2000) in the active crater. The total heat output of 250 MW along the 1-m wide fracture zone is much greater than the 0.9 MW estimated for one fumarolic zone at Comalito (Chiodini et al., 2005). This value is typical of much larger degassing fields (e.g., Karapiti geothermal field, Hochstein and Bromley, 2001; Hakone volcano, Iriyama and Oki, 1978; Solfatara volcano, Chiodini et al., 2001). Smaller heat fluxes can be created by our models, but result in lower temperatures. Our simplified two-dimensional saturated-zone model does ignore potentially important complications such as topography, variations in hydraulic properties, and lateral heterogeneities along and within the fracture. For example, magnetic and GPR measurements suggest that the width of the fracture zone varies along its length. Work by Méheust and Schmittbuhl (2001) and Neuville et al. (2006) has shown that fracture roughness can enhance or inhibit flow. We think that these complex heterogeneities play a role in channeling groundwater and gas flow, but that convection is also a fundamental control.

3.7 Conclusions

Geophysical measurements and numerical modeling show that fluid flux at Masaya volcano is controlled by faults on a local scale at very shallow levels (10s of meters), and by groundwater convection in a flank fracture on the kilometer scale. Magnetic measurements in 2007 detected a NE-SW trending anomaly of 2300 nT to the east of our study area that coincides with surface topographic offset. Modeling of this
data suggests relatively impermeable faults dipping SE at 60°. Numerical models including the faults show fluid flux increasing toward the footwalls and becoming negligible over the faults. Small amounts of circulation also occur in the hanging wall of one modeled fault. This is in excellent agreement with elevated SP and CO₂ flux to the NW of the fault, and small SP values and an absence of CO₂ to the SE.

Numerical models show that the three fumarolic zones observed within the 3-4 km fracture on the flank of Masaya volcano can be explained by convection of groundwater within the saturated zone. The number of convection cells and their dimensions are dependent on fracture geometry, rock permeability, and heat injection rate. The picture is further complicated by heterogeneities within the fracture zone, including faults that control fluid flux within the vadose zone and result in complicated degassing patterns at a local scale.

From our geophysical surveys and models we conclude that within a generally high-permeability fracture zone on the flank of Masaya volcano there are faults and other variations that create localized low-permeability zones. Faults at the central fumarolic zone redirect fluid and heat from a ~150-m-wide diffuse source that results from groundwater convection below the water table. Relatively uniform heat and fluid transport from depth is focused by permeability variations at several scales in the upper ~3 km of the caldera section. Fluids take hours to days to travel from the water table to the surface. A good understanding of the subsurface geology is therefore vital when attempting to understand the sources of both spatial and temporal variations in diffuse degassing.
CHAPTER 4

NUMERICAL MODELING OF FLANK FUMAROLE TEMPERATURE VARIATIONS RELATED TO VOLCANIC ACTIVITY

4.1 Introduction

Fumarole temperature measurements are used as a volcano monitoring tool around the globe. They have three distinct advantages over other methods; 1) fumaroles result directly from degassing of magma, 2) measurements are relatively inexpensive, 3) flank fumaroles can provide easier and safer access than crater sites. However, evidence of a clear link between volcanic activity and fumarole temperatures has proved elusive (e.g., Barquero, 1988; Zimmer and Erzinger, 2003; De Gregorio et al., 2007). Observed variations in fumarole temperature have generally been attributed to changes in gas flux (Richter et al., 2004; Chiodini et al., 2007; De Gregorio et al., 2007), or to variations in mixing between magmatic gases, meteoric waters and hydrothermal waters (Tedesco et al., 1991; Todesco et al., 1997; Zimmer and Erzinger, 2003). However, these conceptual models are difficult to test and may be indeterminate.

Numerical modeling provides a powerful tool to relate measured surface temperature variations to changes in the hydrothermal system at depth. However, this has been limited by the lack of eruptive volcanic activity during sampling periods (e.g., Tedesco et al., 1991; Connor et al., 1993b; Zimmer and Erzinger, 2003), or by sampling
rates on the order of hours (De Gregorio et al., 2007) to weeks (Granieri et al., 2003) to months (Barquero, 1988). Steady-state models of gas flow at fumaroles have shown that surface temperatures are strongly dependent on source depth, mass flow rate, gas velocity, conduit/fracture geometry and surrounding rock properties (Connor et al., 1993b; Stevenson, 1993), but have been unable to describe time-varying properties, for example the dependence of fumarole temperature (and mass flow) on atmospheric pressure at Colima volcano, Mexico (Connor et al., 1993b).

More detailed models of fumaroles have been created that attempt to simulate time-varying parameters. Todesco et al. (2003) created a model of the hydrothermal system at Phlegrean Fields, Italy based on gas composition, which showed that permeability is a major control on surface diffuse degassing. Changes in the source fluid would also be reflected at the surface, but only after several years. Increased injection was shown to cause rock deformation that is detectable much more rapidly than changes in the gas composition (Todesco et al., 2004). Of particular interest, however was the ability to model changes in the hydrothermal system that corresponded to variations in gravity signals recorded at the Phlegrean Fields. By varying the injection rate of gases, their composition, and the duration of injection, both the variable surface gas composition and gravity trends could be replicated (Todesco and Berrino, 2005). These models showed that the changes observed can be explained by a pulsing source of hot fluid, which releases large amounts of CO₂-rich fluid and affects hydrothermal circulation (Todesco and Berrino, 2005). However, a more recent change in gravity and gas enrichment could not be explained numerically by this model, reflecting the complexity of the volcanic system (Todesco et al, 2006).
Here, we model variations in fumarole temperature recorded at Masaya volcano, Nicaragua. We recorded temperatures every five minutes at a low-temperature flank fumarole, including during episodes of minor volcanic activity at the crater (Pearson et al., 2008). This provides an exceptional opportunity to study the details of the relationship between fumarole temperature and volcanic activity. We used the multiphase, multicomponent fluid flow code TOUGH2 to create a numerical model of the system, using constraints provided by previous geophysical studies (MacNeil et al., 2007; Pearson et al., submitted). During almost three years of continuous temperature monitoring we detected four episodes of very distinct temperature signals which corresponded with variations in volcanic activity observed in the crater. Comparison of these signals with TOUGH2 simulations of the hydrothermal system allows us to make quantitative estimates of heat transfer and gas flux, thereby improving our understanding of the response of the hydrothermal system to changes in activity.

