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ABSTRACT

Carbon dioxide emissions are monitored in volcanic and hydrothermal areas to understand volcanic processes, to assess hazards in active regions, and to improve estimates of global volcanic and hydrothermal degassing. Over the last twenty years, significant advances have been made in linking surface emissions of CO₂, SO₂, and other acid gases to volcanic processes at depth. This advancement has been accompanied by improvements in methods to measure and monitor emissions in volcanic regions. Despite these improvements, no tested method exists for obtaining large-scale (km²) estimates of CO₂ degassing. In this work, eddy covariance, a micrometeorological technique, was tested for the first time in volcanic and hydrothermal terrain to measure CO₂ fluxes over large land areas (km²). An eddy covariance (EC) station was deployed at Yellowstone National Park during August 1999 to determine if EC fluxes were consistent with surface flux measurements using the accumulation chamber technique in volcanic regions. A second deployment of EC at Solfatara Crater, Italy, June 8-25, 2001 assessed if EC could continuously measure CO₂ fluxes for volcanic hazards monitoring at this site. Both regions had slopes less than 15 %, but displayed significant variations in CO₂ and heat flux upwind of the EC tower. At Yellowstone, fluxes measured using EC varied over three orders of magnitude (from ~100 to 10,000 g CO₂ m⁻² d⁻¹) and were consistent with fluxes measured using the chamber technique within a factor of 2. At Solfatara, EC measurements of CO₂ fluxes were made continuously for three weeks at six locations. Turbulent (EC) fluxes were calculated in 30-minute averages and varied between 950 and
4460 g CO$_2$ m$^{-2}$ d$^{-1}$ depending on location within Solfatara. Comparing turbulent fluxes with chamber measurements of surface fluxes using footprint models yielded an average difference of 0 ± 4 %, indicating EC measurements were representative of surface fluxes at this hydrothermal site.

Reliable EC measurements (i.e., measurements with sufficient and stationary turbulence) were obtained primary during daytime hours (08:00 and 20:00 local time). EC fluxes measured closest to the degassing pools within Solfatara were the highest measured during the campaign (4392-4459 g CO$_2$ m$^{-2}$ d$^{-1}$). Because EC fluxes include the contribution from degassing pools, where chamber fluxes do not, the difference between the EC measurements and estimates using chamber fluxes yielded emission rates between 12 to 27 t CO$_2$ d$^{-1}$ for the degassing pools in Solfatara. For comparison, emissions for these features was previously estimated at 84 t CO$_2$ d$^{-1}$ following a seismic crisis in 1984 when the area experienced 3 meters of uplift. Daily average EC fluxes varied by ± 50 % with changes in atmospheric pressure, indicating volcanic emissions would have to exceed this for in order to predict volcanic hazard. First-order models of magma emplacement or eruption suggest emissions could exceed this rate for events similar to those observed in the past. In conclusion, eddy covariance was found to provide reliable estimates of surface fluxes both at Solfatara, and Yellowstone, thereby providing a new technique for monitoring significantly larger areas than previous methods. Monitoring larger areas provides new insight to the temporal variability and spatial distribution of degassing in volcanic regions, and thus provides a new and useful technique for monitoring volcanic hazard.
CO₂ emissions were estimated for the Yellowstone volcanic / hydrothermal system using ground-based measurements and through modeling of the volcanic system. The estimates of degassing of Yellowstone were within an order of magnitude of one another, and indicate that Yellowstone likely emits \(3.7 \pm 1.3 \times 10^{11}\) mol CO₂ y\(^{-1}\). This estimate is significant in that it represents up to 16% of the global emission rate estimated for volcanic plumes, and up to 7% of global emissions from volcanic and hydrothermal environments estimated at 6-7 \(\times 10^{12}\) mol CO₂ y\(^{-1}\), suggesting that more measurements are needed in hydrothermal regions to estimate global volcanic and hydrothermal emissions more accurately.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... ix

LIST OF TABLES ............................................................................................................... xi

ACKNOWLEDGMENTS ................................................................................................. xii

Chapter 1 Introduction ................................................................................................. 1
  1.1 Motivation: Improving Global Carbon Dioxide Degassing Estimates ........ 1
  1.2 The Role of Diffuse and Hydrothermal Emissions in Global CO₂ Estimates ................................................................. 2
  1.3 Objectives ........................................................................................................... 3
  1.4 References ......................................................................................................... 5

Chapter 2 Eddy-Correlation Measurement of Hydrothermal Gases ..................... 6
  2.1 Abstract ............................................................................................................... 6
  2.2 Introduction ....................................................................................................... 6
  2.3 Theory of Eddy Correlation ............................................................................ 7
  2.4 Field and Analytical Methods ........................................................................ 11
    2.4.1 Eddy Correlation Measurements .............................................................. 11
    2.4.2 Surface Emissions .................................................................................... 12
    2.4.3 Determining the Source Area ................................................................. 12
  2.5 Results ............................................................................................................. 14
  2.6 Discussion and Conclusions ............................................................................ 15
  2.7 Acknowledgements ......................................................................................... 16
  2.8 References ....................................................................................................... 16

Chapter 3 Monitoring Volcanic Hazard Using Eddy Covariance at Solfatara Crater, Naples, Italy ..................................................... 22
  3.1 Abstract ............................................................................................................. 22
  3.2 Introduction ....................................................................................................... 23
  3.3 Geologic Setting and Current Monitoring ...................................................... 25
  3.4 Methods ............................................................................................................ 27
    3.4.1 Experimental Design and Analysis ......................................................... 27
3.4.2 Surface Flux Measurements ........................................................... 29
3.4.3 Comparing EC and Chamber Measurements using Footprint Models ......................................................... 30
3.4 Results ................................................................................................... 32
3.4.1 Meteorological Conditions ........................................................... 32
3.4.2 Eddy Covariance Fluxes of CO\textsubscript{2} (F\textsubscript{M}) ................................................... 32
3.4.3 Surface Fluxes of CO\textsubscript{2} (E) ........................................................... 34
3.4.4 Comparison of EC fluxes (F\textsubscript{M}) with Predicted Fluxes from Chamber Measurements (F\textsubscript{P}) .......................................................... 34
3.5 Discussion ............................................................................................... 36
3.5.1 Causes for Temporal Variability of Fluxes ...................... 37
3.5.2 Spatial Representation of Surface Fluxes ...................... 38
3.5.3 Causes for Discrepancies Between Measurement Techniques .... 38
  3.5.3.1 Low or non-stationary turbulence ........................................ 39
  3.5.3.2 Incomplete sampling of the surface array: emissions from degassing pools ........................................... 39
  3.5.3.3 Temporal variability of individual surface fluxes .............. 40
  3.5.3.4 Inaccurate weighting of the footprint model during weakly unstable conditions .............................................. 41
3.5.4 Expected Increases in Emissions with Magma Emplacement ..... 43
3.5.5 Conclusions and Recommendations for Monitoring ............... 45
  3.5.5.1 Applicable Sites and Conditions ........................................ 45
  3.5.5.2 Tower placement - footprint considerations ....................... 45
  3.5.5.3 Contemporaneous Measurements ....................................... 46
3.6 Acknowledgements ................................................................. 47
3.7 References .............................................................................................. 48

Chapter 4 CO\textsubscript{2} Emissions from the Yellowstone Volcanic System .......... 63

4.1 Abstract ................................................................................................. 63
4.2 Introduction .......................................................................................... 64
4.3 Magmatic Degassing Based on a Geologic Model ....................... 66
  4.3.1 Source and Evolution of Yellowstone Basaltic Magmas ............ 67
  4.3.2 Estimating Magmatic CO\textsubscript{2} emissions from Yellowstone ..................... 69
    4.3.2.1 Emplacement Rates at Yellowstone (E\textsubscript{M}) ...................... 70
    4.3.2.2 Melt Fraction (F\textsubscript{m}) and Initial Carbon Concentration of the Mantle beneath Yellowstone (C\textsubscript{i}) ...................... 72
    4.3.2.4 Depth of Emplacement....................................................... 73
    4.3.2.5 Solubility of Carbon Dioxide............................................. 74
    4.3.2.6 Constraining the Model Estimates- Bubble Nucleation .... 75
    4.3.2.7 Sensitivity Analysis............................................................ 76
4.4 Results of Magma Emplacement Calculations ....................... 77
4.5 Estimating Surface Emissions of CO\textsubscript{2} ............................................. 77
  4.5.1 Hydrothermal Processes ............................................................... 78
4.5.2 Previous Correlation of Elevated CO₂ through Hydrothermal Soils .................................................................79
4.5.3 Hydrothermal Soil Types .................................................................80
4.6 Methods ..................................................................................................81
  4.6.1 Diffuse Flux Measurement........................................................... 81
  4.6.2 Land Area Estimates .................................................................... 84
  4.6.3 Gas Sampling and Analysis......................................................... 85
4.7 Diffuse Flux Measurements .................................................................86
4.8 Gas Geochemistry ................................................................................. 88
4.9 Discussion of Surface Fluxes and Sources of CO₂............................... 89
  4.9.1 Sampling Considerations.............................................................. 90
  4.9.2 Estimated Contribution of Thermal Features to Total Emissions ................................................................. 92
  4.9.3 Sources of CO₂ and other Gases .................................................. 93
    4.9.4.1 Carbon Isotopes................................................................. 93
    4.9.4.2 Helium Isotopes ................................................................. 95
    4.9.4.3 Carbon and Helium Relations ............................................ 96
4.10 Summary of Surface Emissions .......................................................... 98
4.11 Comparison of Model with Measurements .......................................... 98
  4.11.1 Surface Emissions: Sedimentary Contribution and Changes due to Non-Steady State Conditions ......................... 100
  4.11.2 The Emplacement Model ........................................................... 101
    4.11.2.1 Emplacement Rates.......................................................... 101
    4.11.2.2 Carbon Content ............................................................... 102
    4.11.2.3 Magma Crystallization..................................................... 103
4.12 Conclusions ......................................................................................... 105
4.13 Acknowledgements ............................................................................ 106
4.14 References .......................................................................................... 106

Chapter 5 Conclusions .................................................................................... 124
LIST OF FIGURES

Figure 2–1: Example 3-D Representation of Surface Fluxes and Footprint Function ................................................................. 18

Figure 2–2: Distributions of surface fluxes and EC fluxes. .................................................. 19

Figure 2–3: Comparison of Measured and Predicted Fluxes .............................................. 20

Figure 3–1: Contour Map of CO$_2$ Flux at Solfatara with EC locations. ..................... 51

Figure 3–2: Solfatara EC fluxes and CO$_2$ concentration Location 1. ......................... 52

Figure 3–3: Daily Average EC, Chamber Flux, and Atmospheric Pressure..................... 53

Figure 3–4: Relative Difference between EC and Chamber Fluxes. .......................... 54

Figure 3–5: Relative Difference as Function of Wind Speed / Direction, and Time of Day ................................................................................................................... 55

Figure 3–6: Measured EC Fluxes vs. Predicted Fluxes for all Solfatara Locations... 56

Figure 3–7: Footprint Function as a function of $L$ ......................................................... 57

Figure 3–8: Long-Term Standard Error of Surface Fluxes .......................................... 58

Figure 4–1: Map of Yellowstone National Park ................................................................. 112

Figure 4–2: Yellowstone Geologic Model ........................................................................ 113

Figure 4–3: Bubble Formation as a Function of Depth and Melt Fraction ................. 114

Figure 4–4: Sensitivity Analysis ....................................................................................... 115

Figure 4–5: CO$_2$ Emissions Modeled from Magma Ascent and Based on Measurement .......................................................... 116

Figure 4–6: CO$_2$ Flux Measurements across Yellowstone ............................................ 117
Figure 4–7: Carbon Isotopes for various Yellowstone Reservoirs..............................118

Figure 4–8: C³He as function of Carbon Isotopic Signature......................................119
LIST OF TABLES

Table 2–1: Eddy Correlation Data, Predicted Fluxes, and Meteorological Parameters.............................................................................................................21

Table 3–1: Eddy Covariance Data Collected at Solfatara Crater, June 8-25, 2001.....59

Table 3–2: Range and Mean of Chamber Fluxes Measured over the 200-pt grid, 1997-2001...............................................................................................................61

Table 3–3: Daily Averages of Chamber Flux measured at the continuous station in Solfatara, June 8-25, 2001. .............................................................................62

Table 4–1: Input Parameters used in Calculation of Magmatic Emissions ..........120

Table 4–2: Land Area Extrapolation of Diffuse CO$_2$ Fluxes to estimate Diffuse CO$_2$ Emissions in Yellowstone.................................................................121

Table 4–3: Chemistry and isotopes of gas samples from selected areas in Yellowstone .................................................................122
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Chapter 1

Introduction

1.1 Motivation: Improving Global Carbon Dioxide Degassing Estimates

The primary motivation behind this work was to improve the understanding of the role of volcanic, hydrothermal, and metamorphic (VHM) systems to the long-term carbon cycle. CO₂ degassing from VHM systems is an important source of atmospheric carbon on geologic timescales [Berner et. al, 1983, Berner, 1991, Berner, 1994]. Researchers modeling the global carbon cycle over geologic time suggest that present-day VHM degassing is balanced by CO₂ removal from the atmosphere due to chemical weathering of silicates, giving a present day CO₂ flux of 6-7 x 10^{12} mol y⁻¹ [Berner et al., 1983; Berner, 1991, Berner, 1994].

A few studies have estimated the present-day contribution from VHM systems to the atmosphere (0.4 to 10 x 10^{12} mol y⁻¹ [Kerrick, 2001]), which are generally within an order of magnitude of the mass balance estimates based on weathering. For example, Marty and Tolstikhin [1998] present a comprehensive review of the current estimates of CO₂ emissions from mid-ocean ridges (MOR), convergent margins, and plumes. However, estimates of subaerial volcanic degassing (both arc and plume type) rely on the extrapolation of relatively few measurements acquired from regions of active volcanism to all globally active volcanoes [Marty and Jambon, 1987; Gerlach, 1991; Williams et
al., 1992; Marty and Le Cloarec, 1992; Brantley and Koepenick, 1995; Marty and Tolstikhin, 1998]. Thus, until more measurements are obtained from volcanically active regions, global estimates will inherently contain considerable uncertainty [Kerrick, 2001].

1.2 The Role of Diffuse and Hydrothermal Emissions in Global CO$_2$ Estimates

Until 1991, diffuse degassing along the flanks of volcanoes, and emissions from hydrothermal and metamorphic systems was not recognized as a potentially significant component of VHM CO$_2$ degassing. At this time, Allard et al. [1991] estimated that approximately half of the CO$_2$ emissions from Mt. Etna, Italy, the largest CO$_2$-producing volcano in the world (up to $10^{12}$ mol CO$_2$ y$^{-1}$), were emitted through the flanks of the volcano. This work also highlighted the fact that other quiescently degassing volcanoes and hydrothermal systems might also contribute significantly to global emissions of volcanic CO$_2$.

Estimates of hydrothermal emissions from high heat flow regions suggest that these sources could supply roughly the same amount of atmospheric CO$_2$ as previous estimates of subaerial volcanic emissions [Brantley and Koepenick, 1995; Kerrick et al., 1995]. Very few estimates of hydrothermal emissions based on measurements have been published, but a few include 2.4 to $4 \times 10^9$ mol CO$_2$ y$^{-1}$ at the Mud Volcano thermal area of Yellowstone [Werner et al., 2000a], $1 \times 10^9$ mol CO$_2$ y$^{-1}$ for Solfatara Crater, Italy, and $1.1 \times 10^9$ mol CO$_2$ y$^{-1}$ for the Yangbajain geothermal area in China [Chiodini et al., 1998]. Global estimates of hydrothermal CO$_2$ emissions extrapolated from heat flow measurements in high heat flow, convective systems, suggest that global hydrothermal
emissions could exceed $10^{12}$ mol CO$_2$ y$^{-1}$ [Kerrick et al., 1995; Seward and Kerrick, 1996].  Brantley and Koepenick [1995] incorporated the contribution of diffuse and hydrothermal fluxes into global estimates by normalizing volcanic emissions to crater area, and included the approximate global area of geothermal heat flow, to calculate a total volcanic / metamorphic CO$_2$ emission rate of $6 \times 10^{12}$ mol y$^{-1}$.  They also note that because CO$_2$ emissions tend to follow a power law distribution, that global emissions could be estimated with relatively little error by determining the emission rate from the 10-20 largest volcanic and hydrothermal systems on Earth.

1.3 Objectives

Clearly further measurements of volcanic and hydrothermal emissions are needed to improve the estimates of global present-day CO$_2$ degassing from VHM regions.  Furthermore, more representative measurements (both spatially and temporally) would improve global emission rates as well as improve monitoring in hazardous volcanic regions.  To this end, one goal of this research was to test eddy covariance (EC, also called eddy correlation), a micrometeorological technique, to measure emissions in volcanic and hydrothermal regions.  The advantages of eddy covariance over the typically used accumulation chamber technique are that the method is continuous and spatially representative of the upwind surface.  However, the heterogeneity typically observed in hydrothermal regions both with respect to CO$_2$ and heat fluxes might produce conditions not conducive to EC measurements.  Chapter II presents the results from the first deployment of EC in a hydrothermal region.  In this study we compared EC
measurements to surface fluxes obtained with the accumulation chamber in the Mud Volcano thermal area and demonstrated that within a factor of 2, eddy covariance provides reliable estimates of hydrothermal degassing. The utility of eddy covariance for volcanic hazards monitoring was tested at a second deployment at Solfatara Crater, in Naples Italy, in collaboration with Giovanni Chiodini of the Osservartario Vesuviano. The results of this campaign are presented in Chapter III.

Finally, in Chapter IV the total emissions for the Yellowstone volcanic / hydrothermal system are estimated from surface measurements of CO$_2$ fluxes, and through modeling of the CO2 released with the ascent of basaltic melts from the mantle into the crust. Yellowstone cannot be considered exclusively a volcano or a hydrothermal system. Like many volcanic systems, Yellowstone hosts a hydrothermal system in the shallow subsurface. The heat that drives the hydrothermal system is ultimately derived from basaltic magma that intrudes the crust beneath Yellowstone. The Yellowstone hydrothermal system is one of the largest hydrothermal systems on Earth (> 1000 km$^3$). The results of this study suggest that the Yellowstone volcanic / hydrothermal system contributes significantly to global VHM emissions.

Thus, by introducing a ‘new’ measurement technique to the volcanological community, and providing the first estimate of CO$_2$ emissions from the Yellowstone volcanic / hydrothermal system, this research has both advanced the understanding of the role of VHM systems to the long-term carbon cycle, and provided a new means of further assessing this contribution in the future.
1.4 References


Chapter 2

Eddy-Correlation Measurement of Hydrothermal Gases

2.1 Abstract

In the first application of eddy correlation in a hydrothermal region, we measured turbulent fluxes ranging between -17 and 13,500 g CO\(_2\) m\(^{-2}\) d\(^{-1}\) in Yellowstone National Park (YNP). These turbulent fluxes are similar in magnitude to chamber measurements of diffuse fluxes in the region. Negative turbulent fluxes due to vegetative uptake were measured in non-thermal regions. The flux footprint was used to compare turbulent with surface fluxes within the source area of EC measurements, and turbulent fluxes were consistent within error to the spatial extrapolation of chamber measurements. EC is more representative than chamber techniques, providing a viable alternative to measuring gas emissions in volcanic and hydrothermal terrain.

2.2 Introduction

Monitoring volcanic, hydrothermal, and metamorphic (VHM) emissions of CO\(_2\) is important for quantifying the long-term carbon cycle [Berner and Lasaga, 1989], and for

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evaluating volcanic hazard. [Gerlach et al., 2001]. Recent studies estimating emissions have relied on accumulation chambers to measure diffuse degassing; however, surface disturbances, measurement protocols, and extrapolation procedures introduce uncertainty (up to a factor of two) [Gerlach et al., 2001; Koepenick et al., 1996; Werner et al., 2000a].

Eddy correlation (EC) is a micrometeorological technique that offers a possible alternative to other methods in VHM regions. Although relatively new to the geologic community, EC is extensively utilized for estimating biospheric-atmospheric CO$_2$ exchange (e.g. Ameriflux, etc.) [Wofsy and Hollinger, 1999], and was recently used to measure non-thermal volcanic CO$_2$ fluxes [Anderson and Farrar, 2001]. EC is noninvasive and more representative than chamber measurements [Baldocchi et al., 1988]; however, because CO$_2$ (and possibly also sensible heat) fluxes are larger and spatially more inhomogeneous in hydrothermal regions relative to biogenic fluxes [Werner et al., 2000a], the hydrothermal environment provides an extreme test of EC. Here we use an analytic footprint model [Horst and Weil, 1992; Horst and Weil, 1994] (hereinafter referred to as HW92 and HW94) to compare EC fluxes with surface fluxes for the first time in a hydrothermal region.