4.2 Geologic setting

Masaya volcano in Nicaragua (Figure 4.1) is a shield volcano remarkable for its stable, open and persistently degassing system. The active vents lie within a 12 x 5 km caldera, formed at least in part during Plinian eruptions during the last ~6 ka (Williams, 1983a; van Wyk de Vries, 1993, Wehrmann et al., 2006; Kutterolf et al., 2007). The most recent voluminous eruption occurred in 1772, when lava flows covered the northern part of the caldera floor. Comalito cinder cone is thought to have formed at that time (Rymer et al., 1998). Degassing is currently largely localized at Santiago crater (Figure 4.1), where a small lava lake is sometimes visible (Stoiber et al., 1986; Walker et al., 1993;
Delmelle et al., 2002). During the last decades, activity has been characterized by small ballistic eruptions from Santiago crater and the occasional presence of the lava lake (Horrocks et al., 1999; Duffell et al., 2003; Stix, 2007).

To the northeast of the active summit complex, 3.5 km from and 200 m below Santiago crater, is Comalito cinder cone (Figure 4.1). The two areas are linked by a 3-4 km fracture that is ~100 m wide as suggested by GPR, magnetics, and a topographic offset observed at some points along its length (Pearson et al., in review). The fracture zone hosts outflow of CO₂ and elevated temperatures (~40-80°C) at a number of distinct

Figure 4.1. a) Topographic image of Masaya volcano. Grey lines correspond to groundwater contours at depth (in masl), with the potentiometric low centered about Santiago crater (MacNeil et al., 2007). Arrows show the inferred directions of groundwater flow. The star represents Comalito cinder cone. Inset map shows the location of Masaya volcano in Nicaragua. b) Aerial photograph showing location of studied fumaroles adjacent to Comalito cinder cone on the flank of Masaya (Instituto Nicaraguense de Estudios Territoriales; W. Strauch, 2006, personal commun). Dashed line respresents the fracture zone.
sites along its length (Lewicki et al., 2003; Pearson et al., 2008). One of these fumarole zones, 250 m to the northwest of Comalito cinder cone, has some of the highest known CO₂ fluxes from low-temperature fumaroles (Lewicki et al., 2003). Carbon isotopes indicate that these gases retain a magmatic component (St-Amand, 1999; Lewicki et al., 2003). Pearson et al. (2008) used spectral analysis of time series to show that variations in fumarole temperature at this site correspond to changes in volcanic activity at Santiago crater (Figure 4.1b).

The caldera boundary has comparatively low permeability, which essentially isolates the local hydrologic system (Figure 4.1a; MacNeil et al., 2007). Meteoric recharge in the caldera is balanced by groundwater vaporization at Santiago vent and along the fracture zone and by evapotranspiration, which includes evaporation from Laguna Masaya in the east. As a result, groundwater in much of the caldera, including near the Comalito fumarole zone, flows toward the Santiago vent (Figure 4.1a; MacNeil et al., 2007). Therefore flank degassing is unlikely to result from direct flow of gases at shallow depth from Santiago crater, but rather from a deeper, more widespread source. Numerical modeling shows that the distinct fumarole zones along the fracture could result from convection of groundwater at depth, with gases being redirected locally by faults and similar permeability variations within the caldera section as they travel through the vadose zone to the surface (Pearson et al., in review). Flank fumarole temperatures therefore result from a combination of volcanism, groundwater flow and subsurface geology, and are likely to have complex variations that require both conceptual and numerical modeling to explain.
4.3 Fumarole temperature data

Fumarole temperatures were recorded to five different depths at Comalito cinder cone from May 2006 to November 2009 (Figure 4.2). During this time there were five distinct periods of temperature anomalies, identified primarily from interpretation of the frequency spectrum (Pearson et al., 2008; see Appendix C). The first two, in June and October 2006 (Figure 4.3a and b), corresponded extremely well with a period of vent widening and elevated degassing in the crater, and with development of a small lava lake, respectively. Almost exactly one year later, in June and October 2007, very similar temperature anomalies were recorded (Figure 4.3c and d). Volcanic activity is less obviously correlated, but in July 2007 the degassing changed to a more explosive, ash-rich phase and in October 2007 new fumaroles formed in the active crater.

The fifth temperature excursion, on 29 May 2008, was around the same time as an ash explosion, immediately after Tropical Storm Alma made landfall less than 100 km away (Figure 4.2; Global Volcanism Report, 2010; Tenorio et al., 2010). It was the first tropical storm in recorded history to make landfall on the Pacific coast of Nicaragua (Knabb and Blake, 2008). The intense rainfall can be seen in Figure 4.3e, as can a temporary cooling of the fumarole zone that becomes less distinct with depth. The extremely rapid cooling that was only observed at the shallowest thermocouple and the one 7 m away likely resulted from pooling of rainwater as sealant decay allowed water into the tubes containing the sensors. The thermocouple 7 m away was on a hill in a different area than the other sensors, and its temperature signals changed noticeably with respect to the other thermocouples after it was vandalized in July 2007.
Figure 4.2. Flank fumarole temperature measurements. Numbers represent the depth of each thermocouple in cm. Grey lines highlight the episodes with anomalous temperatures.
The fumarole temperature signals during the first four anomalies have a repetitive and distinct signature that provides constraints on its source. At background state the fumarole temperatures have diurnal and semi-diurnal fluctuations, controlled by solar and tidal variations (Figure 4.3f). During the temperature anomalies their diurnal signal is lost. Instead, there is a rapid increase in temperature over 20 minutes, followed by an exponential decrease, and then a rapid decrease to background level (Figures 4.3a-d). Each of these cycles lasts approximately one day, with 10-16 cycles per episode. The cycles were observed at each thermocouple, although the amplitude of the responses varied between thermocouples. Rainfall appears to be a contributing factor as 34% of the rapid increases in temperature coincided with rainfall events (Figure 4.3a-d). However, 405 of the 611 temperature spikes did not occur during rainfall, and there were 7237 rainfall events (out of 7443) that did not have associated temperature spikes. Similarly, significant rainfall events like Tropical Storm Alma and the first rainfall of the rainy season did not have appear to be related to significant temperature increases (Figure 4.3e and f).

The timescales and amplitudes of the fumarole temperature variations, their repetitive but non-diurnal nature, and their consistent return to background level provide important clues about the change in the hydrothermal system during these anomalous episodes. For example, changes in temperature were far too rapid (both increasing and decreasing over about 20 minutes) to be associated with advection of fluids from near the active crater. TOUGH2 models were developed to explore the heat and mass transfer conditions that could give rise to these cycles.
Figure 4.3. Details of fumarole temperature measurements. Rainfall is shown along the bottom of each graph. Depths of thermocouples are as in Figure 5.2. a) During vent widening in the crater; b) During lava extrusion in the crater; c) Prior to the degassing becoming more ash-rich; d) During new fumarole activity in the crater; e) During Tropical Storm Alma; f) During the first rainfall of the season, after several months with no rain.

4.4 Numerical modeling

The Petrasim interface to the TOUGH2 code was used to simulate the fumarole system at Comalito cinder cone. TOUGH2 is a sophisticated program to model multiphase and multicomponent fluid flow, based on the MULKOM code (Pruess, 2004). TOUGH2 numerically simulates coupled non-isothermal heat and fluid transport through porous media. Thermodynamic conditions according to the steam-table equations (International Formation Committee, 1967) are used to calculate phase transitions,
allowing gases and liquids to be included. The effects of capillary pressure and relative permeability of each phase are calculated as a function of phase volumetric fraction. Full details can be found in Pruess (1991).

The distinctive signals recorded during the anomalous temperature episodes (Figures 4.3a-d) provide constraints on the mechanisms to include in numerical models. In each cycle the initial temperature increases were on the order of minutes, and the entire temperature response generally took less than one day. As flow of groundwater is on the order of meters per day (MacNeil et al., 2007) it would take months for groundwater to flow from the crater to the fumarole, even were it not for the fact that groundwater flows predominantly toward the crater rather than away. Therefore it is unlikely that the anomalies are due to direct flow of gases or heated groundwater from near the crater. Similarly, flow of fluids from an extensive magma source at several kilometers depths would take a minimum of hours but more likely days to reach the surface. For fumarole temperatures to increase by up to 10°C over 20 minutes, the source of these anomalies must be shallow, either within the vadose zone or at the groundwater table at 250 m depth (MacNeil et al., 2007). Numerical models allow us to explore possible sources of these local phenomena.

Previous studies at Comalito cinder cone have shown that within the high-permeability fracture zone, the fumarole zone is a site of constantly elevated gas flux and temperature (Lewicki et al., 2003, Pearson et al., 2008). Gas and heat flux are concentrated along near-vertical profiles controlled by relatively impermeable faults and other small-scale permeability variations (Pearson et al., in review). Therefore we created a model perpendicular to the NE-trending fracture zone, focusing on the central 1-m wide
(assumed for simplicity) high-permeability zone and the surrounding few meters (Figure 4.4a). As this is all within the fracture zone the entire area still hosts outflow of CO$_2$ and elevated temperatures, but the higher permeability means that flow is focused along the central zone and decreases rapidly with distance from it.

To simulate this cross-fracture model we created a 30 by 30 grid, spanning 30 m in width and 250 m in depth (Figure 4.4a). 250 m is the depth to the water table near Comalito cinder cone based on transient electromagnetic soundings (MacNeil et al., 2007), and forms the lower boundary of our vadose-zone model. The model has a permeability of $1 \times 10^{-12}$ m$^2$, except for a 1-m wide zone with permeability of $1 \times 10^{-8}$ m$^2$ that corresponds to the fracture (Pearson et al., in review). The entire model was initially at atmospheric temperature and pressure, containing 99% air to represent the moist air in the vadose zone. The vertical edges of the model space had no-flow conditions. The upper boundary cells represent the atmosphere, and were multiplied by a volume factor of $10^{50}$ so that they had a fixed temperature and pressure but allowed flow to pass from the ground into them. The entire lower boundary was the site of injection of uniform gas at 0.5 kg/s.

The temperature of the injected gas is an important variable, and is determined by its enthalpy. For simplicity, we used air to simulate volcanic gases. As the system is below 100°C, steam is only present as moisture content within the air. Enthalpy is a thermodynamic measure of the heat content of a system, approximated by:

$$h = c_{pa} T + x(c_{pw} T + h_{we})$$
Figure 4.4. a) TOUGH2 model geometry. Flow is concentrated vertically along the NE-trending, high-permeability zone at the center of the fracture zone. The model is perpendicular to the fracture zone, with grey cells corresponding to the high-permeability core. Flow decreases rapidly moving away from this zone. Modeled surface fumarole temperature is from the fracture-core cell below the boundary (output cell). b) Conceptual model of changes in the system that produce the temperature curves to the right.
where $c_{pa}$ is the specific heat capacity of air at constant pressure ($1.006 \times 10^3 \text{ J/kg}$ between -100°C and 100°C), $T$ is the air temperature, $x$ is the humidity ratio (0.01 for our model), $c_{pw}$ is the specific heat capacity of water vapor at constant pressure ($1.84 \times 10^3 \text{ J/kg}$) and $h_{we}$ is the evaporation heat ($2.501 \times 10^6 \text{ J/kg}$). For our system at 70°C, the enthalpy is theoretically $9.7 \times 10^4 \text{ J/kg}$. However, enthalpy is strongly dependent on pressure and this equation is over-simplified for our system. In TOUGH2 enthalpy is calculated from the steam-table equations (International Formation Committee, 1967). We used model-based temperatures, varying the enthalpy until the near-surface model temperature was similar to fumarole temperatures observed at Comalito. The average measured fumarole temperature of ~70°C (Figure 4.2) could be replicated in the near-surface cells of the model with an injected gas enthalpy of $1.496 \times 10^5 \text{ J/kg}$. Other parameters were taken from Chiodini et al. (2005), MacNeil et al. (2007) or were typical of fractured basalt (Table 4.1).