2.3 Theory of Eddy Correlation

In the moving lower atmosphere, mass conservation of CO$_2$ is expressed by
\[
\frac{\partial \tilde{c}}{\partial t} = -\frac{\partial \tilde{u} \tilde{c}}{\partial x} - \frac{\partial \tilde{v} \tilde{c}}{\partial y} - \frac{\partial \tilde{w} \tilde{c}}{\partial z} = -\text{div}\tilde{F}
\]  \hspace{1cm} (2.1)

with \( \tilde{c} \) the concentration (mass/volume) of CO\(_2\). We have neglected molecular diffusion of CO\(_2\), which is unimportant here. \( \tilde{F} = \tilde{u}\tilde{c} = (\tilde{u}\tilde{c}, \tilde{v}\tilde{c}, \tilde{w}\tilde{c}) \) is the CO\(_2\) flux vector defined as the mass of CO\(_2\) passing normal to a unit area per unit time.

The flow near the earth's surface is turbulent, making \( \tilde{c} \), the air velocity \( \tilde{u} \), and the CO\(_2\) flux \( \tilde{F} \) random variables. If we average over many realizations to remove randomness (denoted by an overbar), and write \( \tilde{u} \) and \( \tilde{c} \) as the sum of ensemble-mean and fluctuating parts (e.g., \( \tilde{c} = C + c \)), the ensemble-mean flux is

\[
\tilde{F} = (UC + \overline{uc},\overline{vc},\overline{wc}) \cdot (uc,vc,wc) \text{ is the turbulent or eddy flux of CO}_2.
\]

Under steady mean conditions, and if the mean flow is horizontally homogeneous (eliminating the \( x \) and \( y \) derivatives), the ensemble average of Equation (2.1) then becomes

\[
\text{div}\tilde{F} = \frac{\partial}{\partial z} \left( WC + \overline{wc} \right) = 0
\]  \hspace{1cm} (2.2)

To a good approximation in the lower atmosphere \( \text{div}\tilde{u} = 0 \). Averaging that expression yields
Again under horizontally homogeneous conditions the first two terms in (2.3) vanish. Since \( W = 0 \) at the surface, it follows that \( W = 0 \) everywhere, and (2.2) reduces to

\[
\frac{\partial \overline{w}\c}{\partial z} = 0 , \tag{2.4}
\]

which implies that \( \overline{w}\c(z) \), the vertical component of the mean turbulent flux of CO\(_2\) at height \( z \), is equal to the mean surface flux of CO\(_2\) under horizontally homogeneous and steady mean conditions.

When the mean surface flux \( E \) of a passive constituent is not spatially uniform, the linearity of (2.1) in \( \overline{c} \) allows the vertical turbulent flux to be related to the distribution of flux \( E \) at the surface [HW92]

\[
\overline{w}\c = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E(x', y') f(x - x', y - y', z_m) dx' dy'. \tag{2.5}
\]

The function \( f \) is called flux footprint, and is defined as the contribution, per unit surface flux and area, of each element of upwind surface to \( \overline{w}\c \) at a given point downwind [Schuepp et al., 1990]. As HW92 point out, (2.5) says that for a point surface flux of unit
strength at \((x', y')---i.e., for \(E(x', y') = \delta(x' - x^s)\delta(y' - y^s)---\) the footprint function \(f(x' - x^s, y' - y^s, z_m)\) is equal to the vertical eddy flux \(w_c(x,y,z_m)\).

The equation for the mean concentration downwind of a surface point source during statistically steady and horizontally homogeneous meteorological conditions is

\[
U \frac{dC}{dx} + \frac{d\overline{vc}}{dy} + \frac{d\overline{wc}}{dz} = 0. \tag{2.6}
\]

We have taken the mean wind vector to be in the \(x\)- direction so that \(\overline{U} = (U,0,0)\), and have dropped \(\overline{uc}\) because it is typically small compared to \(UC\). Integrating (2.6) over the lateral coordinate, noting that the lateral turbulent flux \(\overline{vc}\) vanishes well away from the centerline of the mean plume downwind of a point source, yields

\[
U \frac{d\overline{C}^y}{dx} + \frac{d\overline{wc}^y}{dz} = 0, \tag{2.7}
\]

where, for example, \(\overline{C}^y = \int_{-\infty}^{\infty} C(x,y,z)dy\). Since we have equated the footprint function \(f\) with the vertical eddy flux \(\overline{wc}\) downwind of a unit point source, we can replace

\[
\frac{\partial\overline{wc}^y}{\partial z} \text{ with } \frac{\partial f^y}{\partial z} \text{ in (2.7), which is the equation used by HW92 to determine } \overline{f}^y. \text{ The function } f \text{ is determined from } \overline{f}^y \text{ through}
\[ f = \overline{f} \cdot \frac{1}{\sigma_y \sqrt{2\pi}} e^{-\frac{y^2}{2\sigma_y^2}} \]  

(2.8)

where \( \sigma_y \) defines the footprint width (see below).

Within the stated idealizations, (2.7) and (2.8) are exact. HW92 used a model for \( \overline{C}^y \) to solve for \( \overline{f}^y \) (discussed below).

Physical parameters that influence \( f \) include the measurement height \( z_m \) and meteorological conditions during the measurement. Below we demonstrate how we used (2.5) with measurements of \( E \) from the hydrothermal region, and the footprint \( f \) [HW92; HW94] to calculate a predicted turbulent flux \( (F_P) \). \( F_P \) fluxes were compared with measured turbulent fluxes \( (F_M) \) as a means of testing the EC method in a spatially inhomogeneous and high-flux hydrothermal region.

2.4 Field and Analytical Methods

2.4.1 Eddy Correlation Measurements

An infrared CO\(_2\)/H\(_2\)O analyzer (Li-Cor Inc., Model LI-6262) and a three-axis sonic anemometer (Campbell Scientific Inc., Model CSAT3) were deployed during August 1999 at Mud Volcano (MV), YNP. The anemometer was mounted parallel to the terrain (< 4 % slope) at a height \( z_m \) of 3 m. Data were recorded at a rate of 20 s\(^{-1}\). The lag
introduced between the output signals of the vertical wind velocity $w$ and the CO$_2$ concentration $c$ was determined by maximizing their correlation coefficient. Turbulent CO$_2$ fluxes ($F_M$) and temperature fluxes were calculated as the temporal covariance (averaging over 20 to 60 minutes). EC measurements were corrected for misalignment of the anemometer following the axis-rotation procedure in [Baldocchi et al., 1988]. The Webb correction for heat flux [Webb et al., 1980] and meteorological parameters were also calculated (Table 2-1).

2.4.2 Surface Emissions

Diffuse CO$_2$ fluxes and vent emissions ($E$) were measured at Mud Volcano using the accumulation chamber method and a gas channeling system, respectively, during August 1997/98. Diffuse fluxes were measured on a 25-m spacing for areas with high fluxes (adaptive sampling) [Werner et al., 2000a]. Chamber measurements are accurate to within 15 % in laboratory tests [Chiodini et al., 1998], and vent measurements are thought accurate within a factor of two [Werner et al., 2000a]. Because surface fluxes were similar (+/- 30 %) for 1997 and 1998, $E$ in 1999 were assumed similar to $E$ measured in 1998.

2.4.3 Determining the Source Area

For each EC measurement, the maximum upwind distance of the source area (SA) was chosen as 350 m. The width of the SA was chosen as $4\sigma^w = 4\sigma_c x / U$, where $x$ is the
upwind distance along the mean wind trajectory (Figure 2-1), and \( \sigma \) is the root mean square lateral wind velocity. \( E \) and \( f \) were assigned to every mean wind \((x)\) and crosswind \((y)\) location within the SA in 5-m increments. Vent emissions (four measurements had vents within the SA) were averaged over a 5 x 5 m\(^2\) grid and entered into the appropriate \(x, y\) location. Use of the adaptive sampling specified that surface flux measurements should be discontinued in low flux areas [Werner et al., 2000a]. If \( E \) had not been measured within 25 m of the SA location (typically at the edges of the thermal region), a background value of \(-17\) g m\(^{-2}\)d\(^{-1}\) was assigned (based on EC measurements at the edge of the region).

For this work we calculated the footprint function \( f \) from (2.8), using the HW94 model

\[
\bar{f}^y \approx \frac{d\bar{z}}{dx} \frac{z_m U(z_m)}{z^2} \frac{U(z)}{U(z_m)} A e^{\frac{\gamma}{b z}}. \tag{2.9}
\]

\( \bar{z}(x) \) is the mean plume height for the dispersion from a surface source, and is a function of \( z_m, L \) (the Obukhov length), and \( z_o \) (roughness length) [HW94]. \( z_o \) was taken as \( 3 \times 10^{-2} \) m for all runs. \( U(\bar{z}) \) is modeled with similarity expressions, and the variables \( A \) and \( b \) are functions of gamma functions of parameter \( r \) [HW94].
2.5 Results

Twelve EC measurements of $F_M$ were made between 11 A.M. and 5 P.M. under unstable ($L < 0$) conditions. $F_M$ were between -17 and 13,500 g m$^{-2}$ d$^{-1}$ (Table 2-1), and were similar in magnitude to $E$ (Figure 2-2). The correction for anemometer misalignment was typically about 5%. In nonthermal regions (i.e., grasslands) and at the edges of the thermal area, $F_M$ (-11 and -17 g m$^{-2}$ d$^{-1}$) were consistent with vegetative uptake of CO$_2$. Sensible heat fluxes (80 to 355 W m$^{-2}$) were on the order of those over agricultural sites.

Surface fluxes $E$ in the region are spatially variable with maximum values of 7200 g m$^{-2}$ d$^{-1}$ (Figure 2-1a). The footprint function $f$ (Figure 2-1b) weights surface fluxes near the EC station most heavily. Since all $f$ were calculated with the same values of $z_m$ and $z_o$, only changes in atmospheric stability (i.e., the parameter $L$) influenced the shape of $f$ along the mean wind. Unstable ($L < 0$) runs produced $f$ profiles with peaks closer to the EC station. Predicted fluxes $F_P$ were determined by integrating under the surface created by the product of $E$ and $f$ at each $x, y$ location in the SA for each measurement (Figure 2-1c).

Six of the 12 $F_M$ were measured under wind conditions where $E$ had been previously measured upwind of the EC station. Relative differences between $F_P$ and $F_M$ range between 30% and approximately a factor of two (Figure 2-3, Table 2-1), which is within the error of extrapolating chamber measurements spatially in this hydrothermal region [Werner et al., 2000a].
2.6 Discussion and Conclusions

The differences between $F_P$ and $F_M$ in this initial investigation are nominal (between 30% and a factor of 2). Larger differences were expected because (1) the sampling interval of chamber measurements (25 m) cannot capture all spatial variability of $E$ [Werner et al., 2000a], and (2) $E$ in 1999 were assumed equal to those measured in 1998. Vent emissions were also expected to cause difficulties in measuring a representative EC flux; however, the near agreement of $F_P$ and $F_M$ in all four measurements where vents existed upwind suggests EC measurements can be representative in regions that display significant inhomogeneity of surface sources.

Our results are consistent with the results of [Anderson and Farrar, 2001], who found a general agreement between average EC fluxes and surface fluxes upwind of the EC station located in a non-thermal region of high and inhomogeneous fluxes. [Anderson and Farrar, 2001] used various footprint models to determine the distance to the maximum contribution of flux upwind (typically within 100 m), and to define a 90% contribution area of $3-4 \times 10^3$ m² (based on model inputs of $z_m = 2$ m, $z_o = 2.5 \times 10^{-2}$ m, and $L < 0$ m). In the present study the peak of $f$ also lies within 100 m of the EC station (Figure 2-1b), and the area corresponding to the 90% contribution of $f$ is typically $< 5 \times 10^3$ m². However, in inhomogeneous regions, the 90% contribution of $f$ does not correspond uniformly to the 90% contribution of $F_P$ (as seen in Figures 2-1b and 2-1c), because the $F_P$ is highly dependent on the upwind distribution of $E$ (Figure 2-1a).

This analysis indicates that EC yields reliable results in hydrothermal regions, where fluxes can be up to three orders of magnitude larger than productive ecosystems.
The enhanced efficiency of EC over chamber techniques (up to a factor of 10) may facilitate estimation of a global VHM CO\textsubscript{2} flux. Finally, since EC is used to monitor temporal variability of surface fluxes over square kilometers, EC could be used to monitor volcanic unrest continuously.

### 2.7 Acknowledgements

We thank D. Lamb, D. Voigt, and A. Imboden for assistance, T. Horst, J. Weil, and D. Anderson for discussions. The C.E.C.G., Krynine, and Scholten William-Wright funds (PSU), NASA Earth System Science and U.S. Department of Energy, Global Change in Education programs funded this work. Two anonymous referees provided excellent reviews.

### 2.8 References


Figure 2–1: Example 3-D Representation of Surface Fluxes and Footprint Function. The SA for one EC location showing (a) the surface fluxes, (b) the footprint function, and (c) the product of (a) and (b). The dark region in (a) shows the limit of the SA. The EC station was located at 0,0 in all plots. The plateau effect in (a) is a result of the 25-m spacing of $E$, and the 5-m spacing of the SA. Integrating under the surface in (c) gives the FP flux.
Figure 2–2: Distributions of surface fluxes and EC fluxes. Distributions of natural logarithm of surface fluxes (chamber measurements) from August, 1998 (grey), and EC fluxes (black) from August, 1999.
Figure 2–3: Comparison of Measured and Predicted Fluxes. Measured and predicted fluxes for six measurements. The solid line shows 1:1 correspondence. The dashed lines represent a factor of 2 variation about the 1:1 line. The box indicates the approximate range of biogenically produced CO$_2$ fluxes from soils.
Table 2–1: Eddy Correlation Data, Predicted Fluxes, and Meteorological Parameters

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<th>Date</th>
<th>RL a (min.)</th>
<th>EC Flux b (g m$^{-2}$ d$^{-1}$)</th>
<th>Webb$^b$ %</th>
<th>FP Flux c (g m$^{-2}$ d$^{-1}$)</th>
<th>H d (W m$^{-2}$)</th>
<th>U e (m s$^{-1}$)</th>
<th>$s_v^f$ (m s$^{-1}$)</th>
<th>W (m s$^{-1}$)</th>
<th>$u_*$ g (m s$^{-1}$)</th>
<th>L h (m)</th>
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a. RL is the length of the eddy correlation (EC) measurement.
b. Webb % is the ratio of the Webb Flux to the EC Flux, expressed in percent.
c. FP Flux is the predicted flux.
d. H is the estimated heat flux at the surface.
e. U is the mean wind speed for the EC measurement.
f. $s_v$ is the root mean square wind velocity.
g. $u_*$ is friction velocity, a velocity scaling parameter approximately equal to the wind shear at the surface.
h. L is the Obukhow length.
Chapter 3

Monitoring Volcanic Hazard Using Eddy Covariance at Solfatara Crater, Naples, Italy 2

3.1 Abstract

An eddy covariance (EC) station was deployed at Solfatara Crater, Italy, June 8-25, 2001 to assess if EC could monitor CO₂ fluxes continuously at this site. Eddy covariance (EC) measurements of CO₂ fluxes were made at six locations within Solfatara crater continuously over the three-week period. Turbulent (EC) fluxes calculated in 30-minute averages varied between 950 and 4460 g CO₂ m⁻² d⁻¹ depending on location within Solfatara. Comparing turbulent fluxes with chamber measurements of surface fluxes using footprint models yielded an average difference of 0 % (± 4 %), indicating EC measurements are representative of surface fluxes at this hydrothermal site. Reliable EC measurements (i.e., measurements with sufficient and stationary turbulence) were obtained primary during daytime hours (08:00 and 20:00 local time). CO₂ fluxes measured closest to the degassing pools within Solfatara were the highest measured

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during the campaign (4392-4459 g CO$_2$ m$^{-2}$ d$^{-1}$), and the difference between the EC measurements and estimates using chamber fluxes yielded emission rates between 12 to 27 t CO$_2$ d$^{-1}$ for these features. For comparison, emissions for these features were previously estimated at 84 t CO$_2$ d$^{-1}$ following a seismic crisis in 1984 when the area experienced 3 meters of uplift. Daily average EC fluxes varied by ± 50 % as a function of atmospheric pressure. Variations in emissions due to volcanic processes at depth would have to exceed this diurnal variation in order to be useful to predict volcanic hazard. First-order models of magma emplacement suggest emissions could exceed this rate for reasonable assumptions of magma movement. Eddy covariance therefore provides reliable estimates of surface fluxes at Solfatara, and EC can monitor significantly larger areas than can be monitored by previous methods.

3.2 Introduction

Carbon dioxide emissions are often monitored in volcanic and hydrothermal areas in order to assess hazard in active regions [Baubron et al., 1991; Chiodini et al., 1993; Chiodini et al., 1998]. Increases in CO$_2$ degassing have been documented following dike emplacements and prior to volcanic eruptions [McGee et al., 2000; Hernandez et al., 2001], and estimates of CO$_2$ emissions have recently been used as a proxy for magma emplacement rates [Gerlach et al., 2002]. An accurate estimation of CO$_2$ degassing in volcanic and hydrothermal regions can be difficult, however, due to the spatial and temporal variability of emissions. Faults and fractures often act as conduits leading to spatial variability of emissions [Giammanco et al., 1997; Chiodini et al., 2001], and
temporal variability of emissions has been linked to changes in meteorological conditions [Connor et al., 1993; Rogie et al., 2001]. While continuous monitoring helps to establish the dependence of flux on meteorological conditions, the spatial dependence of degassing further complicates monitoring efforts. For example, continuous measurement of flux at a single location (< 1 m$^2$) might not provide sufficient information for predicting hazard in volcanic regions where gas escapes over large areas (km$^2$). Furthermore, global degassing estimates of CO$_2$ would improve by obtaining more large-scale (km$^2$) measurements at active systems [Kerrick, 2001]. Hence, new methods for continuous measurement of volcanic emissions over large regions are needed.

Recent studies have suggested that eddy covariance (EC) provides a reliable and complementary technique for measuring diffuse emissions in volcanic regions [Anderson and Farrar, 2001; Werner et al., 2000b]. Although new to the geologic community, eddy covariance has been extensively utilized in studies of biospheric-atmospheric exchange of CO$_2$ and other trace gases (e.g., FLUXNET) [Baldocchi et al., 2001]. The advantages of using eddy covariance over the chamber technique are that the measurement is (1) made above the surface, which does not disturb natural emissions, (2) continuous, and (3) representative of a spatial average of fluxes over the upwind source area [Baldocchi et al., 1988; Lenschow, 1995]. However, the volcanic environment is potentially too extreme for EC measurements because volcanic regions often have significant topographic relief, CO$_2$ emissions display extreme spatial heterogeneity, and
ground heat fluxes are typically elevated in volcanic environments. For these reasons, not every volcanic region will lead to a successful implementation of EC.

In this study we investigate if eddy covariance (EC) provides a viable technique for continuous monitoring of CO$_2$ fluxes at Solfatara volcano located within the Campi Flegrei caldera (Naples, Italy). We chose Solfatara because the majority of emissions and thermal energy from the Campi Flegrei caldera are released at Solfatara [Chiodini et al., 2001], the area seemed suitable to EC measurements (i.e, flat terrain, ~ 200-300 m homogeneous upwind fetch, < 15% slope), and because emissions and chemistry of volcanic gases have been extensively monitored at Solfatara for over 30 years [Cioni et al., 1984; Martini et al., 1984]. In this study EC measurements are compared with chamber measurements made upwind of the EC tower during the same sampling period. The study demonstrates that EC provides reliable estimates of volcanic fluxes of CO$_2$ at Solfatara. Based on the differences between EC and surface measurements we calculate the emissions from degassing pools for the first time using this technique. The daily variability of EC measurements is used to assess level of volcanic emissions necessary to exceed background variability at Solfatara, and finally, we discuss recommendations for the implementation of EC for continuous monitoring at this and other volcanic sites.