The model was run until it reached steady state, and these pressure and temperature conditions were then used as initial conditions in models where gas injection rate, enthalpy, rock permeability and source depth were varied to try to replicate the cyclic temperature time signal observed during volcanic activity (Figures 4.3a-d).
Table 4.1. Parameters used in TOUGH2 model.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2000</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Permeability (fracture)</td>
<td>$1 \times 10^{-8}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Permeability (surroundings)</td>
<td>$1 \times 10^{-12}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
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<td>W/m°C</td>
</tr>
<tr>
<td>Specific heat capacity</td>
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<td>J/kg°C</td>
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<tr>
<td>Air mass fraction</td>
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<td></td>
</tr>
<tr>
<td>Initial temperature</td>
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<td>°C</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>$1.013 \times 10^5$</td>
<td>Pa</td>
</tr>
<tr>
<td>Background enthalpy</td>
<td>$1.496 \times 10^5$</td>
<td>J/kg</td>
</tr>
<tr>
<td>Background injection rate</td>
<td>0.5</td>
<td>kg/s</td>
</tr>
</tbody>
</table>

4.5 Results

The goal of our modeling is to explain the very consistent but complex fumarole temperature anomalies observed at Comalito cinder cone. As the signals are rapid and repeatable, changes in the system must be local and elastic. To increase surface fumarole temperature by up to 10°C over 20 minutes, a significant amount of energy must be entering the near-surface system. We modeled variations in the gas injection rate, enthalpy, source depth and rock permeability to determine if they could result in this magnitude of surface-temperature increase. The models must also be able to explain the gradual decrease in surface temperature and the rapid return to background temperature observed after the initial increase.

Varying the rate and enthalpy of gas injected into the base of the model (250 m depth) can result in surface temperature variations similar to those observed at Comalito
fumarole (Figure 4.5). A background injection rate of 0.5 kg/s results in a model that attains steady state in 9.4 years. The rapid increase in temperature from approximately 72°C to 79°C in 20 minutes can be simulated by a sudden injection of hot gas at 50 kg/s, a hundred-fold increase. The exponential decrease in temperature corresponds to an almost negligible gas flow rate of 0.05 kg/s or less. The rapid drop to background level is recreated by a slightly higher injection rate of 5 kg/s, but with background-temperature gases.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>3e4</th>
<th>3.3e4</th>
<th>9.5e4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate (kg/s)</td>
<td>0.5</td>
<td>50</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>Enthalpy (J/kg)</td>
<td>1.52e5</td>
<td>1.6e5</td>
<td>1.55e5</td>
<td>1.52e5</td>
</tr>
</tbody>
</table>

Figure 4.5. Changes in surface fumarole temperature are modeled with abrupt changes in mass flux and fluid enthalpy. The box shows where these abrupt changes occur.
Each thermocouple at Comalito fumarole records different temperatures (Figures 4.2 and 4.3), which can be modeled with different enthalpies of the injected gas. The two deepest thermocouples, at 150 cm depth, measure average temperatures of ~62°C, while the shallower thermocouples recorded temperatures between ~67 and 75°C. This corresponds to a modeled enthalpy of injected gas between approximately 1.4 and 1.6 x 10^5 J/kg. For example, the 72 to 79°C temperatures measured at the thermocouple at 66 cm depth correspond to enthalpies of 1.52 to 1.6 x 10^5 J/kg, respectively (Figure 4.5). The 70 to 76°C temperatures observed at the thermocouple at 95 cm depth correspond to enthalpies of between 1.496 and 1.55 x 10^5 J/kg (Figure 4.6). The different amplitude fumarole temperature cycles observed at each thermocouple can therefore all be recreated by using different enthalpy ranges.

The shape of the temperature cycles is sensitive to both the enthalpy and the rate of gas being injected into the base of the model (Figure 4.6). With a low injection rate the system takes longer to heat up, and with an injection rate of 1 kg/s it does not even reach the maximum temperature of 76°C within the 2 days modeled (Figure 4.6b, left panel). With a low enthalpy the system reaches a lower equilibrium temperature, for example 75°C with an enthalpy of 1.55 x 10^5 J/kg compared to 85°C with an enthalpy of 1.65 x 10^5 J/kg (Figure 4.6c). For the final stage of the curve, a high injection rate results in a rapid change, with an increase of up to 0.5°C and then a larger decrease of up to 2°C corresponding to an injection rate of 50 kg/s (Figure 5.6b, far right). With an injection rate of 1 kg/s or less the temperature does not increase first, and the return to background state is much more gradual, taking over a day. The minor increase in temperature prior to the rapid decrease is sometimes observed in the fumarole temperate measurements also
Figure 4.6. Simulation of near-surface temperature, modeled with abrupt changes in gas enthalpy and injection rate. a) Curve that we are trying to recreate. Dashed grey line and box above show when injection rate and enthalpy changed. b) Relationship between gas temperature and injection rate. Numbers on the curves show injection rate in kg/s. Enthalpy of system at different times is shown in boxes in (a). c) Relationship between gas temperature and enthalpy. Numbers on the curves correspond to enthalpy in J/kg. Gas injection rates are shown in the boxes in (a).
(Figure 4.3a and d). The timescale of the temperature response is therefore controlled by the injection rate, while the amplitude of the response is controlled by the enthalpy of the injected gas. An optimum combination of the gas flux and enthalpy can be found to model each cycle at each thermocouple.

Gas fluxes and temperatures are also affected by changes in permeability (Figure 4.7), although changes in permeability alone cannot cause the amplitude of temperature variations observed at Comalito cinder cone. If the fracture permeability decreases relative to the surrounding rock, the near-surface temperatures vary more rapidly and with higher amplitude. For a low permeability of $1 \times 10^{-9} \text{ m}^2$, the initial temperature response is large, up to 78°C, but the more gradual decrease afterwards is at a lower temperature, around 71°C for a permeability of $1 \times 10^{-9} \text{ m}^2$ compared to 75°C with a permeability of $1 \times 10^{-4} \text{ m}^2$ (Figure 4.7a).