3.3. Geologic Setting and Current Monitoring

Solfatara is a volcanic crater located in the Campi Flegrei caldera complex near Naples, Italy. The complex is a nested caldera structure formed during two eruptions that occurred approximately 25 and 37 ka [Orsi et al., 1996]. Activity at Solfatara has been
inferred from volcanic products at 3.8 to 4.1 ka, but phreatic eruptions occurred as recently as the 12th century. The most recent volcanic activity in Campi Flegrei was the 1538 eruption at Monte Nuovo (an eruptive volume of 0.04 km$^3$ over 10 days) [Allard et al., 1991], which was preceded by several meters of ground uplift over a few decades [Tedesco and Scarsi, 1999]. Two periods of seismic unrest and uplift ('bradyseism') occurred between 1970-1972 and 1982-1984 causing a net uplift of 3.4 m [Corrado et al., 1976], and were accompanied by changes in the gas (mainly CO$_2$) / steam ratio [Cioni et al., 1984]. A shorter period of increased seismicity occurred in 1994 and was preceded by significant changes in gas chemistry (CH$_4$, H$_2$, He) in Solfatara emissions [Tedesco and Scarsi, 1999]. These periods of unrest are most likely the result of increased heat input at the base of the hydrothermal aquifers located at 1-2 km depth [Tedesco and Scarsi, 1999; Chiodini et al., 2001]. Although increases in heat are thought to ultimately originate from deeper magmatic sources, direct evidence of magmatic input was only first observed in 1994 when $\delta^{13}$C-CO$_2$ decreased from typical values of -1.7 to -1.9 to values of -3.5‰ [Tedesco and Scarsi, 1999]. The depth to the magma chamber has been inferred at ~5 km depth from gravimetric anomalies, seismic data, petrologic data, and the geothermal gradient, and the mantle (elevated across the region) is estimated at 25 km depth [Ferrucci et al., 1989].

Solfatara is a volcanic crater with steep walls (dip > 70°) on the north, east, and south sides [Chiodini et al., 2001]. To the west the crater wall is missing. The crater floor is flat (< 1.5 m of relief over ~500 m), hosts a large area of intense diffuse degassing (0.5 km$^2$), and contains a few degassing pools (the Fangaia, Figure 1). Several
high-temperature fumaroles (140-160°C) also exist near the SE crater wall [Allard et al., 1991]. In addition to continued fumarolic gas sampling, extensive work has been conducted to estimate rates of diffuse CO₂ degassing at Solfatara [Chiodini et al., 2001]. CO₂ fluxes are periodically measured using the chamber method over a sampling array that covers the crater floor (see Figure 3-1, measurements at 20-m spacing), and temporal variability in CO₂ flux is measured hourly by a permanent instrument in the crater.

3.4. Methods

3.4.1 Experimental Design and Analysis

Eddy covariance (EC) measurements were made at 6 locations at Solfatara, June 8-25, 2001. EC measurements were made at one primary location (location 1, Figure 3-1) for approximately 165 hours (331 30-minute measurements). This location was chosen because the primary wind direction during daytime hours was from the west, and location 1 had the largest (~300 m) uniform upwind source area (SA), or upwind region contributing to the EC measurement.

EC measurements were made at five additional locations (2-6) in an area of high surface emissions of CO₂ (the Fangaia, Figure 3-1) to test if EC and chamber measurements would be consistent in regions containing fumaroles and degassing pools. Measurements were made progressively closer to degassing pools within the Fangaia region (locations 4-6, Figure 3-1) and downwind of a region with no pools (locations 2-3,
Figure 3-1), but potentially downwind of small fumaroles. The EC measurements at these locations were made using 2-m and 1.5-m towers because only 200-m of uniform upwind fetch existed for these locations.

At each location, an infrared CO$_2$/H$_2$O open-path gas analyzer (LI-COR, Inc., Model LI-7500) and a three-axis sonic anemometer (Campbell Scientific Inc., Model CSAT3) were mounted on tower (tower heights are listed in Table 3-1). CO$_2$ and H$_2$O concentrations, the three components of wind speed, and atmospheric pressure and temperature were sampled continuously at a rate of 20 measurements per second. Turbulent fluxes ($F_M$) of CO$_2$, H$_2$O, and temperature were each calculated as the temporal covariance of the scalar ($c$) with vertical wind velocities ($w$) for 30-minute intervals

\[ F_M = w'c' \]  

(3.1)

where the prime (‘) indicates instantaneous deviations about the mean variable [Baldocchi et al., 1988].

Misalignment of the anemometer was corrected following the axis rotation procedure of [Baldocchi et al., 1988]. The Webb correction was applied for both heat and water vapor (Table 3-1) [Webb et al., 1980]. Measurements with low mechanical turbulence (i.e., those with low values of friction velocity, $u_*$ [Stull, 1988] indicate low wind shear at the surface, and are generally not considered reliable measurements [Anderson and Farrar, 2001]. For example, our measurements suggested that flux tended to decrease for $u_* < 0.1$ m s$^{-1}$, and measurements with $u_* > 0.1$ m s$^{-1}$ were
generally constant between mean wind speeds of 1.5 to 4.6 m s\(^{-1}\) (Figure 3-2a.). In other studies using EC, \(u_*\) thresholds are typically chosen between 0.23-0.25 m s\(^{-1}\) [Anderson and Farrar, 2001]. However, the magnitude of \(u_*\) is a function of the roughness and slope of the SA and wind velocity, and therefore, a \(u_*\) threshold is a site-specific value. Because Solfatara is flat and uniform site, choosing a threshold in the range of 0.23 to 0.25 m s\(^{-1}\) would not have been appropriate, and would have eliminated the majority of the data (Figure 3-2a). We chose a liberal threshold to retain as much data as possible.

We also applied tests for stationarity following the procedures of [Foken and Wichura, 1996; Vickers and Mahrt, 1997] to evaluate the error in the EC data. Following these guidelines, 30-min measurements were broken down into 5-min segments. If individual 5-min calculations of flux or wind velocity were within 25 % of the 30-min calculated values, then the measurement was considered stationary. Measurements that failed stationarity tests, or low-turbulence measurements (\(u_* < 0.1\) m s\(^{-1}\)) were not included in average daily values (Table 3-1), but are included in the figures in this paper to demonstrate how including this data in analyses could affect results.

### 3.4.2 Surface Flux Measurements

Surface measurements of diffuse CO\(_2\) degassing (\(E\)) using the accumulation chamber method [Chiodini et al., 1996] were performed over two grids during the same period as the EC measurements. Chamber measurements were made over a detailed (15-m) grid in the Fangaia region (Figure 3-1). Surface fluxes were also measured over the 20-m grid that covers the crater floor that has been sampled periodically since 1997
(Table 3-2). Figure 3-1 shows the locations chosen for EC measurements with respect to the locations of the chamber measurements. Surface fluxes measured using the chamber technique and contoured using Surfer® are also plotted (Figure 3-1). In addition to surface flux sampling, temporal variability of CO$_2$ flux, atmospheric pressure, air temperature, soil temperature, soil moisture, and wind velocity were measured hourly at the continuous flux station located in Solfatara (Figure 3-1). The continuous flux station and regular 20-m grids are maintained by Osservatorio Vesuviano in Naples, Italy.

### 3.4.3 Comparing EC and Chamber Measurements using Footprint Models

Eddy covariance (EC) measurements are representative of the weighted average of the upwind surface flux [Schuepp et al., 1990; Horst and Weil, 1992], where locations closer to the EC tower are more likely to be represented by the EC measurement than locations further from the tower. For this reason, EC measurements cannot be directly compared to the average of surface measurements upwind of the tower in regions of heterogeneous flux. In heterogeneous regions the contribution of each element of the upwind surface to the EC measurement must be determined. This contribution is called the 'footprint' ($f$), which can be modeled based on the meteorological conditions during the EC measurement. The footprint function $f$ is defined over the source area (SA), the upwind extent of which was chosen to be 100 $z_m$ for each measurement, where $z_m$ is the measurement height [Baldocchi et al., 1988], and the lateral extent was chosen as $4\sigma_y = 4\sigma_y x/U$, where $x$ is the upwind distance along the mean wind ($U$) trajectory, and $\sigma_y$ is the root mean square lateral wind velocity. Surface fluxes of CO$_2$ ($E$) and $f$ were assigned to
every mean wind ($x$) and crosswind ($y$) location within the SA in 5-m increments following the procedures in Werner et al. [2000b]. If $E$ had not been measured within 25 m of the SA location (typically at the edge of the thermal region), a background value of 30 g m$^{-2}$ d$^{-1}$ was assigned [Chiodini et al., 2001]. The convolution of surface chamber measurements of CO$_2$ flux ($E$) with the footprint ($f$) at each $x$ and $y$ location results in a predicted flux ($F_p$)

$$F_p = \int \int E(x', y') f(x - x', y - y', z_m) dx' dy'$$

(3.2)

that theoretically should correspond to the measured EC flux ($F_M$). Further, the integral of $f$ over all $x$ and $y$ in the SA should equal one [Horst and Weil, 1992; Horst and Weil, 1994]. We used the [Horst and Weil, 1992; Horst and Weil, 1994] analytical footprint model to calculate $F_p$ to be consistent with our previous work [Werner et al., 2000b].

Comparisons between predicted CO$_2$ fluxes ($F_p$) solved from (3.2) and the EC measurements of CO$_2$ flux ($F_{M-CO2}$, herein after referred to as $F_M$) were made for 162 (49%) of the 331 measurements at location 1 and for 60 measurements for locations 2 through 6. During periods of weak and variable mean wind speeds, the lateral extent of the SA sometimes exceeded ± 90° about the mean wind trajectory. Such a large SA does not result in an unreliable flux, but such measurements are not suitable for footprint calculations. Thus, comparisons between $F_M$ and $F_p$ were not performed for these measurements (25% of location-1 measurements). Comparisons were also not made if the winds were from the east, where the upwind fetch was not uniform with respect to
topography for location 1 (26 % of location 1 measurements), and was not the area of interest for locations 2-6. Comparisons were made, however, for EC measurements that were below the $u_* = 0.1 \text{ m s}^{-1}$ threshold, and also for measurements that were considered non-stationary to determine if EC measurements during these conditions were consistently over- or underestimated with respect to predicted fluxes.

3.4 Results

3.4.1 Meteorological Conditions

Wind speeds varied between 0.09 and 4.71 m s$^{-1}$ and were bimodally distributed with dominant directions centered at S70W (250°) and N80E (80°). Daytime winds were almost exclusively from the southwest, averaging S54W (234°). Nighttime winds were from both dominant directions, but easterly winds occurred primarily at night. Only one short precipitation event occurred during the measurement campaign, but this event did not significantly wet surface soils.

3.4.2 Eddy Covariance Fluxes of CO$_2$ ($F_M$)

Turbulent fluxes of CO$_2$ ($F_M$) measured using eddy covariance (EC) at location 1 varied between -1800 and 2800 g m$^{-2}$ d$^{-1}$ (Figure 3-2a). Fluxes measured at mean wind speeds $< 1.5 \text{ m s}^{-1}$ tended to decrease and become more variable, and negative fluxes
were measured during periods of low wind speeds (< 0.5 m s\(^{-1}\), Figure 3-2b). Typically negative fluxes were measured during nighttime hours and corresponded to increases in mean CO\(_2\) concentration above typical daytime values (up to a factor of 3) (Figure 3-2c). Eliminating non-stationary measurements and measurements with \(u_* < 0.1\) m s\(^{-1}\) resulted in average 30-minute fluxes that varied between 1500 and 350 g m\(^{-2}\) d\(^{-1}\) at location 1 (squares in Figure 3-2b), and uniform mean CO\(_2\) concentrations (squares in Figure 3-2c).

Daily mean \(F_M\) at location 1 varied between 1163 (± 183) to 619 (± 136) g m\(^{-2}\) d\(^{-1}\) after screening for non-stationary and low-\(u_*\) measurements (Table 3-1). Daily variations in the mean \(F_M\) were consistent with the changes observed in mean hourly CO\(_2\) fluxes measured at the continuous chamber station (Figure 3-3a). Temporal variability in flux (both chamber and EC) correlated positively to changes in atmospheric pressure during the measurement campaign (Figures 3b and 3c).

Daily mean \(F_M\) measured in the Fangaia region (locations 2-6, Figure 3-1) were elevated with respect to \(F_M\) measured at location 1. Fluxes increased progressively from location 2 to location 6 as the thermal pools in the Fangaia region were included in the source area of the EC measurement (Table 3-1). The highest EC measurements (4559 - 4834 g m\(^{-2}\) d\(^{-1}\)) were measured at location 6, or directly downwind of a degassing pool (location 6, Figure 3-1). Measurements of sensible heat were slightly higher at the locations directly downwind of thermal features, as were water vapor fluxes, unrotated mean vertical velocities, and mean CO\(_2\) concentrations (Table 3-1). The contribution to flux due to the Webb correction remained a constant percentage of the measured EC flux (Table 3-1).
3.4.3 Surface Fluxes of CO$_2$ (E)

Chamber measurements of surface CO$_2$ fluxes (E) varied between 18 and 25000 g m$^{-2}$ d$^{-1}$ (Figure 3-1) depending on location within Solfatara. The average flux of the 20-m grid (n = 203) was 1732 ± 222 g m$^{-2}$ d$^{-1}$, and the average of the 15-m grid (n = 176) in the southwest region of Solfatara was 1121 ± 188 g m$^{-2}$ d$^{-1}$ (Figure 3-1). The error expressed here is the standard error of the mean defined as $\sigma / \sqrt{n}$. Fluxes varied over several orders of magnitude over spatial scales of meters (Figure 3-1).

The daily mean CO$_2$ flux measured hourly at the permanent station varied between 421 and 466 g m$^{-2}$ d$^{-1}$ during the measurement campaign (G. Chiodini, unpublished data). The standard error of the daily mean flux was typically less than 4% of the mean value (Table 3-3). Hourly CO$_2$ fluxes were positively correlated with changes in atmospheric pressure (Figure 3-3b) with a lag periods of 12 to 24 hours (Figure 3-3c).

3.4.4 Comparison of EC fluxes ($F_M$) with Predicted Fluxes from Chamber Measurements ($F_P$)

The relative error between EC-measured fluxes ($F_M$) and predicted fluxes based on chamber measurements ($F_P$) at location 1 were centered about zero (Figure 3-4a), but negatively skewed. The relative error was defined as the EC-measured flux ($F_M$) minus the predicted flux ($F_P$). The relative error were normalized by $F_M$ and expressed as a percent. Thus, negative relative errors represent $F_M < F_P$, or EC fluxes that were less than predicted fluxes calculated from chamber measurements. Many of the cases in
which $F_M$ was more than 50% lower than $F_P$ were eliminated by filtering out non-stationary EC measurements and measurements with $u_* < 0.1 \text{ m s}^{-1}$ (Figure 3-4b and 4c). The resulting mean difference after filtering was $0 \pm 4\%$ (mean ± standard error of mean) (Figure 3-4c).

Cases in which $F_M$ was more than 50% lower than $F_P$ at location 1 correlated with wind speeds $< 2 \text{ m s}^{-1}$ before filtering (grey points in Figure 3-5a). In other words, at low wind speeds ($< 2 \text{ m s}^{-1}$) EC measurements ($F_M$) were often less than what was predicted from chamber measurements ($F_P$), indicating there was not enough turbulence for a reliable EC measurement. This trend was eliminated after filtering for low-turbulence (low $u_*$) and non-stationary measurements (squares in Figure 3-5a). The relative differences between $F_M$ and $F_P$ were not found to vary with wind direction or with time of day (Figures 3-5b and 3-5c) either before or after filtering.

At locations 2-6 the EC-measured fluxes ($F_M$) were consistently higher than the flux predicted from chamber measurements ($F_P$) (Figure 3-6a). The relative error between $F_M$ and $F_P$ varied from 18 to 82% depending on location. Higher differences corresponded to $F_M$ that contained a larger percentage of the degassing pools within the source area. For example, $F_M$ from location 6 were found to have $> 12\%$ of the footprint derived from the area of the Fangaia degassing pools and differed significantly from the chamber-based measurements. Smaller discrepancies were calculated at sites (location 1) and during measurement periods when winds blew on average from directions away from the degassing pools (e.g. location 2) or for measurements far from the degassing pools (Figure 3-6b). Typically, less than 0.5% of the footprint for $F_M$ from location 2 derived
from the upwind surface containing the degassing pools. For a few measurements at location 2, nearly 10% of the footprint was calculated to be derived from the degassing pools (Figure 3-6b). For comparison, $F_M$ from location 1 typically had < 1% contribution from the degassing pools, and on average showed a lower relative error between $F_M$ and $F_P$ than location 2. Locations 3 through 6 also showed more contribution from the degassing pools that the typical measurement at location 2. EC measurements at locations 2-6 were made primarily during daytime hours, and the relative differences between $F_M$ and $F_P$ from location 2 - 6 were not found to vary as a function of wind speed or time of day.

### 3.5 Discussion

The results of this study indicate that EC provides a reliable means to monitor CO$_2$ emissions continuously over large regions of Solfatara volcano. The temporal variability of daily mean $F_M$ at location 1 was consistent with the variability in chamber flux measurements at the continuous station (Figure 3-3a), and EC-measured fluxes were spatially representative of the upwind surface, as shown by the good agreement between $F_M$ and $F_P$ (Figure 3-4c). The successful implementation of EC at Solfatara is largely due to the fact that winds typically come from the west to southwest during daytime hours (i.e., not obstructed by the crater walls), and because the crater floor of Solfatara is large (~ 500 m across) and displays little relief (< 1%). However, because EC measurements of flux were typically only reliable (i.e., $u_* > 0.1$ m s$^{-1}$ and stationary) during daytime hours when wind speeds were > 1.5 m s$^{-1}$ (e.g., squares in Figure 3-2a
and 3-2b), EC complements, but cannot replace, the monitoring capability of continuous chamber measurements. We turn now to further discussion of the temporal and spatial variability observed in the EC and chamber measurements to address how EC could be employed to detect hazards related to volcanic and hydrothermal activity.

3.5.1 Causes for Temporal Variability of Fluxes

In order to assess the capacity of EC to detect changes in CO$_2$ flux with increases in volcanic activity, we must first document and understand background variability during periods of quiescent degassing. Because changes in the EC-measured flux tended to correlate with changes in hourly chamber measurements (Figure 3-3a), and because 75% of the variability in hourly chamber measurements of flux were explained by changes in atmospheric pressure (Figure 3-3c), we suggest the daily variability observed in CO$_2$ flux measured using EC at location 1 (up to a factor of 2, Figure 3-3a) was most likely due to the daily variability in atmospheric pressure (Figure 3-3b). In previous studies in volcanic regions, diffuse fluxes of CO$_2$ measured using the chamber technique were positively correlated to non-diurnal changes in atmospheric pressure with observed lag times from 12-72 hours [Rogie et al., 2001]. At Solfatara, the lag tends to fall between 12 and 24 hours (Figure 3-3c).
3.5.2 Spatial Representation of Surface Fluxes

One advantage of EC over chamber measurements is that the area monitored by EC is much larger than chamber measurements [Baldocchi et al., 1988]. The source area of the EC measurement scales with increasing height of the measurement [Finn et al., 1996]. Thus, source area for all EC measurements is on the order of ~100 m$^2$ to 10s of km$^2$. This compares to 100 cm$^2$ for most chamber measurements. In Figure 3-7 the footprint (i.e., the predicted contribution to the EC measurement) is plotted as a function of distance upwind from the tower. During typical daytime conditions the area contributing > 90 % to the EC measurement was situated within 70 to 170 meters upwind of the tower for 2.5 m tower. This area represents ~ 25 to 50 % of the distance across the degassing area of the crater floor at Solfatara. Thus, the area at Solfatara monitored by EC with a 2.5 m tower is a significant portion of the degassing region, allowing more thorough volcanic monitoring.

3.5.3 Causes for Discrepancies Between Measurement Techniques

The average relative error between EC fluxes ($F_M$) and predicted fluxes ($F_P$) based on chamber measurements (0 ± 4 % after screening for low-$u_*$ and non-stationary measurements, Figure 3-4c) suggests that EC yields reliable results (on average) for monitoring volcanic fluxes at Solfatara. However, the range of the relative errors between $F_M$ and $F_P$ at location 1 varied between -50 and 50 %. In this section we discuss the causes for discrepancies.
3.5.3.1 Low or non-stationary turbulence

As previously noted, instances where $F_M < F_P$ are most likely related to low turbulence or non-stationary conditions. Indeed our analysis suggests that during low turbulence ($u_* < 0.1 \text{ m s}^{-1}$) and non-stationary conditions, the turbulent flux ($F_M$) was underestimated relative to predictions based on chamber measurements ($F_P$), resulting in negative differences in Figure 3-4.

3.5.3.2 Incomplete sampling of the surface array: emissions from degassing pools

Positive differences (i.e., $F_M > F_P$) could be due to a contribution to flux measured by EC but not measured within the surface array. This was most evident for the EC measurements made in the Fangaia region downwind of degassing pools (Locations 2-6) (Figure 3-6). EC measurements made downwind of degassing pools in Yellowstone also displayed this trend, but at Yellowstone, emission rates of the degassing pools had been previously estimated [Werner et al., 2000a] and were included in the surface array [Werner et al., 2000b]. At Yellowstone the near agreement of $F_M$ and $F_P$ for measurements downwind of degassing pools suggested that EC was representative of surface flux in regions that display significant inhomogeneity. The near agreement also suggests that the difference between $F_M$ and $F_P$ can be used as a new method to estimate the emission rates of the pools. The differences between $F_M$ and $F_P$ in the Fangaia region yielded emission rates between 12 to 27 t CO$_2$ d$^{-1}$ for the degassing pools, which compares to 84 t CO$_2$ d$^{-1}$ estimated for these features in 1984 following an episode of
uplift and seismicity [Italiano et al., 1984]. The vent emissions measured at Solfatara is comparable to the estimates of vent emissions measured directly at Mud Volcano in Yellowstone, which ranged from < 1 to 24 t d\(^{-1}\) [Werner et al., 2000a]. The decrease in emissions from the degassing pools in the Fangaia region since 1984 is consistent with declining mean surface fluxes at Solfatara over the last 4 years of (Table 3-2).

3.5.3.3 Temporal variability of individual surface fluxes

The relative differences between \(F_M\) and \(F_P\) could also be in part due to temporal variability of flux at each measurement location in the upwind source area. Surface measurements of CO\(_2\) flux were performed on two separate grids, and each location was measured only once during the campaign. Thus, the temporal variability of flux at each grid location over the period of sampling is unknown. While the daily mean flux measured at the continuous station varied typically < 10 % over the sampling period, daily mean \(F_M\) were found to vary ± 50 % from the mean flux (Figure 3-3a), suggesting that surface fluxes upwind of the EC tower varied more on average than the flux measured at the continuous station. This variability in surface flux would have been captured by the EC measurement, but not represented by the two grids of chamber measurements made once during the campaign. The continuous flux station is located in a medium-to-low flux area (average ~ 450 g m\(^{-2}\) d\(^{-1}\) compared to an average of > 1700 g m\(^{-2}\) d\(^{-1}\) for the 200-pt. grid, Tables 3-2 and 3-3). This suggests that the variability observed at the continuous site could possibly be lower than other locations in Solfatara.
period, we analyzed surface fluxes measured over the 200-m grid for four consecutive months in 1997 (unpublished data, G. Chiodini). Fluxes measured at each location varied on average 35 % ± 0.5 % month to month, with variability ranging from < 1 to 70 % of the mean value at each grid location. Month-to-month variability over this range (up to 70 % of the mean) was observed at each grid location regardless of the mean flux. Thus, it is reasonable to suggest that the relative differences between $F_M$ and $F_P$ (± 50 %) was in part related to short-term temporal variability of the surface fluxes. However, we also observed that the long-term standard error of the mean flux at each grid location over a 4-year period was 10 % of the mean flux (Figure 3-8), with a range varying from 4 to 30 %. Because the long-term standard error of mean surface fluxes (10 %) is significantly less than average month-to-month errors (35 %), we suggest long-term comparisons between EC and chamber measurements could potentially converge from ± 50 % to a lower value if temporal variability of surface flux degassing were indeed the reason for the discrepancies. Because no significant changes in the volcanic activity have occurred since 1997, we consider these observations a good measure of background variability of surface degassing. Furthermore, changes in flux above background variability detected by EC could be used to determine the timing of diffuse flux surveys, allowing for a better understanding of the spatial-temporal dynamics of flux in volcanic regions.

3.5.3.4 Inaccurate weighting of the footprint model during weakly unstable conditions

Our analysis also suggests that differences on the order of ± 50 % between $F_M$ and $F_P$ could also be due to the footprint model not accurately weighting the upwind source
area during weakly unstable conditions. The shape of the footprint was largely dependent on the stability of the atmosphere, largely quantified through parameter $L$, the Obukhov length, which is measure of the relative importance of mechanical mixing (i.e., $u_*$) to buoyancy-induced turbulence [Stull, 1991]. When $L$ is negative and small, mixing due to buoyancy exceeds mechanical mixing, and the atmosphere is highly unstable (i.e., well mixed). When $L$ is negative and large, mechanical mixing exceeds mixing due to buoyancy, and the atmosphere is weakly unstable (i.e., not well mixed if low values of $u_*$ have been eliminated).

As $L$ decreased to more negative values (weakly unstable conditions, less well mixed), the peak magnitude of the footprint function decreased and was located further from the tower (Figure 3-7a). Comparisons between $F_M$ and $F_P$ during weakly unstable periods ($L << 0$) also often corresponded to a large discrepancy between the measured turbulent flux and the predicted flux (Figure 3-4d). Systematically observing the distribution of errors as a function of $L$ between -2 and -200 suggested that the footprint function lead to larger negative differences between $F_M$ and $F_P$ at values of $L < -7$ (Figure 3-4d). These negative differences were attributed to weakly mixed atmospheric conditions leading to underestimation of the $F_M$. Such observations are similar to those observed for $F_M$ during periods with low $u_*$, suggesting that $L$ might also be useful as a parameter for distinguishing periods when the turbulent flux does not represent the surface flux.

We also observed that the footprint function $f$ did not integrate to one for measurements with $L < -3.5$ (Figure 3-6b). This means that for these measurements the
upwind extent of the source area (initially set at 100 z\textsubscript{m}) was not large enough. Beyond 100 z\textsubscript{m} the upwind source area was no longer uniform; thus, we did not choose to extend the source area to enable \( f \) to integrate to one. Instead, the source area was not fully weighted for these measurements, which likely lead to an underestimation of \( F\textsubscript{P} \), or positive measured differences between \( F\textsubscript{M} \) and \( F\textsubscript{P} \) in Figure 3-4d. The underestimation of \( f \) increased with decreasing \( L \) (Figure 3-6b), suggesting that the measurements with \( L < -7 \) in Figure 3-4d also were likely the result of low integrated \( f \) values. The combined effect of weakly unstable conditions (\( L < -7 \)) causing negative differences between \( F\textsubscript{M} \) and \( F\textsubscript{P} \), and inaccurate weighting of the footprint function \( f \) causing positive differences between \( F\textsubscript{M} \) and \( F\textsubscript{P} \) is a possible explanation of the bimodal distribution of differences observed in Figure 3-4d.

### 3.5.4 Expected Increases in Emissions with Magma Emplacement

One of the ultimate goals of this study was to determine if EC measurements of volcanic fluxes of CO\textsubscript{2} can be used to monitor volcanic unrest. We have shown above that the daily variability in flux across large portions of Solfatara varies as a function of changes in atmospheric pressure: at location 1 the variability was on the order of 500-600 g m\textsuperscript{-2} d\textsuperscript{-1}. Thus, for this location, the increase in CO\textsubscript{2} flux due to an increased volcanic signal would have to exceed this threshold in order to use EC-measured fluxes as a predictive tool. Here we investigate two scenarios to demonstrate if the CO\textsubscript{2} released from depth as the magma rises to the surface would lead to CO\textsubscript{2} fluxes that exceed the background variability at this site.
The first scenario we consider is if magma were to rise to the surface from the magma chamber beneath the Campi Flegrei system. The magma chamber is estimated at 5 km depth and is thought to contain 0.3 - 0.5 wt. % CO$_2$ [Allard et al., 1991]. If a small eruptive event were to occur, say on the order of the Monte Nuevo 1538 eruption (estimated at 0.04 km$^3$ over 10 days), and all the emissions were released through the region actively degassing at Solfatara (0.5 km$^2$ [Chiodini et al., 2001]), then the average increase in flux over the entire region would be 8300 g m$^{-2}$ d$^{-1}$. This predicted increase in average flux is similar to that measured at Usu volcano in Japan, where average diffuse fluxes on the flanks of Usu increased from 1800 g m$^{-2}$ d$^{-1}$ during a period of quiescent degassing, to 7000 g m$^{-2}$ d$^{-1}$ immediately prior to an eruptive event [Hernandez et al., 2001].

The second scenario we consider is if mantle basalt would migrate from the crust-mantle boundary (estimated at 25 km depth in this region, [Ferrucci et al., 1989]) to the magma chamber beneath Campi Flegrei (~ 5 km) and release all CO$_2$ to the solubility limit at that pressure over a one-year period. Assuming an initial mantle carbon content of 500 ppm [Allard et al., 1991], 10 % partial melt, and emplacement of 0.04 km$^3$ of magma, the average daily increase in flux over that year would be ~ 3000 g m$^{-2}$ d$^{-1}$. Significant changes in the measured flux would also be observed if the magma took longer to degas: increases in flux above 500 g m$^{-2}$ d$^{-1}$ could be measured even if the time to degas increased to 3 years. Thus, the increases in flux predicted for any of these events (increases above background by at least + 50 %) would exceed daily changes in flux measurements due to fluctuations in atmospheric pressure as observed in our work.
3.5.5 Conclusions and Recommendations for Monitoring

3.5.5.1 Applicable Sites and Conditions

Despite potential complications with advection due to crater walls, Solfatara has proven an excellent site to deploy a permanent EC station to monitor CO$_2$ fluxes. The contribution to the average flux from degassing pools or fumaroles was not measurable by chamber methods, but were easily measured by EC. The success of using EC to measure degassing at Solfatara demonstrates that EC will be useful at other volcanic sites. Ideal sites should be relatively flat (<15% slope, [Baldocchi et al., 1988]), not be in the lee of a hill, and have fairly constant wind direction with at least 150-200 m of degassing area upwind of the tower location. Any implementation of EC to monitor for volcanic hazard should take care to eliminate measurements during low-turbulence or non-stationary conditions. At Solfatara, low turbulence and non-stationary measurements were observed primary during nighttime hours (Figure 3-2b and 3-2c) and at wind speeds < 2 m $s^{-1}$ (Figure 3-5a), suggesting that nighttime and low wind periods should be avoided during data collection. Based on these criteria, other applicable sites would likely include many hydrothermal areas and large caldera systems.

3.5.5.2 Tower placement - footprint considerations

In section 3.5.2 we show that the area monitored by EC is much larger than that of chamber measurements, and that EC can be used to measure the temporal variability of
flux over large regions (1000s of m$^2$ to ~ 1 km$^2$). At Usu volcano in Japan, a series of three diffuse flux surveys showed increases in flux at all locations preceding a volcanic eruption, but diffuse fluxes tended to increase most around areas displaying high degassing rates prior to the onset of volcanic activity [Hernandez et al., 2001]. If this study is typical of the changes in diffuse degassing rates prior to eruptions, then this indicates that high-flux regions would likely respond more to increases in volcanic activity. This hypothesis is also supported by the observation that degassing in volcanic areas is often elevated along well-defined fault and fracture patterns [Giammanco et al., 1998; Hernandez et al., 2000] that serve as preferential conduits for degassing. Fracture-controlled degassing is also observed at Solfatara [Italiano et al., 1984; Chiodini et al., 2001]; thus, monitoring fluxes using EC at Solfatara should attempt to contain high-flux regions within the EC source area because these regions are most likely to show the greatest response to volcanic unrest. For example, a 2.5-m tower should be located within 50 to 150 m downwind of a high-flux region given our footprint calculations.

3.5.5.3 Contemporaneous Measurements

EC can bridge the gap between continuously monitored chamber measurements and spatial surveys of surface fluxes. EC seems appropriate for detecting large-scale changes in the volcanic systems, and could be used to better plan the timing for surface mapping of CO$_2$ flux. Due to missing data during periods of low turbulence, EC is not as convenient for determining the processes causing trends in flux as continuous chamber measurements. However, continuous chamber measurements by necessity only monitor
changes at one point. The combined use of both techniques provides the most
information regarding processes and the spatial representativeness of individual chamber
measurements. Furthermore, while we have not focused our discussion on the variability
in H$_2$O fluxes, we suggest the combined measurement of H$_2$O and CO$_2$ fluxes using EC
could provide more insight to volcanic and hydrothermal processes, especially given the
history of changing gas/steam ratios preceding periods of uplift and seismicity at
Solfatara [Cioni et al., 1984]. In conclusion, we find eddy covariance provides reliable
estimates of surface fluxes at Solfatara, and EC can monitor significantly larger areas
than previous methods. Monitoring larger areas provides new insight to the temporal
variability and spatial distribution of degassing at Solfatara, and thus provides a new and
useful technique for monitoring volcanic hazard.

3.6 Acknowledgements

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allowing us to perform our experiment.
3.7 References


Tedesco, D., and P. Scarsi, Chemical (He, H-2, CH4, Ne, Ar, Na) and isotopic (He, Ne, Ar, C) variations at the Solfatara crater (southern Italy): mixing of different sources in relation to seismic activity, *Earth and Planetary Science Letters*, **171** (3), 465-480, 1999.


Figure 3–1: Contour Map of CO$_2$ Flux at Solfatara with EC locations.
The map shows locations of chamber measurements (stars) and eddy covariance measurement locations (numbered circles) occupied during June 9-25, 2001. Locations 2-6 in the Fangaia region (a region of high surface degassing in Solfatara) were occupied progressively closer to the degassing pools. EC measurements made directly downwind of the degassing pools were used to determine emission rates of the pools (see text).
Figure 3–2: Solfatara EC fluxes and CO$_2$ concentration Location 1.
All plots show the 331 EC measurements made at location 1, (a) CO$_2$ flux plotted against $u_*$ (friction velocity, a measure of wind shear at the surface, m s$^{-1}$). $u_*$ is used as a means to determine if measurements have sufficient turbulence for a reliable EC measurements. The line is a running mean calculated over a window of 0.05 m s$^{-1}$ of $u_*$. Note the decrease in flux with $u_* < 0.1$ m s$^{-1}$, indicating insufficient turbulence for a reliable EC measurements below this value. (b) EC measurements of CO$_2$ flux plotted as a function of wind speed. Grey dots indicate measurements with $u_* < 0.1$ m s$^{-1}$ or were non-stationary (see text). Dark squares indicate the measurements retained after filtering out non-stationary measurements and measurements with $u_* < 0.1$ m s$^{-1}$. Note most measurements were retained for wind speeds $> 1.5$ m s$^{-1}$, (c) CO$_2$ concentrations vs. time of day (local time). Most measurements retained were collected during daytime hours (8:00 to 20:00). Often during nighttime hours the wind speed drops, and the atmosphere becomes stable. During these conditions, CO$_2$ concentrations increase, sometimes reaching a factor of three higher than background.
Figure 3–3: Daily Average EC, Chamber Flux, and Atmospheric Pressure.
(a) Daily mean CO$_2$ fluxes measured using EC (dots) at location 1 plotted with the standard error of the mean value (bars) along with a one-day running mean of hourly chamber measurements (line) from the continuous station. The running mean was used to smooth high frequency variability. Note the similar trend between the temporal variability of both measurements. Although not a one-to-one correspondence, fluxes measured using both methods tend to show similar relative changes over periods of days. (b) One-day running mean of hourly measurements of CO$_2$ flux plotted with atmospheric pressure over the sampling period. (c) The correlation coefficient calculated between hourly CO$_2$ measurements and atmospheric pressure. Note the high value of correlation (up to 0.75) with CO$_2$ lagging 12 to 24 hours behind changes in atmospheric pressure.
Figure 3–4: Relative Difference between EC and Chamber Fluxes.
The relative differences between EC-measured fluxes ($F_M$) and fluxes predicted from chamber measurements and the footprint ($F_P$). All relative differences are defined as $F_M - F_P$, expressed as a percentage of $F_M$. Thus, negative error is when $F_M < F_P$, and positive error implies $F_M > F_P$. See text for causes of positive and negative relative error. In (a), the relative error is shown for all 162 comparisons between $F_M$ and $F_P$ at location 1. In (b), the relative error is plotted for those comparisons with $u_* > 0.1$ m s$^{-1}$. Note many negative differences are removed. In (c), the relative error is plotted for stationary measurements with $u_* > 0.1$ m s$^{-1}$ (see text). The resulting mean difference is 0 +/- 4 %. In (d), the relative error is plotted for comparisons with $L < -7$ (measurements made during weakly unstable conditions when the atmosphere is not well mixed). Footprints for these measurements did not typically integrate to 1 by the 300-m upwind limit of the source area (see Figure 3-3-6).
Figure 3–5: Relative Difference as Function of Wind Speed / Direction, and Time of Day

The relative difference between $F_M$ and $F_P$ plotted as a function of (a) wind speed, (b) wind direction, and (c) time of day. Grey dots indicate comparisons that failed tests for stationarity and low $u^*$, squares represent stationary measurements with $u^* > 0.1 \text{ m s}^{-1}$. Note how the relative errors are negatively skewed at low wind speeds, but that filtering for low $u^*$ and non-stationary measurements eliminated these measurements. Relative errors were not found to vary as a function of wind direction (b) or time of day (c).
Figure 3–6: Measured EC Fluxes vs. Predicted Fluxes for all Solfatara Locations.
The predicted flux ($F_p$) determined from chamber measurements plotted against EC-measured flux ($F_m$) for all locations within Solfatara (a). The error for the EC measurements are based on the recommendation of Vickers and Mahrt [1997], and the error of the predicted fluxes is based on the long-term variability of mean surface fluxes (Table 2). Comparisons between $F_m$ and $F_p$ at location 1 cluster around the one-to-one line. At all other locations (2-6), $F_m$ exceeds $F_p$ because the EC measurements were made downwind of degassing pools. The contribution from the degassing pools in the Fangaia region was not included in the surface array used to calculate $F_p$. The differences between $F_m$ and $F_p$ were used to calculate the emission rates of the pools in the Fangaia region: 12 to 27 td$^{-1}$ (see text). In (b) the relative differences between $F_m$ and $F_p$ is plotted as a function of the % contribution to the footprint from the area of the degassing pools in the Fangaia region. The relative difference increases with increasing contribution from the degassing pools in Fangaia. Location 6 (located directly downwind of the degassing pools) shows the highest contribution to the footprint (up to 16%) from these features. The measurements from location 2 have between ~1 and 10% contribution from the degassing pools, and location 1 has the least contribution from the degassing pools (< 0.5%).
Figure 3–7: Footprint Function as a function of $L$
(a) Three examples of the footprint function plotted as a function of distance upwind of the EC tower. The different examples show how the footprint changes with varying atmospheric conditions, as expressed by parameter $L$ (in m). The peak of the footprint function indicates the maximum weight applied to a location upwind of the tower such that the EC measurement is most representative of that location within the source area. As $L$ becomes more negative, the atmosphere is less well mixed, and the peak magnitude of the footprint function becomes lower and further from the tower. In (b), the cumulative footprint function is plotted as a function of distance upwind of the EC tower. Note with low negative values of $L$ the footprint function does not integrate to 1 by the 300 m upwind (i.e., the maximum upwind distance of the source area). Also note that ~ 90 % of the footprint function is obtained by 70 to 170 m upwind of the tower in all cases.
The long-term standard error of the mean of surface fluxes measured over 13 surveys from 1997 to present (Table 3-2) is approximately 10% of the mean flux, regardless of the mean flux at the site.

**Figure 3–8: Long-Term Standard Error of Surface Fluxes**

The long-term standard error of the mean of surface flux plotted as a function of the mean from each location within the 200-pt. grid of surface fluxes, measured over 13 surveys from 1997 to present (Table 3-2). The standard error of the mean fluxes is ~ 10 % of the mean flux, regardless of the mean flux at the site.
Table 3–1: Eddy Covariance Data Collected at Solfatara Crater, June 8-25, 2001

<table>
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<th>Site</th>
<th>UTM</th>
<th>UTM</th>
<th>Julian Day</th>
<th>n</th>
<th>Height (m)</th>
<th>Mean $F_m$ (g m$^{-2}$ d$^{-1}$)</th>
<th>$1\sigma$ (g m$^{-2}$ d$^{-1}$)</th>
<th>$1\sigma \ n^{0.5}$ (g m$^{-2}$ d$^{-1}$)</th>
<th>$1\sigma \ n^{0.5}$ (% of $F_m$)</th>
</tr>
</thead>
<tbody>
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<td>4520230</td>
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* each measurement represents a 30-min. time average
** Of 333 30-minute averages, 180 had sufficient turbulence to calculate an eddy correlation flux

(cont. on next page)
### Table 3-1 (cont.)

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Table 3–2: Range and Mean of Chamber Fluxes Measured over the 200-pt grid, 1997-2001 \(^a\).

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\(^a\) Data collected by G. Chiodini, unpublished data.
Table 3–3: Daily Averages of Chamber Flux measured at the continuous station in Solfatara, June 8-25, 2001.