The effect is similar but with a smaller amplitude if the permeability of the surrounding rock is lowered relative to a constant fracture permeability (Figure 4.7b). For example, a fracture permeability of $1 \times 10^{-11} \text{ m}^2$ corresponds to a near-surface temperature of 72°C during the gradual decrease in temperature; while a fracture permeability of $1 \times 10^{-9} \text{ m}^2$ results in a near-surface temperature of 73°C.
Figure 4.7. Correlation between fumarole temperature and permeability. (a) Numbers on the curves represent fracture permeability as a negative power in m$^2$ (e.g. 4 corresponds to 1 x 10$^{-4}$ m$^2$). Wall rock permeability is kept constant at 10$^{-12}$ m$^2$. (b) Numbers represent negative power of wall rock permeability in m$^2$. Fracture permeability is kept constant at 1 x 10$^{-8}$ m$^2$. Other parameters are as in Figure 4.5.

In both cases, higher permeability causes a lower initial temperature response but a higher near-surface temperature during periods of low gas flux. This is probably due to associated changes in mixing between the fracture fluids and those in the surrounding rock. However, higher permeability of the fractured rock corresponds to a greater contrast with the surrounding rock, while higher permeability of the surrounding rock translates to a lower permeability contrast with the fracture. This suggests that the bulk permeability is more important than the relative permeabilities between the two rock types. When the permeability of the surrounding rock is close to or greater than the fracture permeability (1 x 10$^{-8}$ to 1 x 10$^{-7}$ m$^2$), however, the rapid temperature response is lost. In both cases, if the permeability is reduced below the values modeled in Figure 5.7, the injection rate or the number of injection cells must be reduced for the model to remain stable.
The temperature response is found to be relatively insensitive to the depth to the source (Figure 4.8). With a deeper source the gases have more time to react with surrounding fluids and the response is slightly enhanced, but the effect is generally less than 1°C. Unless the water table rose by 200 m, it is unlikely that any change would be detectable at the surface. As the water table is unlikely to rise by so much, it appears that fluctuations in the water table are not an important factor in either the timescales or the amplitudes of the fumarole temperature cycles.

Figure 4.8. Relationship between surface temperature and depth to the gas source. Numbers represent depth in m. Even with an increase in the water table elevation of 150 m, the change is temperature is less than 1°C.

4.6 Discussion

Numerical models of the system at Comalito cinder cone suggest that the distinctive temperature signals observed during volcanic activity result from short-term
increases in gas flow rate and enthalpy. There is a trade-off between the two; increased enthalpy requires a lower gas flow rate to reach the same temperature, but that slows the response time. The most realistic model corresponds to an influx of hot gas that drops to a very low flux rate after about 20 minutes. We suggest that during this time the more stable fluid in the less permeable surrounding rock is kept out of the fracture and pressurized by the flow of hot gas (Figure 4.4b). When the flux of hot gas drops to essentially zero, the gases at background enthalpy then flood back in, causing an increase in flow rate and a second smaller temperature spike at the surface. The system then quickly reequilibrates to background temperature and gas flow rates with the rock both within the fracture and outside.

The large number of repetitive cycles suggests that there is a non-destructive source at depth causing the injection of hot fluid. Faulting or fracturing is therefore not a feasible mechanism. A change in the heat source of the fluid is insufficient either to cause the magnitude and timescale of fumarole temperature variations directly, or to increase buoyancy-driven fluid flow. We suggest that either a sudden release of gases from a storage area within the volcanic edifice or a change in the pressure distribution is a more likely source for the changes in fumarole temperature that are related to volcanic activity. For example, degassing of the magma source at depth could result in an abrupt change in the pressure distribution that causes a pressure wave to travel through the water table. This in turn could enhance groundwater circulation and/or boiling, increasing fluid flow and fumarole temperatures. Slight differences in enthalpy and gas flow rates resulting from minor variations in either process could explain the variations between the different cycles within an episode. Constant magma degassing has been inferred from tremor at
Masaya (Métaxian et al., 1997), but no changes in seismic energy were identifiable related to the observed volcanic activity.

The correlation of surface temperature with rainfall (Figures 4.3a-d) suggests that this may be an important factor in creating the temperature cycles. As rainfall events fall within the same 5-minute sampling window as increasing surface temperature, the effect must be extremely shallow. For rainfall to percolate through the system, either affecting the water table or fluid flow in the vadose zone, timescales on the order of hours to days are required. Rainfall is known to increase pore pressure (Wang and Sassa, 2003), and we instead hypothesize that rainfall affects the pressure within the system, perhaps increasing it past some threshold value that allows increased transport of fluids to the surface. The number of rainfall events without an associated increase in temperature, and the lack of correlation between the amount of rainfall and magnitude of near-surface temperature changes suggest that this is not the dominant mechanism, however.

Chemical reactions may contribute toward changes in soil temperature, particularly as there is a positive correlation of temperature with rainfall. The heat of wetting can be significant, although the soil temperature time series associated with wetting are different from those observed at Masaya (Figure 4.9; Prunty and Bell, 2005). In addition, the lack of anomalies at the beginning of each rainy season after several months without rain (Figure 4.3f) indicates that this is not a major factor in causing observed temperature changes.
Figure 4.9. Heat of wetting curve according to Prunty and Bell (2005). The temperature does not drop as observed in the fumarole temperatures.

Reactions of water, particularly with sulfur dioxide (known as scrubbing), are exothermic (Stiles and Felsing, 1926) and could give off heat and affect gas fluxes at Comalito cinder cone. Chiodini et al. (2005) did not detect any sulfur species from the fumaroles at Comalito, although the magma at Masaya volcano is known to be a significant sulfur source (Stoiber et al., 1986; Williams-Jones et al., 2003). The decrease in sulfur dioxide fluxes in the crater prior to a phreatic explosion (Duffell et al., 2003) may suggest that scrubbing is occurring at Masaya volcano. Although this could release significant amounts of heat, we discard it as a dominant mechanism because some, but not all, cycles correspond to rainfall events. It is also unlikely that the SO$_2$ would have degassed from the magma and traveled through the saturated and vadose zones, only to react with water near the surface. Nevertheless, we do not rule out the possibility that the
changes in soil temperature may in part result from increased flux of SO\textsubscript{2} and exothermic reactions during scrubbing.