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<td>0.64</td>
</tr>
<tr>
<td>176</td>
<td>431</td>
<td>52.1</td>
<td>15.1</td>
<td>3.5</td>
<td>1006.4</td>
<td>63.8</td>
<td>0.52</td>
</tr>
</tbody>
</table>

* Data collected by G. Chiodini, unpublished data.
Chapter 4

CO₂ Emissions from the Yellowstone Volcanic System

4.1 Abstract

Two methods were used to estimate CO₂ degassing from the Yellowstone magmatic-hydrothermal system. The amount of magmatic CO₂ released as basaltic magma emplaces from the mantle into the crust beneath the Yellowstone caldera is calculated and compared to CO₂ fluxes measured in three different types of hydrothermal regions within Yellowstone. Comparison of modeled estimates with surface measurements suggests that $3.7 \pm 1.3 \times 10^{11}$ mol y$^{-1}$ ($45 \pm 16$ Kt d$^{-1}$) of CO₂ are released from Yellowstone due to diffuse degassing. Flux measurements suggest that fluxes in acid-sulfate regions were significant in total calculations (> 96 % of the total), whereas the fluxes in neutral-chloride and travertine-precipitating areas were not significant. Analyses of carbon and helium isotopes suggest that ~ 50 % of the CO₂ emitted is derived from sedimentary sources at locations outside the caldera, whereas locations inside the caldera likely have sedimentary contributions < 30 %. In addition to release of CO₂ with emplacement, magma crystallization in the subsurface is thought to contribute significantly to the CO₂ emissions at the surface. The contribution of CO₂ from
Yellowstone to global volcanic CO$_2$ emissions ($\sim 6-7 \times 10^{12}$ mol y$^{-1}$) is comparable to the CO$_2$ contribution from other large volcanic systems like Popocatepetl, Mexico and the combined contribution from the Hawaii hotspot. Likewise, the amount of CO$_2$ emitted per land area from Yellowstone (on average $10^8$ mol CO$_2$ km$^{-2}$ y$^{-1}$) is also a significant when compared to other large volcanic and hydrothermal systems worldwide.

4.2 Introduction

Determining the volatile transfer of CO$_2$ from mantle or crustal reservoirs to the exosphere has received considerable recent attention due to the important implications to the long-term climate of Earth [Marty et al., 1998; Kerrick, 2001]. The amount of CO$_2$ released from volcanic, hydrothermal, and metamorphic (VHM) systems is relatively unconstrained, yet, is an important component of the long-term global carbon cycle [Berner et al., 1983; Kerrick, 2001]. Over geologic time, CO$_2$ released to the atmosphere from VHM systems is balanced by the atmospheric drawdown due to the weathering of silicate minerals, thereby maintaining a habitable climate on Earth. However, perturbations in the Earth’s climate have been linked to changes in the atmospheric CO$_2$ concentration, highlighting the need for a better understanding of the long-term carbon cycle [Berner, 1991; Berner, 1994].

In order to estimate variability of CO$_2$ in the Earth’s atmosphere over geologic time, it is first necessary to quantify and understand the processes controlling emissions of CO$_2$ on Earth today [Berner and Lasaga, 1989]. Several authors have attempted to quantify the global release of CO$_2$ from VHM systems, but estimates are hindered by a
lack of data for most active systems. Estimates for volcanic degassing vary over an order of magnitude (from 0.4 to 10 x 10^{12} mol y^{-1}) [Williams et al., 1992; Brantley and Koepenick, 1995], but are generally consistent with estimates inferred from the atmospheric drawdown due to weathering (6-7 x 10^{12} mol y^{-1}) [Berner, 1991; Berner, 1994]. Active hydrothermal systems likely contribute significantly to global VHM emissions (> 10^{12} mol y^{-1}) [Brantley and Koepenick, 1995; Kerrick et al., 1995], but estimates are less constrained than estimates for volcanic systems. Until more VHM systems are assessed for CO_{2} emissions, global estimates will inherently contain considerable uncertainty [Kerrick, 2001].

This study is aimed at quantifying the CO_{2} emissions for the Yellowstone magmatic-hydrothermal system. Yellowstone is unique compared to other global volcanic and hydrothermal systems. The volcanism at Yellowstone is driven by a mantle hotspot located beneath the North American Plate, which has been active for > 12.5 my. The Yellowstone volcanic system supports one of the largest hydrothermal systems on Earth (up to 1000 km^{2}) [Rowley, 1982]. Previous estimates of CO_{2} emissions from the Mud Volcano thermal region of Yellowstone (~0.4 km^{2} of degassing area, > 2 x 10^{9} mol y^{-1} or > 290 t d^{-1} CO_{2}, [Werner et al., 2000a]) are equivalent to emissions measured at some active volcanoes (e.g., Vulcano, ~ 1.6 x 10^{9} mol y^{-1} CO_{2} [Chiodini et al., 1996]). Given that Mud Volcano represents less than one percent of the hydrothermally altered land area in Yellowstone (Figure 4-1), it is likely that the Yellowstone system could contribute significantly to present-day VHM emissions. Estimating the emissions from the whole of Yellowstone, however, is particularly challenging given that Yellowstone
contains > 10,000 active thermal features [Fournier, 1989] and > 190 km$^2$ have been affected by hydrothermal activity (Figure 4-1) [Rodman et al., 1996]. While hydrothermal activity is concentrated in basins, most regions are either too extensive or remote to measure completely using ground-based techniques (Figure 4-1).

In this study, we use two methods to estimate CO$_2$ degassing from the Yellowstone magmatic-hydrothermal system. First, we calculate the amount of magmatic CO$_2$ that would be released with the emplacement of mantle basalts into the crust beneath the Yellowstone caldera. Such calculations are only possible given the wealth of data that has been collected over the last three decades, providing geological and geochemical constraints for the Yellowstone system. We then compare CO$_2$ fluxes measured in several different types of hydrothermal regions within Yellowstone to estimate the total emissions of CO$_2$ based on land area affected by various types of hydrothermal activity. Because the volatile flux of deep CO$_2$ can be the product of multiple sources at depth, we use carbon and helium isotopes to assess the contribution of each source to the total degassing estimate. We then compare the estimate of magmatic CO$_2$ derived from surface measurements and isotopic analysis to the calculations of magmatic degassing of CO$_2$ based on magma emplacement. Finally, both estimates are evaluated in the context of globally important volcanic and hydrothermal systems.

### 4.3 Magmatic Degassing Based on a Geologic Model

In this section we estimate the amount of CO$_2$ released as mantle basalts emplace beneath the Yellowstone caldera. A geological model for Yellowstone (Figure 4-2),
compiled from 3-D tomographic inversions of seismic velocities, petrologic observations, studies of heat flow and uplift, and geochemistry of hydrothermal waters and gases [Fournier, 1989; Dzurisin et al., 1990; Smith et al., 1994; Saltzer and Humphreys, 1997; Wicks et al., 1998; Miller and Smith, 1999], provides the needed constraints for predicting the sources and fate of CO₂ for the Yellowstone system.

4.3.1 Source and Evolution of Yellowstone Basaltic Magmas

Volcanism along the Yellowstone-Snake River Plain (YSRP) occurs in distinct stages. Yellowstone is currently in the stage in which basaltic magma generated in the upper mantle (< 240 km) rises due to density differences, and pools at the base of the crust (~ 40 km, Figure 4-2). Injection of this basaltic magma into the lithosphere melts crustal rocks and forms silicic magmas (Figure 4-2) [Hildreth et al., 1991; Smith et al., 1994; Dzurisin et al., 1999].

Petrology of erupted basalts reveals information regarding the evolution of mantle-derived magmas in crustal reservoirs. Most basaltic magmas erupted in the Yellowstone region are hypersthenne-normative tholeiites that contain sparse olivine and plagioclase phenocrysts. Few basalts are primitive and most show evidence of mixing with up to 30% rhyolitic magma in crustal reservoirs. The only xenoliths of deep origin brought to the surface in basalts include partially melted deep-to-mid-crustal granulite, indicating that basaltic magma was transported through or resided at this level in the crust. However, the general lack of mantle xenoliths as well as high-pressure
phenocrysts is stronger evidence that basalts typically ascend slowly and have long crustal residence times before eruption [Hildreth et al., 1991].

Tomographic imaging of a high-velocity layer at the base of the upper crust (at ~15-25 km depth) [Sparlin and Braile, 1982] indicates that basalts arrest at this level (Figure 4-2). The input of basaltic magmas to this level would supply a continuous source of heat to sustain the production of large amounts of silicic magma over periods of millions of years. However, phenocryst populations support residence in both mid- and deep-crustal reservoirs. Finally, because the geochemistry of basaltic units suggests that magmas evolve independently in crustal reservoirs, and because the volumes of individual basaltic eruptions lie between <1 to 25 km$^3$ [Hildreth et al., 1991], it follows that the crust has been intruded by thousands of > km-scale parcels of basalts [Hildreth et al., 1991] over the 2.2 Ma period of evolution of the current Yellowstone system.

Whether or not the Yellowstone system is ultimately connected to a deep mantle plume remains unknown. Most evidence suggests that convection in the asthenosphere drives the propagation of the Yellowstone system [Hildreth et al., 1991; Humphreys et al., 2000] rather than continuous input from a deep mantle source. It is not evident whether basalts have been derived from an evolved (MORB-like) upper mantle, or from a more enriched (OIB-like) deeper source because the original geochemical natures of the emplaced basalts have been overprinted by crustal signatures. The isotopic signatures of He found in fluid inclusions in olivines along the YSRP hotspot track are high in $^3$He (max $R_c/R_a = 17$, [Craig, 1997]) and similar to the present-day Yellowstone emissions [Kennedy et al., 1985], revealing that the mantle source is more enriched in primordial
He than typical asthenosphere (e.g., MORB). Hence, a purely convecting-asthenosphere model can not explain the primitive mantle signature as expressed by high $^3$He contents in gases, which tend to suggest either a continuous or non-waning input from a deep mantle source throughout the evolution of the hotspot system.

4.3.2 Estimating Magmatic CO$_2$ emissions from Yellowstone

We utilize magma emplacement rates estimated for the Yellowstone system and studies on the carbon content and degassing of magmas (e.g., [Bottinga and Javoy, 1990; Dixon et al., 1997; Dixon and Clague, 2001] and references therein) to determine the amount of magmatic CO$_2$ that could be released during the emplacement of upper mantle basalt into the crust at Yellowstone. If we assume that a partial melt with melt fraction $F_m$ (i.e., the fraction of the volume of rock that undergoes melting) forms in the mantle from a source rock with an initial carbon content of $C_i$ (wt. % as CO$_2$), and is emplaced at a rate $E_M$ (km$^3$ y$^{-1}$) into the crust, then the emission rate of CO$_2$ from the Yellowstone magmatic system ($F_{YVS}$, mol CO$_2$ y$^{-1}$) can be calculated from

$$
F_{YVS} = E_m \cdot \left( \frac{C_i}{F_m} - C_{so} \right) \cdot d \cdot k.
$$

Here, $C_{so}$ (wt. % CO$_2$) is the solubility of CO$_2$ in the magma emplaced to a depth $D$, and $d$ is the density of a basaltic magma (2900 kg m$^{-3}$). $k$ (2.27 x $10^8$ m$^3$) is a units conversion factor that converts wt. % CO$_2$ to mol CO$_2$ and km$^3$ to m$^3$. It is assumed that
carbon partitions completely into the melt phase at the location of magma generation in the mantle (e.g., [Bottinga and Javoy, 1990]). We assume that as the melt rises, CO₂ degasses from the melt, and that the melt and the gas phase reach equilibrium at depth due to long crustal residence times [Hildreth et al., 1991]. Bottinga and Javoy [1990] argue that an equilibrium state is quickly established once a melt obtains a supersaturation ≥ 1.5 with respect to CO₂, which is consistent with our initial conditions (discussed below). Finally, as CO₂ exsolves from the melt we assume that the gas phase escapes from the magma chamber to shallower depths beneath the caldera (e.g., to the hydrothermal systems) and potentially to the surface. The emission rates calculated in this exercise are the result of magmatic degassing, and would not necessarily equal surface emissions if (1) a large component of surface degassing is derived from the decomposition of limestones and sediments, (2) if CO₂ reacts with subsurface hydrothermal waters and rocks and exits the Yellowstone system as bicarbonate, (3) if significant amounts of carbon precipitates as calcite in the subsurface or travertine at the surface, or (4) if surface emissions are not at steady state due to episodic release or storage of volatiles regulated by rupturing and healing of precipitate layers in the subsurface [Fournier, 1999]. The ranges and sensitivity of the calculation of Yellowstone emissions to input parameters $E_M$, $F_m$, $C_i$, and $C_{SD}$ are discussed below.

4.3.2.1 Emplacement Rates at Yellowstone ($E_M$)

The emplacement rate of basaltic magma from the mantle beneath Yellowstone ($E_M$) can be estimated from seismic imaging, uplift, and heat flux studies. Hildreth et al.
[1991] estimated that ~ 10,000 km$^3$ of basaltic magma have emplaced into the crust beneath Yellowstone over the last 2.2 Ma, yielding an average magma emplacement rate of ~ 0.005 km$^3$ y$^{-1}$. More recently Humphreys et al. [2000] imaged an 115,000 km$^3$ sill beneath Yellowstone, only half of which was expected to be basalt originally from the mantle. If we assume half of the volume of the sill was emplaced over the same 2.2 Ma history, this results in an average rate of 0.025 km$^3$ y$^{-1}$. The lower of these rates is comparable to an estimate of the average emplacement rate for Yellowstone compiled from various studies (0.002 ± 0.0005, [Crisp, 1984]. However, Shaw [1985] suggested that a minimum of 0.01 km$^3$ y$^{-1}$ of mafic input from the mantle is needed on average to maintain an active silicic system such as Yellowstone, supporting higher emplacement rates.

Magma emplacement rates have also been estimated from measured uplift and heat flux within Yellowstone. One model suggests that uplift is due to the emplacement of 0.017 km$^3$ y$^{-1}$ of basaltic magma beneath the caldera system [Dzurisin et al., 1994]. However, a second model suggests that uplift and subsidence could be the result of pressurization and depressurization of the hydrothermal system through the sealing and rupture of fractures. Deformation studies since 1923 suggest that the timescale of uplift supports the hydrothermal model over the magma emplacement model [Dzurisin et al., 1999]; yet, emplacement of magma from the mantle may be responsible for lower-frequency periods (1000-y timescale) of uplift and subsidence. Heat flux studies indicate that the thermal flux needed to drive the hydrothermal system could result from either crystallizing and cooling 0.08 km$^3$ y$^{-1}$ of basaltic magma, or from crystallizing 0.2 km$^3$ y$^{-1}$
of rhyolite magma beneath the caldera [Fournier, 1989]. Emplacement rates of 0.08 km$^3$ y$^{-1}$ of basaltic magma would cause uplift rates that are ~ 7 times too high given the measured historic uplift rates [Fournier, 1989]; thus, the heat flux is most likely derived from the crystallization or cooling of rhyolite in the shallow crust. This hypothesis is supported by the tomographic imaging of partial melts at shallow depths beneath the caldera [Miller and Smith, 1999]. However, crystallizing 0.2 km$^3$ of rhyolite magma would in turn cause a volumetric decrease of 0.014 km$^3$ y$^{-1}$ [Fournier, 1989] that has not been observed in deformation studies over the last 12 ka [Locke and Meyer, 1994; Dzurisin et al., 1999]. Thus, we argue that on average 0.014 km$^3$ y$^{-1}$ of mantle basalt should have emplaced beneath Yellowstone, or else a long-term decrease in the elevation in the caldera would have been observed.

Finally, the chosen range of emplacement rates for basalt magma beneath Yellowstone in this study (0.0015 to 0.025 km$^3$ y$^{-1}$) is comparable to extrusion and emplacement rates observed at other hotspots such as Hawaii (0.001 to 0.4 km$^3$ y$^{-1}$, long term mean of 0.015 km$^3$ y$^{-1}$) and Iceland (0.05 to 0.13 km$^3$ y$^{-1}$) [Shaw, 1985; Clague, 1987].

4.3.2.2 Melt Fraction ($F_m$) and Initial Carbon Concentration of the Mantle beneath Yellowstone ($C_i$)

The fraction of partial melt $F_m$ most likely lies between 5 to 10 % based on increased seismic velocities of depleted mantle surrounding the Yellowstone hotspot [Saltzer and Humphreys, 1997; Humphreys et al., 2000]. This estimate is supported by
the work of White and McKenzie [1995], who suggest that 5% is the lower limit of melt fraction in plume environments.

The carbon concentration of the mantle has been estimated using several approaches, but due to the insoluble nature of CO$_2$ in melts at crustal depths and pressures, obtaining samples that have not undergone degassing of CO$_2$ is difficult. Thus, an accurate value of the upper mantle C concentration remains unknown. For this study the carbon concentrations of upper mantle xenoliths were compiled assuming that these samples represent relatively ‘undegassed’ upper mantle sources [Mathez et al., 1984; Nadeau et al., 1990; Pineau and Mathez, 1990; Trull et al., 1993]. The range in C from these whole rock samples (7 to 766 ppm C) is comparable to model estimates for the upper mantle (50-500 ppm C) derived from measured C/$^4$He ratios in xenoliths from hotspot locations [Trull et al., 1993]. We, therefore, initially allowed the carbon content of the upper mantle to vary between 50 and 500 ppm C, which equates to $C_i$ values between 0.018 to 0.18 wt. % CO$_2$ in Equation (4.1).

4.3.2.4 Depth of Emplacement ($D$)

The CO$_2$ solubility in the melt beneath Yellowstone depends on the pressure at the depth of magma emplacement, which can be inferred from seismic imaging of stratigraphy and petrology of Yellowstone basalts. A minimum depth of emplacement is 15 km, directly beneath the cooling granitic pluton imaged in the upper crust (2-14 km) [Miller and Smith, 1999]. The maximum emplacement depth is located near the base of the crust imaged at 40 km [Sparlin and Braile, 1982] (Figure 4-2). Emplacement depths
between 40-15 km are thus possible; however, we consider 25 to 15 km as a more applicable range because hot mantle melts need to emplace to shallow depths to maintain the production of several large silicic systems (Figure 4-2) [Smith et al., 1994], and because these depths are consistent with seismic images of high-velocity mid-crustal layer along the YSRP [Sparlin and Braile, 1982; Smith et al., 1994; Humphreys et al., 2000].

4.3.2.5. Solubility of Carbon Dioxide

Experiments on the solubility of CO$_2$ in basaltic magma demonstrate that solubility is more dependent on pressure and composition than on temperature [Blank and Brooker, 1994]. The solubility of CO$_2$ decreases as the magma becomes less mafic and as pressure decreases. Pressure was calculated as a function of depth ($P_D$) based on the following relationship

$$P_D = \int_{0}^{z=40} \rho \text{gd}D + P_{\text{atm}}$$

where $\rho$ is the density of the crust beneath Yellowstone estimated from seismic velocities, $D$ is the depth in km, and $P_{\text{atm}}$ is the atmospheric pressure. The magma is assumed to be tholeiitic in composition [Hildreth et al., 1991]. The proportion of CO$_2$ dissolved in the melt at each emplacement depth ($C_{sD}$) was calculated based on the relationship presented in Pan et al. [1991] for tholeiitic compositions.
4.3.2.6 Constraining the Model Estimates- Bubble Nucleation

Some constraints can be placed on possible combinations of the parameters $C_{sd}$, $C_i$, and $F_m$ that result in degassing of the emplaced magma. For example, if a combination of parameters results in equilibrium CO$_2$ concentration ($C_{sd}$) that exceeds the CO$_2$ concentration of the source magma ($C_i/F_m$), no magmatic emission is considered to occur. Furthermore, Bottinga and Javoy [1990] suggest that CO$_2$ bubbles will not nucleate in a basaltic melt unless the melt is 50% supersaturated (i.e., $C_i/F_m > 1.5 C_{sd}$), thereby further narrowing the range of possible initial combinations that result in degassing of a magmatic body at depth. In Figure 4-3 isoconcentration lines of $C_i$ were plotted as a function of melt fraction and emplacement depth for the condition $C_i/F_m = 1.5 C_{sd}$ [Bottinga and Javoy, 1990]. Based on this model, combinations of $F_m$ and depth of emplacement that lie above the isoconcentration line would not result in bubble nucleation, and thus, no magmatic degassing would occur. For combinations below the isoconcentration line, bubble nucleation would occur, and degassing should proceed to equilibrium [Bottinga and Javoy, 1990]. Hence, with increasing depth of emplacement or fraction of partial melt, a higher initial carbon concentration is necessary to ensure magmatic degassing occurs. If we consider exclusively a 15-km emplacement depth, $C_i$ would have to exceed ~0.06 wt. % CO$_2$ to reach 50% supersaturation when $F_m \leq 0.05$ (Figure 4-3). Thus, our initial starting conditions for $C_i < 0.016$ wt. % CO$_2$ (or < ~180 ppm C) would not result in a magmatic emission based on Equation (4.1).
4.3.2.7. Sensitivity Analysis

A sensitivity analysis was performed by calculating the percent change in the emission rate ($F_{YVS}$) calculated from Equation (4.1) as a function of the percent change in each input parameter (Figure 4-4). The sensitivity was calculated by varying each input parameter over the estimated possible range listed in Table 4-1, while holding all other input parameters constant at the mean value. These calculations suggest the emission rate is least sensitive to CO$_2$ solubility over the range of depths and pressures of emplacement (varying $D$ over its possible range only changed $F_{YVS}$ by 32% from the mean value). The emission rate was also less sensitive to the fraction of partial melt ($F_{YVS}$ changed by ~70% from the mean when $F_m$ varied from 0.05 to 0.1 (Figure 4-4). Calculated emission rates were most sensitive to the initial carbon content, causing a variation in $F_{YVS}$ of almost a factor of 2 for $0.018 \leq C_i \leq 0.18$ wt. % CO$_2$. Emplacement rates were next most strongly influenced by the range in calculated emission, varying $F_{YVS}$ by almost 90% from the mean over the specified range. In the final calculation of Equation (4.1) the depth of emplacement was set at 15 km (i.e., the lowest pressure, which minimizes $C_sD$) and the melt fraction at 0.05, which maximizes the $C_i/F_m$ term in Equation (4.1). These conditions maximize CO$_2$ released upon emplacement of basalt magma into the crust and are indicated by the star in Figure 4-3.
4.4 Results of Magma Emplacement Calculations

Magmatic emissions ($F_{YVS}$) calculated using equation (4.1) varied from $< 1 \times 10^9$ to $4.5 \times 10^{10}$ mol y$^{-1}$ (up to 5.4 Ktd$^{-1}$) (Figure 4-5). The higher emissions rates are consistent with estimates for other volcanic and hydrothermal systems such as the Taupo Volcanic Zone [Kerrick et al., 1995], and Oldoinyo Lengai [Koepenick et al., 1996]. The lower rates are less than the total emissions at the Mud Volcano thermal region of Yellowstone based on surface measurements, estimated between $2.4$ and $4 \times 10^9$ mol y$^{-1}$ [Werner et al., 2000]. The CO$_2$ released from Mud Volcano is, however, likely derived from both magmatic and sedimentary sources. In the following sections we will estimate the total emissions for Yellowstone and determine the sedimentary contribution to the total degassing from various regions including Mud Volcano. The magmatic contribution to the total degassing from Mud Volcano will establish an absolute lower limit to the magmatic emission rates calculated for the whole of Yellowstone from Equation (4.1).

4.5 Estimating Surface Emissions of CO$_2$

Groundtruthing the estimate for magmatic degassing at Yellowstone will take many years of flux measurements over the full 195 km$^2$ of thermally altered land area. However, spot measurements have been made to test the consistency of the magma emplacement model with field observations. The chemistry of the soils resulting from various hydrothermal processes is used as a means to extrapolate surface fluxes across Yellowstone. Carbon and helium isotopes are then used to determine the proportion of
the total CO\textsubscript{2} released from the decomposition of limestones and other sedimentary sources. This estimate is then compared with that estimated from the magma emplacement model described in section 4.3.

4.5.1 Hydrothermal Processes

Yellowstone supports extensive hydrothermal activity that is related to at least one large hydrothermal reservoir at depth with an estimated temperature in excess of 300\textdegree C \cite{Fournier, 1989}. The type, distribution, and extent of hydrothermal activity and accompanying CO\textsubscript{2} emissions observed across Yellowstone are primarily related to subsurface hydrothermal processes and structural control. Faults and fractures serve as conduits for deeply-derived gases and circulating groundwaters creating hydrothermally-altered areas at the intersection of these faults and fractures with the ground surface. These regions are predominantly located along the 0.6 Ma caldera rim and ring fracture zone boundaries, and along major N-S fault traces in the corridor between Norris and Mammoth (Figure 4-1).

Yellowstone’s hydrothermal activity can be broadly categorized by liquid- and vapor-dominated systems. The type of system varies with local subsurface geology, and the level of the water table. Liquid-dominated systems occur when the subsurface is liquid-saturated at shallow depths. The majority of the liquid-dominated systems are located within the western regions of the 0.6 Ma caldera rim \cite{Fournier, 1989}. Waters in these systems are often neutral-chloride and typically have high SiO\textsubscript{2} concentrations that lead to the deposition of sinter. In the Mammoth region, hot waters flow through a thick
sequence of sedimentary rocks, leading to high concentrations of Ca, Mg, and HCO$_3$ in waters that precipitate travertine.

Vapor-dominated hydrothermal systems occur in regions where the subsurface is unsaturated with respect to liquid water. Steam and gases are released when waters boil in a reservoir at depth, forming acid-sulfate thermal features at the surface due to the oxidation of H$_2$S in the condensed steam. Fumaroles are also sometimes present in vapor-dominated regions if the flow of gas and steam is great enough to penetrate the condensate zone below the surface. Vapor-dominated systems are thought to exist throughout the eastern half of Yellowstone, but Mud Volcano is the only thermal region that has been documented as vapor-dominated through scientific drilling [White et al., 1971].

### 4.5.2 Previous Correlation of Elevated CO$_2$ through Hydrothermal Soils

Previous work estimating CO$_2$ emissions in the Mud Volcano region demonstrated that diffuse CO$_2$ fluxes were highest in and around active thermal areas [Werner et al., 2000a; Werner et al., 2000b]. Degassing elevated above biogenic fluxes (> 30 g m$^{-2}$ d$^{-1}$) was observed in areas with elevated heat flux and altered soils with little to no vegetation (grasses) [Werner et al., 2000a] aligned with local faults and fractures. Elevated degassing was also observed in non-thermal regions with hydrothermally altered soils that had been revegetated (grasses and logdepole pine). These regions were typically within 150 m of active thermal features. Given the correlation between elevated
CO$_2$ and hydrothermally altered soils, Werner et al. [2000a] concluded that mapped soil units could be used as a means to detect regions of elevated degassing rates.

### 4.5.3 Hydrothermal Soil Types

Hydrothermally-altered volcanic rocks and secondary minerals make up the parent materials for ~ 195 km$^2$ of soils in Yellowstone [Rodman et al., 1996]. Hydrothermal soil types in Yellowstone form from reactions of unaltered volcanics with thermal waters and gases that issue at the surface. The varying water chemistries found in Yellowstone (neutral-chloride, travertine-depositing, acid-sulfate) and the processes occurring at depth (decompressional boiling, discussed below) largely affect the soil chemistry and soil type found in hydrothermal regions across Yellowstone.

Hydrothermal soil types are generally categorized using the same classification as the fluid chemistry: (1) neutral-chloride, (2) travertine, and (3) acid-sulfate [Rodman et al., 1996]. Neutral-chloride soils form in regions where neutral-chloride waters deposit siliceous sinter around springs. These deposits weather into soils with siliceous rock fragments. In travertine-precipitating regions, soils are characterized by travertine fragments. Acid-sulfate soils form in regions where hydrothermal gases rich in H$_2$S and CO$_2$ are released to the surface from hydrothermal waters boiling beneath the surface. As gases typically follow fractures to the surface, acid regions are found aligned with fracture zones in the vapor-dominated regions of Yellowstone (eastern regions).

Acid-sulfate soils can also be found associated with liquid-dominated regions. As hydrothermal waters migrate toward the surface from a deep reservoir, many systems
undergo decompressional boiling with vapor separation [Kennedy et al., 1985; Fournier, 1989]. When boiling occurs, CO$_2$ and other dissolved gases are lost to the vapor phase, which does not typically follow the same migration pathway to the surface. Vapor release at the surface results in acid-sulfate regions at the borders or in close proximity to silica-precipitating regions in liquid-dominated systems. Such acid regions have been observed at the Shoshone Geyser basin [Hearn et al., 1990] and other western caldera geyser basins. Acid-sulfate features can also occur in liquid-dominated regions when the hydrothermal waters boil at shallow depths directly beneath the surface, creating acid-sulfate regions on topographic highs. Based on these observations, in this study, we considered it important to classify degassing regions not by the type of hydrothermal system (liquid- or vapor-dominated), but rather by soil chemistry that best represents hydrothermal processes (subsurface boiling and gas loss).

4.6 Methods

4.6.1 Diffuse Flux Measurement

Diffuse fluxes were measured in various regions of Yellowstone using the accumulation chamber method following the procedures in Werner et al. [2000a]. STP-normalized fluxes were calculated from the change in concentration ($c$) with time ($dc/dt$ in ppm s$^{-1}$).
where $T$ is the measured temperature (K), $V$ is the volume of the entire system (m$^3$), and $A$ is the area of the base of the chamber. The $V/A$ ratio in this study was 14.05 and $k$ was 155.87 m$^{-3}$. $T_o$ and $P_o$ are included to normalize the flux to STP (298 K and 101.3 kPa). Throughout this paper diffuse fluxes are denoted in units of g CO$_2$ m$^{-2}$ d$^{-1}$. In controlled settings the error of accumulation chamber measurements has been estimated at ± 15 % [Chiodini et al., 1996] and -12 % [Evans et al., 2001]. This latter estimate emphasized that chamber measurements in model systems tend to be 12 % lower than the true flux.

During 1997 and 1998, CO$_2$ fluxes were measured in the following regions: Upper Geyser Basin, Mammoth Hot Springs, Mud Volcano and Roaring Mountain, Crater Hills, and in the Lamar River Valley (all described below) (Figure 4-1). Fluxes were measured along transects in each region (except Mud Volcano) at a spacing of 25 m. At Mud Volcano fluxes were measured in 1996 using a transect, and in 1997 and 1998 using a stratified-adaptive sampling design [Werner et al., 2000a]. In 1998, the sample size was increased to compare with our results from 1997 [Werner et al., 2000a]. However, because sampling was more extensive in Mud Volcano relative to other acid-sulfate regions in this study, we use the data here only to compare average fluxes. Given the high degassing rates documented at Mud Volcano [Werner et al., 2000a; Werner et al., 2000b], and the large land area occupied by acid soils opposed to other hydrothermal soil types in Yellowstone (Table 4-2), we focused more attention on acid systems to assess if degassing was consistently high in these regions. We chose Roaring Mountain
because it is an acid-sulfate system that lies outside the caldera along the fault zone that connects Norris Geyser Basin to Mammoth Springs and is potentially underlain by carbonates. We chose Crater Hills because it lies in close proximity to Mud Volcano and should be underlain by the same stratigraphy, but supports a mixed system of both acid-sulfate and neutral-chloride features. One spring that issues at Crater Hills has the highest Cl concentrations in the Park and is thought to have the most direct connection to the deepest and hottest hydrothermal system beneath the caldera [Fournier, 1989]. While silica is currently precipitated around this one feature, the rest of the area supports acid-sulfate features. We investigated the Lamar River Valley because it is an acid-sulfate system that lies significantly outside the caldera rim and has very little discharge of steam at the surface. The Upper Geyser Basin was chosen because it is a neutral-chloride system typical of silica depositing regions that lie in the western half of the caldera. While isolated patches of acid-sulfate regions exist at the edges of the Upper Geyser Basin, the flux measurements here were made on neutral-chloride type soils. Finally, we chose Mammoth Hot Springs because it is the largest travertine-precipitating region within Yellowstone. While clearly a much more extensive sampling in each area would be desirable, comparing the mean from a reconnaissance transect at Mud Volcano collected in 1996 with the mean determined from extensive sampling in 1997 and 1998 [Werner et al, 2000a] suggests that mean fluxes based on transect data are likely within 25 % of means based on more extensive sampling.
4.6.2 Land Area Estimates

Land area estimates for neutral-chloride, travertine-precipitating, and acid-sulfate areas were obtained from a digital database of the 1996 Yellowstone Soil Survey at the Spatial Analysis Center, Yellowstone National Park [Rodman et al., 1996]. The amount of land area associated with neutral-chloride hydrothermal activity was estimated from the Cryorthents-sh and Hydrothermal Materials and Lithis Eutrochrepts Undifferentiated map Group (unit 353Z). This map unit (~ 43 km$^2$) is composed of neutral high-chloride hydrothermal areas and non-thermal areas affected by hydrothermal activity. Travertine-precipitating areas were estimated from the Arrowpeak Family and Greyback Family Lithic Eutrochrepts Undifferentiated Group (map unit 423Z). This unit (7 km$^2$) is a mixture of travertine hydrothermal areas and areas that have been affected by hydrothermal activity. Estimates for land area in or affected by acid-sulfate hydrothermal features were based on the Cryochepts-HT&sh and Hydrothermal Materials and Hanks Family Undifferentiated Group (map unit 358Z) and the Ivywild Family and Hydrothermal Materials and Cryochrepts-HT&sh Undifferentiated Group (map unit 853Z). Both map units are composed of acid-sulphate hydrothermal areas and non-thermal areas that have been affected by hydrothermal activity in the past. The areas of unit 358Z and 853Z are 84 and 61 km$^2$, respectively. Complete descriptions of each map unit can be found in Rodman et al. [1996]. Only the proportion of each map unit that was classified as actively thermal within the database (annual temperatures > 8 °C) was used in the land area extrapolations, resulting in 34, 2, and 35 km$^2$ of neutral-chloride, travertine, and acid-sulfate soils, respectively (Table 4-2).
4.6.3 Gas Sampling and Analysis

Gas samples were collected in 1997 across eastern regions of Yellowstone in order to determine the sources of gas emitting at the surface. Sample locations were chosen to complement the data previously published by other authors [Kennedy et al., 1985; Kharaka et al., 2000]. We sampled acid systems of the eastern portion of Yellowstone because they are less well studied compared to liquid-dominated regions and regions along the Norris-Mammoth corridor. Gas samples were only collected from fumaroles, frying pans, and shallow thermal pools for gas chemistry and isotopic ratios of carbon and helium. Bottle preparation and sampling procedures for gas collection followed Fahlquist and Janik [1992]. Gas samples were collected by inverting and sealing a plastic funnel over the degassing region. The funnel was connected to a pre-evacuated flask containing 4 N NaOH using Tygon tubing. Noncondensable gases collected in the headspace were analyzed for He, H₂, O₂, N₂, CO, CH₄, and C₂H₆ using gas chromatography. Caustic solutions were titrated (using a Mettler DL25 automatic titrator) for carbonate after oxidizing reduced sulfur gases. Sulfide and total sulfur were analyzed by electrode analysis and ion chromatography, respectively. All chemical analyses were performed at Los Alamos National Laboratory, EES-1 Wet Chemistry Laboratory.

Isotopic analyses for carbon and helium were also performed on the samples. Prior to GC analysis, 10-ml aliquots headspace were transferred from the gas sampling bottles into special glass vials. The samples were analyzed for ³He/⁴He ratio (Rₜ) at the University of Rochester (Rochester, New York) within two weeks of sampling following
the procedures of Poreda and Craig [1989]. Helium isotopic ratios are expressed as the ratio $^{3}\text{He}/^{4}\text{He}$ ($R_c$) in the sample to the ratio in air ($R_a$). Aliquots of the caustic solutions from gas samples were analyzed for $\delta^{13}\text{C-CO}_2$ versus PDB ($\pm 0.1\%$) by mass spectrometry within 4 weeks of collection at Geochron Laboratories (Cambridge, Massachusetts).

4.7 Diffuse Flux Measurements

The distribution of fluxes measured in each region was distinctly skewed (Figure 4-6) as indicated by the coefficients of variation (CV, defined as the standard deviation divided by the mean of a sampled population, Table 4-2). The skewed nature of CO$_2$ degassing measurements in high-flux areas was also observed at Mud Volcano [Werner et al., 2000a] as well as many other volcanic and hydrothermal areas [Brantley and Koepenick, 1995; Chiodini et al; 1998; Bergfeld et al., 2001; Chiodini et al, 2001; Gerlach et al, 2001]. While the arithmetic average of a sampled population is an unbiased estimator of the mean, it is also very susceptible to high values in the sampled population [Gilbert, 1987]. This is illustrated if we consider the fluxes measured in the Lamar River Valley. At this location we measured flux at 45 sites, two of which could be considered anomalous, but not unreasonably high considering measurements in other regions (Figure 4-6). The arithmetic average of the sample is 1225 g m$^{-2}$ d$^{-1}$ including the two high values and 189 g m$^{-2}$ d$^{-1}$ when they are not excluded. By excluding these measurements, the CV of the sample distribution reduces from 5.3 to 1.6. Typically, if the CV of a sampled population is greater than 1.2, then alternative methods are often
employed to estimate the mean of the distribution [Gilbert, 1987]. For instance, Bergfeld et al. [2001] used minimum variance estimators developed for lognormal populations [Gilbert, 1987] to estimate the mean and variance of flux populations, and Chiodini et al. [1998] used Sichel’s t-estimator to estimate the mean of flux populations. In this study, each sample distribution was tested for lognormality using the W test (a normality test for low sample sizes [Gilbert, 1987]); however, each sampled distribution failed lognormality tests at the p = 0.001 level. The skewed nature of each sample suggests the mean calculated using minimum variance estimators developed for lognormal distributions might be less sensitive to high values than the arithmetic average (Table 4-2); however, as shown below, the results based on either estimator of the mean were essentially the same. For completeness, we have included the results based on both the arithmetic mean and the results using the mean calculated from unbiased estimators presented in Gilbert [1987].

The arithmetic average of diffuse fluxes was 27 ± 5.0 g m⁻² d⁻¹ in neutral-chloride regions, 89 ± 25 g m⁻² d⁻¹ in travertine-precipitating regions, and 1250 ± 460 g m⁻² d⁻¹ in acid regions (Table 4-2). The standard error of the mean flux (calculated as one standard deviation of the measured population divided by the square root of the number of sites measured) increased with increasing mean flux, from 18 % in neutral-chloride, to 28 % in travertine areas, to 36 % for acid-sulfate regions.

The mean flux (± standard error of the mean) calculated from minimum variance estimators [Gilbert, 1987; Bergfeld et al., 2001] was 37 ± 12 g m⁻² d⁻¹ in neutral-chloride regions, 140 ± 66 g m⁻² d⁻¹ in travertine regions, and 1170 ± 707 g m⁻² d⁻¹ for acid regions.
Throughout the remainder of following discussion the arithmetic average is used to estimate the total emission rate for Yellowstone.

The total Yellowstone diffuse emission rate based on extrapolation of the mean flux over the thermal portion of each type of hydrothermal land area resulted in emission rates of $0.8 \pm 0.14 \times 10^{10} \text{ mol y}^{-1}$ ($0.9 \pm 0.17 \text{ Kt d}^{-1}$) for neutral-chloride, $0.1 \pm 0.04 \times 10^{10} \text{ mol y}^{-1}$ ($0.2 \pm 0.04 \text{ Kt d}^{-1}$) for travertine, and $36 \pm 13 \times 10^{10} \text{ mol y}^{-1}$ ($40 \pm 16 \text{ Kt d}^{-1}$) for acid-sulfate systems (Table 4-2). Summing these estimates gives a total of $3.7 \pm 1.3 \times 10^{11} \text{ mol y}^{-1}$ ($45 \pm 16 \text{ Kt d}^{-1}$) for the total diffuse CO$_2$ emissions at Yellowstone.

### 4.8 Gas Geochemistry

The $^3\text{He}/^4\text{He}$ ratio ($R_c$) with respect to air ($R_a$) ranged from 4.6 to 17.0 (Table 4-3). The highest values of $R_c/R_a$ were sampled at Mud Volcano (16.6 to 17.0). Lower $R_c/R_a$ was measured at the Mushpots located near the eastern caldera rim (6.4), and even lower values were measured in the Lamar River valley (4.6) in the northeast region of Yellowstone (Table 4-3).

Carbon isotopic signatures of gases range from -2.5 to -4.9 ‰, and are similar to the $\delta^{13}\text{C}$ signatures of CO$_2$ collected in other regions of Yellowstone [Craig, 1963; Kharaka et al., 1992] (Figure 4-3). Gases collected in the Mud Volcano region (the region with the most magmatic He isotopic signature) have carbon isotopic signatures between $-3.2$ and $-4.8$ ‰.
4.9 Discussion of Surface Fluxes and Sources of CO\textsubscript{2}

Flux measurements suggest that average degassing rates are higher in acid-sulfate regions than in neutral-chloride or travertine-precipitating regions (Table 4-2 and Figure 4-6). The mean flux measured in neutral-chloride regions (27 g m\textsuperscript{-2} d\textsuperscript{-1}) was not significantly different than fluxes measured in background (i.e., forest) regions of Yellowstone (19.2 g m\textsuperscript{-2} d\textsuperscript{-1} [Werner et al., 2000a]). The mean flux in travertine-precipitating regions (89 g m\textsuperscript{-2} d\textsuperscript{-1}) was elevated with respect to background, but when integrated over the apparent land area was not significant in the total calculations of CO\textsubscript{2} emissions (Table 4-2). In contrast, the mean flux integrated over acid-sulfate regions was significant in total calculations (> 96 % of the total). The mean (~ 1200 g m\textsuperscript{-2} d\textsuperscript{-1}) was similar to the mean estimated from > 600 surface measurements at Mud Volcano (1700 g m\textsuperscript{-2} d\textsuperscript{-1}, [Werner et al., 2000a]), and also similar to estimated mean fluxes from Solfatara crater in the Campi Flegrei caldera (1520 g m\textsuperscript{-2} d\textsuperscript{-1} [Chiodini et al., 2001], the Horseshoe tree kill area of Mammoth Mtn. (1500 - 2100 g m\textsuperscript{-2} d\textsuperscript{-1} [Gerlach et al., 2001], and fluxes measured on the flanks of Usu volcano during periods of quiescence (1800 - 2400 g m\textsuperscript{-2} d\textsuperscript{-1}) [Hernandez et al., 2001]. Finally, the range of fluxes measured in each acid-sulfate region in Yellowstone was similar regardless of sample size (Figure 4-6), lending further confidence to the calculated mean value.