Another variable that may affect gas flow rates, and therefore temperature, is permeability. After earthquakes increased fumarole temperature and gas flux have been observed at a number of sites (Tedesco et al., 1991; Richter et al., 2004). There were no significant changes in seismicity corresponding to our temperature anomalies, but permeability can also change unrelated to seismicity. Wohletz and Heiken (1992) found that hot gases could cause hydraulic fracturing, increasing the effective permeability and therefore increasing gas flux. Todesco et al. (2004) showed that hydrothermal flow causes rock deformation and an associated change in permeability. Enever et al. (1992) showed that pressure curves resulting from hydraulic fracturing could have a very similar shape to our measured fumarole temperature anomalies. In their study the system was closed, and fluid was injected. Fracturing of the rock resulted in an initial rapid increase in pressure. The following exponential decrease in pressure resulted from the fluid entering the crack and the crack tip propagating. When the fluid injection was turned off, the pressure dropped rapidly. Although the system is not closed at Comalito cinder cone, it is possible that cracking of the rock surrounding the fracture could be enhancing the changes in temperature. As the cycles are repetitive, with consistent threshold temperatures, the process must be elastic and so it is unlikely that entirely new fractures are forming in each case. Dilation of existing fractures is however a plausible mechanism, although fluid injection and/or a change in pressure is still required for this to occur.
A similar pattern in soil-temperature variations has been observed in high-
temperature fumaroles at Colima volcano, Mexico, attributed to mixing of fumarole gases
and air (Connor et al., 1993a). This is analogous to our model, where fumarole gases are
mixing with vadose-zone fluids.

The background gas injection rate of 0.5 kg/s translates to a flux of 43 t/d at the
Comalito fumarole. This is in good agreement with the combined CO$_2$ and steam flux of
49 t/d measured by Chiodini et al. (2005). It is rather less than the 4 kg/s of SO$_2$ and 400
kg/s of water vapor emitted from the active crater at Masaya (Galle et al., 1993; Burton et
al., 2001). During volcanic eruptions, SO$_2$ flux rates have been observed to increase by a
factor of 10 at Mt Pinatubo (Daag et al., 1996) and Mt St Helens (Casadevall et al.,
1983). During the temperature anomalies at Masaya our models suggest that the total gas
input increased 100-fold, to a flux rate comparable with large degassing fields like Campi
Flegrei (Chiodini et al., 2005). This is possible, but is probably overestimated due to
contributing factors like subsurface heterogeneity, groundwater table depth and
exothermic reactions. Geochemical flux monitoring is generally carried out at a sampling
rate of a maximum of one hour, and as our anomalies only lasted 20 minutes it is possible
that gas flux monitoring would not have sampled during this time. The flux rate may also
be overestimated due to heat contributions from chemical reactions and heat of wetting.

In our models, the total gas input during a one-day anomaly is 195 tons. At
background levels the daily gas input is 43 tons, suggesting an increase in mass of
between 1520 and 2430 tons during a 10- to 16-day anomaly episode. SO$_2$ flux from
Santiago crater has been observed to triple during increased magmatic degassing (Stoiber
et al., 1986). A 4.5-fold increase in total gas flux during temperature anomalies related to
increased magma degassing is therefore entirely plausible. The change in source flux may be even smaller, as the focusing effect of the fracture zone is only modeled to shallow depths, and the fracture may be concentrating fluids from greater depth.

Our study shows that changes in the volcanic system at Masaya volcano can be detected with fumarole temperature monitoring, and should also be detectable with continuous gas flux monitoring. However, the changes are extremely abrupt, and increases in temperature and gas flux only last 20 minutes, which is less than the sampling rate of most gas flux monitoring systems and some temperature monitoring systems. As the gradual decrease in temperature and the corresponding drop in gas flux lasted longer, approximately one day, it is possible that an increase in volcanic activity at Masaya volcano would actually be detected as a decrease in gas flux at the fumarole zone at Comalito cinder cone.

4.7 Conclusion

During volcanic activity at Masaya volcano, the Comalito fumarole shows a very distinctive, cyclical temperature response that our modeling suggests is due to a rapid but transient influx of hot gas. At background state, fluid is injected along the base of the model at 0.5 kg/s. Hot gas is then injected at 50 kg/s to create a rapid rise in fumarole temperature over 20 minutes. This prevents the gas in the less permeable surrounding rock from entering the fracture. The flux of hot gas drops to a rate of 0.05 kg/s or less, allowing the system to return toward equilibrium. When it is almost at equilibrium, the previously trapped gas in the surrounding rock re-enters the fracture at a slightly higher

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injection rate of 5 kg/s. The rate then gradually drops as the system returns to background state.

Our models suggest that a 100-fold increase in gas flux occurs during these temperature cycles, although this only lasts for approximately 20 minutes. We suggest that the increased gas flux results from a pressure pulse due to pulsing of the degassing magma, which increases fluid circulation and possibly increases permeability by dilating fractures. This is repeatable, resulting in a number of fumarole temperature cycles. The effect may also be enhanced by hydrofracturing or increased pore pressure due to rainfall. Wetting of the soil and chemical reactions also release heat which may contribute to the increases in temperature observed. However, increased gas flux appears to be the simplest physical explanation for the rapid fluctuations in fumarole temperature that we observe at Comalito cinder cone.