The mean fluxes estimated here for each region are consistent with what would be expected based on the subsurface processes. For example, in liquid-dominated systems the vapor phase lost during decompressional boiling as waters migrate to the surface often follows a different path to the surface and creates an area of acid-sulfate chemistry
at the surface. Deeply-derived hydrothermal waters that do not undergo decompressional boiling typically mix with cooler meteoric waters as waters rise to the surface and CO$_2$ remains dissolved in the fluid phase, documented by low Cl/HCO$_3^-$ ratios [Kennedy et al., 1985]. Thus, in either case (boiling or mixing), one would not expect high CO$_2$ emissions through the soils of neutral-chloride regions. Our diffuse degassing measurements support these models since high CO$_2$ fluxes were not observed in areas of neutral-chloride soils. Furthermore, the precipitation of silica or travertine may act as a cap that impedes gas flow to the surface, reducing observed fluxes temporarily or locally in liquid-dominated regions. Supporting this hypothesis, the lowest fluxes observed in both the Upper Geyser Basin and Mammoth Springs were measured in regions of fairly recently precipitated silica or travertine. More elevated diffuse fluxes (up to 630 and 95 g m$^{-2}$ d$^{-1}$ at Mammoth Hot Springs and UGB, respectively) were measured on highly fractured or weathered silica and travertine deposits, but these fluxes were still generally lower than fluxes measured in acid-sulfate systems.

Fluxes were elevated in acid-sulfate regions. High fluxes would be expected given that the majority of the CO$_2$ is lost to the vapor phase through boiling of deep hydrothermal reservoirs and migrates to the surface along faults and fractures creating acid sulfate soils at the surface.

4.9.1 Sampling Considerations

To constrain the surface emissions at Yellowstone in future work, we suggest that fluxes should be measured in more regions, especially those regions that have undergone
a transformation from a liquid-dominated to a vapor-dominated system. Evidence for past liquid-dominated systems is evident from the sinter deposits that are found in many vapor-dominated regions throughout the eastern portion of Yellowstone. The transition from liquid-dominated to vapor-dominated in the eastern portions of Yellowstone is thought to have followed the last glaciation when water levels were elevated with respect to today [Fournier, 1989]. Given the low average flux observed at Crater Hills (389 g m$^{-2}$ d$^{-1}$) relative to other acid-sulfate regions, it is possible that other acid-sulfate systems that were once liquid-dominated and experienced significant silica deposition may also display lower average fluxes. No quantitative data exist for how extensively the acid-sulfate regions of the eastern caldera were once influenced by silica-precipitating waters, except that sinter cones are commonly found throughout the region [Fournier, 1989].

We suggest that future sampling should also include acid-sulfate soils found at the borders of liquid-dominated regions, because these regions were not included in our sampling, and because these areas might provide the best indicator of changes deep in the hydrothermal system. For example, if heat is added to the base of the hydrothermal system, inducing more boiling at depth, the areas where this would be observed first are those areas undergoing minimal boiling currently. Thus, the highest changes in flux in a hydrothermal system due to the input of heat at depth would likely be observed at the borders of liquid-dominated regions.
4.9.2 Estimated Contribution of Thermal Features to Total Emissions

The emission estimates calculated from chamber measurements and extrapolated over land area do not include emissions from thermal features, which were estimated to contribute 30 to 60% of the total emission rate at Mud Volcano. Previous degassing estimates suggest that emissions from thermal features in liquid-dominated regions of Yellowstone [Gunter, 1972] may be up to two orders of magnitude lower with respect to emissions from thermal features in acid-sulfate regions [Gunter, 1972; Werner et al., 2000a]. Thus, we assume that acid-sulfate regions are likely the only regions with significant contributions from thermal features. However, the ratio of vent to diffuse emissions has only been determined for the Mud Volcano region [Werner et al., 2000a]. Mud Volcano lies at the intersection of two major structural features within the caldera that have fault trends perpendicular to one another (Sour Creek Dome and Elephant Back Mountain). It is possible that the subsurface beneath Mud Volcano is more fractured than other acid-sulfate regions, which might lead to a higher vent-to-diffuse ratio. Higher fracturing at Mud Volcano is supported by the high helium isotopic signature relative to other acid-sulfate regions (see below). Therefore, while the emissions from thermal features are sure to add to the total emissions at Yellowstone, we can not estimate what amount this would be. Likely the contribution from vents to the total degassing would be less than that observed at Mud Volcano (30 to 60%).
4.9.3 Sources of CO$_2$ and other Gases

In addition to magmatic degassing, hydrolysis or thermal breakdown of sediments could provide an additional source of CO$_2$. While limestones and sediments outcrop in the northern reaches of YNP [Friedman et al., 1970], several lines of evidence suggest that they also exist at depth inside the caldera. First, travertine deposits and hydrocarbons in thermal waters have been observed near the NE caldera rim [Fournier, 1989; Hutchinson and Thompson, 1992] and the sources of these are thought to be Paleozoic and Mesozoic sediments at depth. Secondly, increases in methane and nitrogen have also been observed in Yellowstone gases collected in the NE of Yellowstone, suggesting an increase in a sedimentary component in these regions (Table 4-2) [Goff and Janik, 2002]. Finally, lead isotopic signatures in hot spring deposits sampled at western caldera locations also suggest mixing of volcanic and sedimentary sources in thermal waters [Leeman et al., 1977]. In this section carbon and helium isotopes are used to calculate the fraction of CO$_2$ related to magmatic degassing versus sedimentary sources.

4.9.4.1 Carbon Isotopes

The carbon isotopic signature of CO$_2$ is often used to determine the proportion of CO$_2$ derived from distinct isotopic reservoirs. However, given the overlap in the isotopic signatures of limestones near Yellowstone and magmatic endmembers (Figure 4-7), the carbon isotopic signature alone can lead to ambiguous results. The $\delta^{13}C$-CO$_2$ measured in fumaroles in this study (-2.3 to -4.9 ‰) is consistent with previous studies (-1 to -5 ‰,
Craig, 1963]). Craig [1963] suggested that if a magmatic component of CO$_2$ existed at Yellowstone, then the isotopic signature had been overprinted by sedimentary sources based on the comparison of $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-HCO$_3^-$ at Yellowstone with those measured at other systems with no known sources of limestone. Limestones near Yellowstone have carbon isotopic signatures between -2.3 and +3.3‰ [Friedman, 1970]. This range overlaps significantly with bicarbonate in spring waters (-3 to +1‰) [Craig, 1963] suggesting a sedimentary source for the bicarbonate (Figure 4-7). The isotopic signature of CO$_2$ in equilibrium with this bicarbonate is temperature-dependent such that $^{13}$C concentrates in HCO$_3^-$ if the temperature is below ~150°C, and $^{13}$C concentrates in CO$_2$ at temperatures greater than 150°C [Malinin et al., 1967]. Given that the estimated reservoir temperatures for most hydrothermal systems in Yellowstone lie between 180 to 340°C [Fournier, 1989], and that the $\delta^{13}$C-CO$_2$ is depleted with respect to $\delta^{13}$C-HCO$_3^-$ (Figure 4-7), this implies that CO$_2$ is probably not in equilibrium with HCO$_3^-$ at reservoir temperatures, and thus could be derived from multiple sources. CO$_2$ in equilibrium with HCO$_3^-$ at reservoir temperatures would have isotopic signature ranging between -1.4 to +8.1‰, depending on the fractionation factor adopted [Malinin et al., 1967]. Thus to achieve a maximum $\delta^{13}$C of -2‰ for CO$_2$ at the surface, this would require a minimum of 60% magmatic and 40% limestone-derived components assuming an average magmatic endmember ($\delta^{13}$C-CO$_2$ = -6). Alternatively, HCO$_3^-$ and CO$_2$ could have distinct sources. In other words, as hydrothermal waters pass through limestone reservoirs, the HCO$_3^-$ in waters would increase. Meanwhile, CO$_2$ could be derived directly from degassing of mantle-derived magmas. The full range of $\delta^{13}$C-CO$_2$
measured from fumaroles at Yellowstone is consistent with the \( \delta^{13}C \) documented for hotspot magmas (Figure 4-7), accounting for a 2‰ enrichment in \( \delta^{13}C \)-CO\(_2\) relative to the \( \delta^{13}C \) of the basaltic magma source [Mattey, 1991]. However, without knowing the isotopic signature of the mantle beneath the Yellowstone system, carbon isotopic signatures alone cannot definitively identify the contribution from mantle vs. sedimentary sources.

4.9.4.2 Helium Isotopes

The magnitude and spatial distribution of \( R_c/R_a \) measured in this study indicate a significant source of primordial mantle helium within the caldera and increasing contamination from crustal sources outside of the caldera boundary. The magnitude and spatial distribution of \( R_c/R_a \) is consistent with the findings of Kennedy et al. [1985], suggesting the helium isotopic signature is constant over decadal timescales. The \( R_c/R_a \) values measured at Mud Volcano (max 17.0) were slightly higher than those measured by Kennedy et al. [1985] (max 15.8) and Craig [1997] (max 16.5). The \( R_c/R_a \) measured in the Mushpots and the Lamar River Valley were lower than those measured at Mud Volcano. Kennedy et al. [1985] interpreted the decrease in \( R_c/R_a \) as dilution that occurs with increasing transport distance from the primordial He source to locations outside the caldera. The helium ratios in this study are also equivalent to the highest values measured in fluid inclusions in olivine and clinopyroxene phenocrysts along the Yellowstone hotspot track [Craig, 1997], indicating a relatively constant and high proportion of primordial helium (\(^{3}He\)) over the life of the hotspot track (17 Ma). \( R_c/R_a \)
values as high as 35 have been measured in Hawaiian hotspot gases, which suggests that primordial helium could be diluted up to ~50% by crustal sources ($R_c/R_a = 0.05$) assuming that Yellowstone and Hawaii have similar mantle source regions. Alternatively, the signature at Mud Volcano could be uncontaminated with respect to crustal sources and reflect a Yellowstone hotspot source region that has resulted from mixing of depleted upper mantle (MORB-like, $R_c/R_a \sim 8$) and less depleted lower mantle (Hawaii-like, $R_c/R_a = 35$).

4.9.4.3 Carbon and Helium Relations

Numerous authors have employed the technique described in Sano and Marty, [1995] to estimate relative contributions from mantle, limestone, and organic-rich sedimentary sources in gas emissions based on the relative abundance of carbon and $^3$He and the carbon isotopic signature. Using the technique, the proportion of magmatic (M), limestone (L), and organic sedimentary (S) sources can be estimated from

$$
(\frac{^{12}C}{^{12}C})_{\text{obs}} = M \left(\frac{^{13}C}{^{12}C}\right)_M + L \left(\frac{^{13}C}{^{12}C}\right)_L + S \left(\frac{^{13}C}{^{12}C}\right)_S \tag{4.4}
$$

$$
1/(^{12}/^{3}He)_{\text{obs}} = M/(^{12}/^{3}He)_M + L/(^{12}/^{3}He)_L + S/(^{12}/^{3}He)_S \tag{4.5}
$$

$$
M + S + L = 1 \tag{4.6}
$$
if the δ13C and C3He of each reservoir (M, L, and S) can be determined. The difficulty in using this technique in Yellowstone is that (1) the isotopic signature of the mantle endmember for Yellowstone is not well constrained, and (2) hydrothermal processes may affect the total concentration and isotopic signature of carbon and helium in gas samples. The gas samples in this study fall within the range of C3He (from 2-20 x 10⁹) [Trull et al., 1993] and δ13C predicted for hotspots (Figure 4-8). This range overlaps with ratios determined for MORB glasses and arc-volcanic gases [Marty and Jambon, 1987] and thus could be consistent with a 100% mantle source of CO2. Such a conclusion suggests that the mantle beneath Yellowstone is more like other hotspots than MORB. However, by setting the C3He of the magmatic endmember in equations (4.4 – 4.6) to the lowest measured value (2.31 x 10⁹) (Table 4-3), the maximum amount of possible contamination by sedimentary sources can be determined. The δ13C for limestone and sediment endmembers were taken from studies at Yellowstone [Friedman, 1970; Des Marais, 1991], and the C3He for these reservoirs was chosen to be consistent with [Sano and Marty, 1995]. Given these initial conditions, the maximum contribution of CO2 from the combined sedimentary sources (both limestone and organics) was estimated at 54 % at Mammoth Hot Springs. Similarly, gases from the Lamar river valley indicate a 51 % contribution from sedimentary sources, whereas gases from Mud Volcano suggest a contribution between 35 and 17 % (Table 4-3). An average contribution of 40 % is consistent with the estimates based purely on carbon isotopic signatures described above.

In the above discussion, we have assumed that minimal CO2 has reacted with Na-silicates to form HCO3-, which would reduce the C3He ratio in the measured samples.
Such a decrease in the initial C/\(^3\)He ratio would act to increase the calculated apparent amount of carbon derived from sedimentary sources. Thus, if these reactions are occurring at depth and causing a significant decrease in the C/\(^3\)He ratio, then potentially a 40 % average allocation to sedimentary sources is too high.

### 4.10 Summary of Surface Emissions

Based on measurement, diffuse CO\(_2\) fluxes in Yellowstone are \(3.7 \pm 1.3 \times 10^{11}\) mol \(\text{y}^{-1}\) (45 ± 16 Kt \(\text{d}^{-1}\)) with > 96 % originating from acid-sulfate hydrothermal soils. Based on carbon and helium isotopes, ~ 50 % of the CO\(_2\) emitted at the surface is derived from sedimentary sources outside the caldera. Within the caldera, the fraction of CO\(_2\) from sedimentary sources likely decreases to < 30 %. An average contribution of 40 % from sedimentary sources leads to diffuse magmatic CO\(_2\) emissions in Yellowstone that range from 0.9 to 3 \(\times 10^{11}\) mol \(\text{y}^{-1}\).

### 4.11 Comparison of Model with Measurements

The emission rate calculated from the emplacement model \((F_{YVS})\) minimally has to exceed the magmatic emissions estimated for Mud Volcano based on detailed measurements [Werner et al., 2000a] and the proportion of magmatic degassing expected at this site based on carbon and helium isotopes (a minimum of 65 %, discussed above). Thus magmatic emissions for Mud Volcano lie in the range of 1.3 to 2.6 \(\times 10^9\) mol \(\text{y}^{-1}\) (0.16 to 0.31 Ktd\(^{-1}\)), which sets the lower limit for \(F_{YVS}\). Note that this estimate includes
vent emissions. Furthermore, given that similar high fluxes were measured in three thermal areas of similar size (Figure 4-1) in addition to Mud Volcano, we argue $F_{YVS}$ likely exceeds four times the emission rate of Mud Volcano, or roughly $\geq 8 \times 10^9$ mol y$^{-1}$. Based on this constraint, $C_i$ is expected at $\geq 0.07$ wt. % CO$_2$ if emplacement rates are below $0.01$ km$^3$ y$^{-1}$. Likewise, $E_M$ must exceed $0.003$ km$^3$ y$^{-1}$ even for the highest carbon contents. However, considering that $\geq 0.01$ km$^3$ y$^{-1}$ of mafic magma input has been suggested to sustain the production of large rhyolitic magmas over millions of years [Shaw, 1985], our preferred range of emissions ($F_{YVS}$) ranges from $\sim 1$ to $4.5 \times 10^{10}$ mol y$^{-1}$.

The preferred estimate of $F_{YVS}$ ($\sim 1$ to $4.5 \times 10^{10}$ mol y$^{-1}$) is within an order of magnitude of magmatic emissions determined from chamber measurements and isotopes ($0.9$ to $3 \times 10^{11}$ mol y$^{-1}$). Minimally $4.5 \times 10^{10}$ mol CO$_2$ y$^{-1}$ is needed in addition to the estimate based solely on the emplacement of basaltic magma from the mantle into the crust to agree with the minimum estimate of magmatic emissions based on measurements at the surface (Figure 4-5). The discrepancy between the degassing model and measurements is nominal given that several of the parameters used in the emplacement model vary over several orders of magnitude. In the following discussion we address conditions that would lead to convergence of the model estimates and surface measurements.
4.11.1 Surface Emissions: Sedimentary Contribution and Changes due to Non-Steady State Conditions

Carbon and helium isotopes indicate that on average ~ 40% of the emissions at Yellowstone could be contributed from sedimentary sources, the majority of which is limestone (Table 4-3). Thus, the decarbonation of additional limestone to produce a contribution in excess of 40% could help to explain the differences between degassing measurements and model predictions. A 40% contribution from sedimentary sources to the total CO$_2$ emissions from Yellowstone would equate to the decarbonation of $\geq 6650$ m$^3$ of limestone each day, or a sheet of carbonate 1.6 by 1.6 km by 1 m thick each year (assuming limestone has a density of 2.5 g cm$^{-3}$). At this rate, a ~ 2.5 km thick sequence of limestone existing beneath the volcanic deposits across the area of the caldera (~ 60 by 40 km) could be decarbonated in 2.5 Ma years, emitting on average $6.7 \times 10^{10}$ mol y$^{-1}$ (~8 Kt d$^{-1}$). If the sequence was much less than 2.5 km thick, then the carbonate reservoir could potentially be exhausted by the present time given that volcanic activity began in the region at 2.2 Ma. Additional limestone in excess of what is suggested above, however, cannot explain the remaining difference between degassing measurements and model predictions given what is known about the subsurface stratigraphy at Yellowstone. No more than an additional 5% limestone (up to ~ 7000 m$^3$ d$^{-1}$ limestone decarbonation) could be expected, whereas an additional 30% (up to 8650 m$^3$ d$^{-1}$ limestone decarbonation) would be needed for agreement between the measurements and the model.

Surface emissions could also vary with cycles of uplift and subsidence at Yellowstone that are most easily explained by rupturing and healing of the self-seal layer
at the top of the hydrothermal system [Dzurisin et al., 1999; Fournier, 1999]. Over the period of 1976 to 1984, the central area of the caldera experienced on average 22 mm y\(^{-1}\) uplift, and was followed by a period of subsidence of at a rate of 19 mm y\(^{-1}\) from 1985 to 1995 [Dzurisin et al., 1999]. The volumetric change of the land surface with either of these events (uplift or subsidence of ~ 0.24 km\(^3\) over 10 years) would lead to a storage or release of 2 x 10\(^{10}\) mol CO\(_2\) y\(^{-1}\) assuming CO\(_2\) makes up 5 % of the total gas phase, and conditions in the deep hydrothermal system are 374 °C and 22.1 MPa [Henley et al., 1984]. Thus, it seems reasonable that historic changes in the elevation of the Yellowstone caldera could explain a portion (< 50 %) of the minimum discrepancy (4.5 x 10\(^{10}\) mol CO\(_2\) y\(^{-1}\)) observed between calculated and measured emission rates.

4.11.2 The Emplacement Model

4.11.2.1 Emplacement Rates

An increase in the magma emplacement rate could elevate emission rates to levels consistent with degassing measurements. Alternatively, the magma emplacement rate may not be indicative of the flux of plume material degassing in the upper mantle. In order to explain the observed discrepancy between our model and measurements, the magma emplacement rate would have to exceed 0.04 km\(^3\) y\(^{-1}\) (Figure 4-5). Such rates are consistent with emplacement rates from other hotspot systems such as Hawaii [Clague, 1990]; however, historical uplift measurements in Yellowstone do not support magma
emplacement rates in excess of 0.017 km$^3$ y$^{-1}$ [Dzurisin et al., 1994]. Thus, we would
have to suggest that the plume impingement rate (the rate of melt accumulating at the
base of the crust) is higher than the emplacement rate, and that CO$_2$ is lost to the surface
as melts accumulate at the base of the crust. However, estimates of the buoyancy flux at
Yellowstone (the flux of material necessary to induce topographic uplift) are on the order
of 0.016 km$^3$ y$^{-1}$ [Sleep, 1990], which does not suggest high impingement rates.
Furthermore, our calculations suggest that magma accumulating at 40 km depth would
not exceed saturation with respect to CO$_2$ given our initial carbon content (up to 0.18 wt
% CO$_2$, Figure 4-3). Thus, neither higher emplacement rates nor impingement rates can
alone yield the higher fluxes needed to match the observations based on chamber
measurements.