We conclude that fumarole gas and temperature monitoring can be a useful way to detect changes in a volcano-hydrologic system, provided that a sufficiently small (<< 1 hour) sampling rate is used. Fumarole temperature monitoring can also be used to infer changes in gas flux at depth. A good conceptual and/or numerical model is however vital to be able to relate any detected changes in fumarole activity to changes in volcanic activity.
LIST OF REFERENCES


APPENDIX A

Finite difference model of 2D heat transfer
% Matlab program to calculate 2D heat transfer by conduction and convection. Top and bottom boundaries are fixed temperature, right boundary is no-flow and left boundary is convective.
close all       % Start with a clear workspace
clear all

Tnew=0;       % Set the starting temperature at 0
nptx=25;       % Set the number of points in the horizontal direction
nptz=25;       % Set the number of points in the vertical direction
len=300;       % Set the maximum number of iterations
dx=(nptx-1)*0.02;    % Calculate the grid spacing

% Create a square mesh for the model domain
T=200*ones(nptz,nptx,len+1);

% Set the boundary conditions
T(1,:,:)=10;       % Fixed temperature at the top to represent air
T(nptz,:,:)=800;    % Fixed temperature at the bottom to represent heat source
for i=2:nptz       % Fixed heat flux condition
    T(i,:,:)=(T(nptz,:,:)-T(1,:,:))/(nptz-1)+T(i-1,:,:);
end

% Start the iterations to calculate solution
for j=1:len
    for q=1:1000000
        % Calculate convective boundary
        % Call subroutine convect to calculate boundary condition
        [T(:,nptx,j),alpha,k,h,Tave]=convect(T(:,nptx-1,j),dx,T(nptz,1,1));
        Bi=h*dx/k;    % Calc how much of temp is transferred to adjacent cell
        T(1,nptx,j)=(1/(1+Bi))*[(T(1,1,j)+T(2,nptx,j))/2+(Tave*Bi)]; % Calculate new temperature from adjacent cells
        % Explicit, finite difference approximation for wall rock conduction
        [T,dt]=transient(T,nptx,nptz,j,alpha,k,h,dx);
        %Test for convergence within a cell
        diff=abs(Tnew-T);
        if diff<1
            break % If the temp difference is less than 1°C, calculate the next cell
        end
    end
    Tnew=T;        % Otherwise update the temp conditions and try again
end

if  j>=2
Appendix A (continued)

```matlab
difft=abs(T(:,:,j)-T(:,:,j-1));  % Calculate temp diff between iterations
    if difft<1              % If less than 1°C, simulation converged
        break
    end
end

% Plot the results
x=1:nptx;
x=dx*x;
figure
[C,h] = contour((max(x)-x),(x-(1*dx)),T(:,:,j));
set(gca,'YDir','rev')
xlabel('Distance from conduit (m)')
ylabel('Depth from surface (m)')
clabel(C,h);
```

% Subroutine convect.m
% Subroutine called from conduct.m. Required inputs are temperature (Tw), length of cell (dx), and temperature at base (Ten)
function [T,alpha,k,h,Tavg]=convect(Tw,dx,Ten)
load steam.mat –ASCII
% Some constants, held in an external file
a=0.1;  % Radius of conduit through which hot gas flows
len=length(Tw);  % Calculate how many cells there are in the boundary

% Renumber the cells because they are upside down
for k=1:len
    Twr(k)=Tw(len-k+1);
end
Tw=Twr;

%Calculate new cell values
for m=1:len
    Tex=(Tw(m)+Ten)/2;  % Exit temperature is average of previous temperature and input
    Tavg=exp((log(Tex)+log(Ten))/2);  % Calculate average temperature
    Texold=0;  % Make sure exit temperature of each cell is 0 for 1st calc
    for n=1:100000  % Call subroutine vars to find the properties of the fluid
        [rho,cp,k,viscw,Pr,alpha]=vars(Tw(m),steam);
        [rho,cp,k,visc,Pr,alpha]=vars(Tavg,steam);
        v=10;  % Velocity of the fluid
        ```
Appendix A (continued)

k=3;  \% Thermal conductivity, set at 3 to match COMSOL model

\% Call subroutine nusselt to calculate convection heat transfer coefficient
[h]=nusselt(a,rho,v,visc,viscw,Pr,k);

\% Calculate new values for the temperature in each cell
dif=Ten-Tw(m);
expt=-2*h*dx/(v*rho*a*cp);
Tex=dif*exp(expt)+Tw(m);
Tavg=exp((log(Tex)+log(Ten))/2);

\% See if cells in convective boundary have converged to a solution
conv=abs(Tex-Texold);
if conv<=0.001
    break \% If converged, exit if loop
end
Texold=Tex; \% If not converged, update temperatures and start cycle again
end
Ten=Tex; \% Update temperatures for next iteration
T(len-m+1)=Ten;
end

% Subroutine vars.m
% Subroutine to find the relevant properties of water/steam based on the temperature,
called from convect.m
function [rho,cp,k,visc,Pr,alpha]=vars(T,steam);

if T<325
    i=1;
elseif (T>=325) & (T<375)
    i=2;
elseif (T>=375) & (T<425)
    i=3;
elseif (T>=425) & (T<475)
    i=4;
elseif (T>=475) & (T<525)
    i=5;
elseif (T>=525) & (T<575)
    i=6;
elseif (T>=575) & (T<650)
    i=7;
end
Appendix A (continued)

\[
\text{elseif } (T \geq 650) \& (T < 750) \\
i = 8;
\text{elseif } (T \geq 750) \& (T < 850) \\
i = 9;
\text{elseif } (T \geq 850) \& (T < 950) \\
i = 10;
\text{elseif } (T \geq 950) \\
i = 11;
\text{end}
\]

\[
rho = \text{steam}(i,2); \quad \text{% Density}
\]
\[
cp = \text{steam}(i,3); \quad \text{% Specific heat}
\]
\[
k = \text{steam}(i,4); \quad \text{% Thermal conductivity}
\]
\[
\text{visc} = \text{steam}(i,5); \quad \text{% Dynamic viscosity}
\]
\[
v = \text{steam}(i,6); \quad \text{% Kinematic viscosity}
\]
\[
Pr = \text{steam}(i,7); \quad \text{% Prandtl number}
\]
\[
\alpha = \text{steam}(i,8); \quad \text{% Thermal diffusivity}
\]

% Subroutine nusselt.m
% Subroutine to calculate the convection heat transfer coefficient
function [h]=nusselt(a,rho,v,visc,viscw,Pr,k)

D=2*a; \quad \text{% Diameter of pipe}
Re=rho*v*D/visc; \quad \text{% Calculate Reynold’s number}
\text{if } \text{Re} < 2200
\quad \text{Nu}=8.66; \quad \text{% Nusselt number for laminar flow}
\text{else}
\quad \text{Nu}=0.027*(\text{Re}^{0.8}*(\text{Pr}^{1/3})*((\text{visc}/\text{viscw})^{0.14}); \quad \text{% Nusselt number for turbulent flow}
\text{end}
\quad h=\text{Nu}*k/D; \quad \text{% Convection heat transfer coefficient}

% Subroutine transient.m
% Subroutine to calculate conduction within model
function [T,dt]=transient(T,nptx,nptz,j,alpha,k,h,dx)

sigma=0.2; \quad \text{% Multiplication factor}
dt=sigma*(dx)^2/alpha; \quad \text{% Time step}
\text{%interior nodes, transient, explicit solution (couldn’t get implicit to work)}
\text{for } l=2:nptz-1
\quad \text{for } m=2:nptx-1
\quad \quad T(l,m,j+1)=\text{sigma}*[T(l,m-1,j)+T(l,m+1,j)+T(l-1,m,j)+T(l+1,m,j)]...

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\[(1-4*\sigma)T(l,m,j)\]

end
end

% File steam.mat, containing properties of water/steam (White, 1984)

<table>
<thead>
<tr>
<th>Temp K</th>
<th>Density Kg/m³</th>
<th>Specific heat J/kgK</th>
<th>Thermal conductivity W/mK</th>
<th>Dynamic viscosity PaS</th>
<th>Kinematic viscosity m²/s</th>
<th>Prandtl number</th>
<th>Thermal diffusivity m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0253</td>
<td>2041</td>
<td>0.0181</td>
<td>0.91e-5</td>
<td>36.1e-5</td>
<td>1.03</td>
<td>35.1e-5</td>
</tr>
<tr>
<td>350</td>
<td>0.258</td>
<td>2037</td>
<td>0.0222</td>
<td>1.12e-5</td>
<td>4.33e-5</td>
<td>1.02</td>
<td>4.22e-5</td>
</tr>
<tr>
<td>400</td>
<td>0.555</td>
<td>2000</td>
<td>0.0264</td>
<td>1.32e-5</td>
<td>2.38e-5</td>
<td>1.00</td>
<td>2.38e-5</td>
</tr>
<tr>
<td>450</td>
<td>0.491</td>
<td>1968</td>
<td>0.0307</td>
<td>1.52e-5</td>
<td>3.10e-5</td>
<td>0.95</td>
<td>3.17e-5</td>
</tr>
<tr>
<td>500</td>
<td>0.441</td>
<td>1977</td>
<td>0.0357</td>
<td>1.73e-5</td>
<td>3.92e-5</td>
<td>0.96</td>
<td>4.09e-5</td>
</tr>
<tr>
<td>550</td>
<td>0.401</td>
<td>1994</td>
<td>0.0411</td>
<td>1.93e-5</td>
<td>4.82e-5</td>
<td>0.94</td>
<td>5.15e-5</td>
</tr>
<tr>
<td>600</td>
<td>0.367</td>
<td>2022</td>
<td>0.0464</td>
<td>2.13e-5</td>
<td>5.82e-5</td>
<td>0.93</td>
<td>6.25e-5</td>
</tr>
<tr>
<td>700</td>
<td>0.314</td>
<td>2083</td>
<td>0.0572</td>
<td>2.54e-5</td>
<td>8.09e-5</td>
<td>0.93</td>
<td>8.74e-5</td>
</tr>
<tr>
<td>800</td>
<td>0.275</td>
<td>2148</td>
<td>0.0686</td>
<td>2.95e-5</td>
<td>10.7e-5</td>
<td>0.92</td>
<td>11.6e-5</td>
</tr>
<tr>
<td>900</td>
<td>0.244</td>
<td>2217</td>
<td>0.078</td>
<td>3.36e-5</td>
<td>13.7e-5</td>
<td>0.95</td>
<td>14e.4e-5</td>
</tr>
<tr>
<td>1000</td>
<td>0.220</td>
<td>2288</td>
<td>0.087</td>
<td>3.76e-5</td>
<td>17.1e-5</td>
<td>0.99</td>
<td>17.3e-5</td>
</tr>
</tbody>
</table>

Figure A-1. Early numerical simulations, of magma conduit and wall rock next to it. Convective left boundary simulates flow along the conduit to the surface. MATLAB results using my finite difference code (a) show excellent agreement with results using COMSOL multiphysics (b), although the horizontal extent of the models is slightly different.
APPENDIX B

Fumarole temperature data plotted by year
Figure B-1. Fumarole temperature data in 2006.
Figure B-2. Fumarole temperature data in 2007.
Figure B-3. Fumarole temperature data in 2008.
Figure B-4. Fumarole temperature data in 2009.
APPENDIX C

Spectrograms
Figure C-1. Top: Spectrogram from thermocouple at 33 cm depth. Bottom: Fumarole temperature time series at 33 cm depth.
Figure C-2. Top: Spectrogram from thermocouple at 63 cm depth. Bottom: Fumarole temperature time series at 63 cm depth.
Figure C-3. Top: Spectrogram from thermocouple at 95 cm depth. Bottom: Fumarole temperature time series at 95 cm depth.
Figure C-4. Top: Spectrogram from thermocouple at 150 cm depth. Bottom: Fumarole temperature time series at 150 cm depth.
Figure C-5. Top: Spectrogram from thermocouple 7 m away. Bottom: Fumarole temperature time series 7 m away.
Figure C-6. Top: Spectrogram of air temperature time series. Bottom: Air temperature time series.
ABOUT THE AUTHOR

Sophie Pearson was born in Emsworth, Hampshire, England. She received her MGeophys in Geophysical Sciences from Leeds University, UK in 2005, which included a year studying at Penn State University, USA. A week after obtaining her degree she joined the Department of Geology at the University of South Florida (USF) as a PhD student under the supervision of Dr. Charles Connor. She received a Presidential Fellowship from USF to support her throughout her PhD, which included full funding for five years. As well as working at USF, Sophie participated in conferences and fieldwork in USA, Ecuador, Nicaragua, Taiwan, Japan, and Iceland. Her work has been published in international journals and in 2009 she received the Outstanding Service Award from the Department of Geology. She has now accepted a permanent position as a Geothermal Geophysicist with GNS Science in New Zealand.