4.11.2.2 Carbon Content

A portion of the magma feeding Yellowstone could be derived from a deeper,
possibly more enriched, carbon source given the high $^3$He/$^4$He observed in Yellowstone
gases and the geochemistry of late-and early-stage basalts [Hildreth et al., 1991]. A melt
formed from 5 % batch melting of a mantle containing 1.14 wt % CO$_2$ (derived from
3100 ppm C [Trull et al., 1993]) would result in magmatic emissions from Equation (4.1)
that are consistent with our degassing measurements. However, this would also imply a
primary magma (i.e, $C_i/F_m$) with > 11 wt % CO$_2$, which is over twice the value reported
by Dixon et al. [1997] for alkaline magmas at Hawaii (5.4 ± 0.4 wt. % CO$_2$). Mixing
between upper and lower mantle components is also likely in plume environments and
could explain the differences observed between the model calculations and measurements. *Marty et al.* [1998] suggest that ≤ 2.5 % of the lower mantle mixes with upper mantle in plume environments. If the discrepancy in our results was due to 2.5 % lower mantle contamination, then the lower mantle carbon content would have to exceed the carbon equivalent of 3.67 wt. % CO$_2$ (assuming $C_i$ of the upper mantle = 0.07 wt % CO$_2$), which is over three times the carbon concentration for the lower mantle suggested by *Trull et al.* [1993] (1.14 Wt. % CO$_2$). Alternatively, if we accept the value of $C_i$ = 1.14 Wt. % CO$_2$ for the lower mantle suggested by *Trull et al.* [1993], this implies a lower mantle contribution of > 10 % would be necessary to fully explain the discrepancy between the model and the measurements in this study. Thus, to remain consistent with the results of both *Trull et al.* [1993] and *Marty et al.* [1998], mixing of upper and lower mantle components creating an enrichment of carbon in the mantle beneath Yellowstone could account for no more than 25 % of the observed discrepancy between model results and measurements. However, it is important to note similar degassing studies typically assume source (tholeiitic) magmas with ≤ 1.2 wt. % CO$_2$ [*Gerlach and Graeber*, 1985; *Dixon and Clague*, 2001; *Gerlach et al.*, 2002], which is lower than the CO$_2$ content of the source magma estimated from 5 % partial melt in this study (estimated here as 1.4 to 3.6 wt. % CO$_2$).

4.11.2.3 Magma Crystallization

In contrast to the previous factors, crystallization of magmas residing either in the crust or at the crust-mantle boundary could explain a large portion of discrepancy
between the degassing model and surface measurements. As crystallization occurs, CO₂ preferentially partitions into the melt phase such that melts could eventually exceed CO₂ solubility limits and continue to degas. As an example, if on average 0.025 km³ of basaltic magma crystallizes in the crust each year, this would release an additional 4.1 x 10¹⁰ mol y⁻¹ (or 4.9 Kt d⁻¹) thereby increasing the calculated emission rate to ~ 0.9 x 10¹¹ mol y⁻¹, which is the lower limit of what was estimated for surface emissions based on chamber measurements. This conclusion is consistent with other studies that model crystallization in addition to magma ascent to explain emission patterns at other shallower volcanic systems [Harris and Rose, 1996].

In summary, one major and two minor potential mechanisms exist that would result in an increase in the degassing estimates produced by the model. Foremost, the emission of CO₂ with crystallization of the emplaced magma could easily explain a large portion of the discrepancy between measured emissions and those predicted by the emplacement model (4.1 of the 4.5 x 10¹⁰ mol CO₂ y⁻¹ if \( E_M \) is on the order of 0.025 km³ y⁻¹). Secondly, non-steady release of volatiles from the deep hydrothermal system could cause changes of surface emissions on the order of 2 x 10¹⁰ mol CO₂ y⁻¹. Finally, mixing of upper and lower-mantle melts could potentially increase the melt carbon concentration, thereby explaining a portion of the difference between the model estimates and the surface measurements (~ 1.1 x 10¹⁰ mol CO₂ y⁻¹). Thus, the model supports the estimate based on surface measurements, indicating that CO₂ is likely released from Yellowstone at a rate of 3.7 ± 1.3 x 10¹¹ mol y⁻¹ (45 ± 16 Kt d⁻¹).
4.12 Conclusions

The estimate of total CO₂ emissions at Yellowstone (3.7 ± 1.3 x 10¹¹ mol y⁻¹ or 45 ± 16 Kt d⁻¹) is ~100 times the values estimated for the Mud Volcano region [Werner et al., 2000a]. Based on this estimate Yellowstone supplies ~8 to 16% of the global emissions from plume (i.e., hotspot) environments estimated at 3 x 10¹² mol y⁻¹ [Trull et al., 1993; Marty et al., 1998]. Assuming 40 hotspots exist worldwide [Davies, 1999], an average hotspot emission rate of 7 x 10¹⁰ mol y⁻¹ is expected, which is slightly lower than the emission rate for Yellowstone. While our estimate is comparable to the combined CO₂ emissions from the Hawaiian hotspot (1.2 x 10¹¹ mol y⁻¹ or 15 Kt d⁻¹ combining the estimates of Ryan [2001] and Gerlach et al. [2002]), it is an order of magnitude higher than that estimated for Reunion Island (2 x 10⁹ mol y⁻¹ over the last 50 years) [Bureau et al., 1998].

Our estimate for the CO₂ emissions from Yellowstone is also similar to the second highest emission rate measured at a large volcano (Popocatepetl, 3.1 x 10¹¹ mol y⁻¹ or 38 Kt d⁻¹), which likely has a strong sedimentary component of degassing [Goff et al., 2001]. Yellowstone, however, emits less CO₂ than Mt. Etna (up to 10¹² mol y⁻¹ or 120 Kt d⁻¹) [Allard et al., 1991]. These comparisons highlight that, on a per-volcano basis, Yellowstone contributes significantly to global volcanic CO₂ emissions estimated at ~6-7 x 10¹² mol y⁻¹ [Brantley and Koepenick, 1995]. Likewise, Yellowstone is also a significant contributor to global emissions per land area. The Yellowstone volcanic system supports one of the largest hydrothermal regions in the world (~1000 km² [Rowley, 1982]), for which our estimate gives an average of 10⁸ mol CO₂ km⁻² y⁻¹. This
estimate is roughly 2 orders of magnitude higher flux per km$^2$ than other geothermal areas such as the Taupo Volcanic Zone [Seward and Kerrick, 1996], suggesting that further investigation of globally significant hydrothermal regions is necessary to better estimate global volcanic- hydrothermal emissions.

4.13 Acknowledgements

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4.14 References


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Figure 4–1: Map of Yellowstone National Park
Map of Yellowstone National Park showing the locations of hydrothermally affected land area (black regions) and the outline of the caldera rim and ring-fracture zone of the Yellowstone caldera (From White et al. [1992] their Figure 1). The letter A refers to acid-sulfate regions, NC to neutral-chloride regions, T to travertine regions, and C to regions with little output of steam at the surface.
Figure 4–2: Yellowstone Geologic Model
A geological cross-section of the Yellowstone volcanic system inferred from seismic velocities. The hotspot is in the upper mantle extending to depths no more than 150 km [Saltzer et al., 1997]. Pooling of basaltic magma is expected at the base of the crust [Dzurisin et al., 1994], and injection of basaltic magma to minimum depths of 25 km is responsible for creating silicic magmas in the upper crust. (modified from Smith et al. [1994] their Figure 35).
Figure 4–3: Bubble Formation as a Function of Depth and Melt Fraction
Isoconcentration lines determined for conditions in which the melt concentration exceeds solubility by 50% plotted as a function of depth of emplacement and melt fraction. Any region above the isoconcentration line represents conditions in which bubbles would not form in the melt. Below the line, the magma would result in degassing of CO$_2$. For example, an initial carbon content of 0.07 wt. % CO$_2$ would not result in bubble nucleation unless emplacement depths were very shallow (15 km) beneath Yellowstone and only for very low partial melts ($F_m \leq 0.05$) (see the star). Similarly for emplacement depths > 35 km no magmatic degassing would occur for mantle source regions with initial carbon contents between 0.018 and 0.18 wt. % CO$_2$. 

Figure 4–4: Sensitivity Analysis

Plotted is the percent change from the mean in the calculated emission rate from Equation 4.1 as a function of varying each variable over the range indicated while holding all other variables at the mean value. Emplacement rates varied from 0.0015 to 0.025 km$^3$y$^{-1}$, the melt fraction varied from 0.05 to 0.1, the initial carbon concentration of the mantle source region varied from 0.018 to 0.18 Wt.% CO$_2$ (equivalent to 50 to 500 ppm C), and the depth of emplacement varied between 15 to 40 km. Equation 4.1 is least sensitive the range of depths of emplacement and melt fraction. These variables were set at 15 km and 0.05 for further calculations to maximize the emission rate calculated in Equation 4.1.
Figure 4–5: CO₂ Emissions Modeled from Magma Ascent and Based on Measurement
The dotted lines are the modeled CO₂ emission rate plotted as a function of the emplacement rate of basalt magma from the mantle into the crust for different initial CO₂ concentrations in the upper mantle. The arrows indicate the possible range of emplacement rates published in the literature (see text). The range of magmatic emissions for Mud Volcano is shown at the bottom determined from detailed surface measurements and isotopic constraints. The solid line shows the maximum diffuse emission rate calculated for Yellowstone based on chamber measurements. The shaded region for Yellowstone magmatic emissions was based on the range in the estimated total (Table 4-2) minus the average contribution from sedimentary sources (40 %) determined from isotopes (see text). The emission rates for the other volcanic systems are from the following references: (a) Brantley and Koepenick [1995], (b) Allard et al., [1991]; Gerlach [1991], (c) Goff et al., [2001], (d) Ryan [2001]; Gerlach et al. [2002], (e) Brantley and Koepenick [1995], (f) Wardell et al., [2001], (g) Chiodini et al. [2001], (h) Seward and Kerrick, [1996], (i) modified from Werner et al. [2000a], and (j) Gerlach et al. [2001].
**Figure 4–6: CO₂ Flux Measurements across Yellowstone**

Shown are the distributions of the fluxes of CO₂ measured in various regions of Yellowstone using the accumulation chamber technique. The box represents the 25th to the 75th percentile of the data, and the line represents the median. The bars indicate the range of the data, and any circles are considered outliers. The number beneath the distribution indicates the number of sample locations. The first 5 distributions were measured in the Mud Volcano thermal area in 1997/1998. MVBG stands for Mud Volcano ‘background’, or measurements made in forests, GU97 is the Guuper region of Mud Volcano measured in 1997, GU98 was measured in 1998. Similarly, GO97 and GO98 represent sampling in 1997 and 1998 in the Goose Regions of Mud Volcano. RM is Roaring Mtn.(acid-sulfate region), CH is Crater Hills (mixed acid-sulfate / silica-precipitating region), LAM is Lamar Valley (cold degassing region), MHS is Mammoth Hot Springs (travertine depositing), and UGB is Upper Geyser Basin (silica precipitating region).
Figure 4–7: Carbon Isotopes for various Yellowstone Reservoirs
The bar represents the range of carbon isotopic signatures recorded for various reservoirs in Yellowstone in comparison to magmatic reservoirs. The range for MORB and hotspots taken from Trull et al [1993], calcites from Sturchio [1990], bicarbonate Craig [1963], soil gases from Werner et al. [2000a] and Rightmire [1974], fumarole gases from this study and Craig [1963], and limestones from Friedman [1970].
The $\text{C}^3\text{He}$ ratio is plotted as a function of the $\delta^{13}\text{C}$ of $\text{CO}_2$. Sedimentary isotopic signatures were chosen based on the isotopic signatures of organic gases released from sediments and from limestones that outcrop near Yellowstone. The mantle endmember was chosen as the most primitive sample collected in Yellowstone, and is shown by the two-component endmember mixing lines extending from it (dotted lines). All samples are consistent with the range observed at other hotspots [Trull et al., 1993]. Maximum sedimentary contributions were observed for Mammoth Hot Springs and the Lamar River valley and minimum contributions were observed at Mud Volcano (Table 4-3).
Table 4–1: Input Parameters used in Calculation of Magmatic Emissions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Min Flux</th>
<th>Max Flux</th>
<th>Range</th>
<th>Δ Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_M$</td>
<td>km$^3$ y$^{-1}$</td>
<td>0.0015</td>
<td>0.025</td>
<td>0.013</td>
<td>6.2</td>
<td>104</td>
<td>97.8</td>
<td>89</td>
</tr>
<tr>
<td>$C_i$</td>
<td>wt. % CO$_2$</td>
<td>0.07</td>
<td>0.18</td>
<td>0.12</td>
<td>--</td>
<td>151</td>
<td>~ 192</td>
<td>175</td>
</tr>
<tr>
<td>$F_m$</td>
<td>%</td>
<td>5</td>
<td>10</td>
<td>0.075</td>
<td>25.6</td>
<td>114</td>
<td>88.1</td>
<td>80</td>
</tr>
<tr>
<td>$D$</td>
<td>km</td>
<td>15</td>
<td>40</td>
<td>0.195</td>
<td>37.4</td>
<td>72.6</td>
<td>35.2</td>
<td>32</td>
</tr>
</tbody>
</table>

*a* Emplacement Rate

*b* Initial carbon dioxide concentration of the mantle source region

*c* Melt fraction in mantle

*d* Depth of emplacement

*e* The emission rate changed by this amount from the mean value by varying each variable over the range indicated while all others were held at the mean value.
Table 4–2: Land Area Extrapolation of Diffuse CO$_2$ Fluxes to estimate Diffuse CO$_2$ Emissions in Yellowstone.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Neutral (N)</th>
<th>Travertine (T)</th>
<th>Acid (A)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermally Altered Land</td>
<td>km$^2$</td>
<td>43</td>
<td>7</td>
<td>145</td>
<td>195</td>
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<tr>
<td>Thermal$^a$ Altered Land Area</td>
<td>km$^2$</td>
<td>34</td>
<td>2</td>
<td>35</td>
<td>70</td>
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</table>

(Based on Arithmetic Average)

<table>
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<th></th>
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<th>Travertine (T)</th>
<th>Acid (A)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Flux</td>
<td>g CO$_2$ m$^{-2}$ d$^{-1}$</td>
<td>27</td>
<td>89</td>
<td>1250</td>
<td></td>
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<tr>
<td>Std. Error of mean</td>
<td>g CO$_2$ m$^{-2}$ d$^{-1}$</td>
<td>5</td>
<td>25</td>
<td>457</td>
<td></td>
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<tr>
<td>Coefficient of variation (CV)</td>
<td>---</td>
<td>0.9</td>
<td>1.5</td>
<td>3.4</td>
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<td>Emission Rate</td>
<td>Kt CO$_2$ d$^{-1}$</td>
<td>0.91</td>
<td>0.15</td>
<td>43</td>
<td>45</td>
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<tr>
<td>Error</td>
<td>Kt CO$_2$ d$^{-1}$</td>
<td>0.17</td>
<td>0.04</td>
<td>16</td>
<td>16</td>
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<tr>
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<td>0.12</td>
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<td>0.03</td>
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(Based on Minimum Variance Estimators)

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<th></th>
<th>Unit</th>
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<th>Acid (A)</th>
<th>Total</th>
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<tr>
<td>Mean Flux</td>
<td>g CO$_2$ m$^{-2}$ d$^{-1}$</td>
<td>37</td>
<td>140</td>
<td>1170</td>
<td></td>
</tr>
<tr>
<td>Std. Error of mean</td>
<td>g CO$_2$ m$^{-2}$ d$^{-1}$</td>
<td>12</td>
<td>66</td>
<td>707</td>
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</tr>
<tr>
<td>Emission Rate</td>
<td>Kt CO$_2$ d$^{-1}$</td>
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<tr>
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<td>0.11</td>
<td>25</td>
<td>25</td>
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<tr>
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<td>1.0</td>
<td>0.19</td>
<td>34</td>
<td>35</td>
</tr>
<tr>
<td>Error</td>
<td>$10^{10}$ mol CO$_2$ y$^{-1}$</td>
<td>0.37</td>
<td>0.91</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ The annual soil temperature was > 8°C [Rodman et al., 1996].
Table 4–3: Chemistry and isotopes of gas samples from selected areas in Yellowstone (values in dry gas mole %).

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Description</th>
<th>Date</th>
<th>Type Feature</th>
<th>Temp. (°C)</th>
<th>Xg</th>
<th>CO2</th>
<th>H2S</th>
<th>He</th>
<th>CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-0</td>
<td>Buffalo Ford Warm Spring</td>
<td>9/10/93</td>
<td>S</td>
<td>43.0</td>
<td>29.6</td>
<td>99.7</td>
<td>0.0000</td>
<td>0.0017</td>
<td>0.0315</td>
</tr>
<tr>
<td>LA-4</td>
<td>Buffalo Ford Warm Spring</td>
<td>9/10/93</td>
<td>S</td>
<td>43.0</td>
<td>29.1</td>
<td>99.7</td>
<td>0.0000</td>
<td>0.0017</td>
<td>0.0297</td>
</tr>
<tr>
<td>LA-47</td>
<td>Churning Caldron area</td>
<td>9/04/93</td>
<td>FP/MP</td>
<td>98.0</td>
<td>29.1</td>
<td>97.5</td>
<td>0.0101</td>
<td>0.0262</td>
<td>0.0293</td>
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<tr>
<td>PSU-08</td>
<td>Gumper area - southern frying pan</td>
<td>9/06/93</td>
<td>FP</td>
<td>91.5</td>
<td>30.4</td>
<td>99.6</td>
<td>0.1376</td>
<td>0.0012</td>
<td>0.0266</td>
</tr>
<tr>
<td>LA-10</td>
<td>Gumper</td>
<td>9/06/93</td>
<td>MP</td>
<td>72.9</td>
<td>32.8</td>
<td>96.5</td>
<td>0.1687</td>
<td>0.0016</td>
<td>0.0318</td>
</tr>
<tr>
<td>LA-2</td>
<td>Gumper</td>
<td>9/06/93</td>
<td>MP</td>
<td>72.9</td>
<td>29.3</td>
<td>99.4</td>
<td>0.3747</td>
<td>0.0037</td>
<td>0.0281</td>
</tr>
<tr>
<td>LA-5</td>
<td>30 m from Dragons Mouth</td>
<td>9/10/93</td>
<td>FP</td>
<td>96.0</td>
<td>10.6</td>
<td>99.4</td>
<td>0.4032</td>
<td>0.0017</td>
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<tr>
<td>LA-54</td>
<td>Mud Geyser</td>
<td>9/04/93</td>
<td>MP</td>
<td>90.0</td>
<td>9.3</td>
<td>99.6</td>
<td>0.2148</td>
<td>0.0015</td>
<td>0.0249</td>
</tr>
<tr>
<td>PSU-02</td>
<td>Hilltop frying pan- N of Mud Volcano</td>
<td>9/01/93</td>
<td>FP</td>
<td>90.0</td>
<td>29.6</td>
<td>99.6</td>
<td>0.0907</td>
<td>0.0014</td>
<td>0.0222</td>
</tr>
<tr>
<td>PSU-01</td>
<td>Mudpot northwest of Sulfur Caldron</td>
<td>9/01/93</td>
<td>MP</td>
<td>89.9</td>
<td>18.6</td>
<td>99.3</td>
<td>0.1733</td>
<td>0.0016</td>
<td>0.0257</td>
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<tr>
<td>PSU-14</td>
<td>Sulfur Caldron</td>
<td>9/03/93</td>
<td>FP</td>
<td>88.9</td>
<td>16.2</td>
<td>99.4</td>
<td>0.2981</td>
<td>0.0015</td>
<td>0.0258</td>
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<tr>
<td>PSU-11</td>
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a S stands for spring, FP for frying pan, MP for mudpot, F for fumarole, G for cold bare ground
b Xg is the mol % gas / (gas+steam)
c M is the CO2 derived from the magmatic component, L the limestone component, and S the organic sedimentary component (cont. on next page)
**Table 4-3 (cont.)**

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**Note:** C²³⁹²³⁸He values are not available for all samples.
In summary, carbon dioxide emissions are monitored in volcanic and hydrothermal areas to understand volcanic processes, to assess hazards in active regions, and to improve global estimates of volcanic and hydrothermal degassing. In this work, two major goals have been accomplished that advance the capability to monitor active volcanic regions for hazard assessment, and also to improve the understanding of the long-term carbon cycle. First, eddy covariance, a micrometeorological technique, was demonstrated to be a reliable method for measuring fluxes of carbon dioxide in two volcanic / hydrothermal environments. Secondly, this work contains the first estimate of CO$_2$ emissions from the Yellowstone volcanic / hydrothermal system, one of the largest systems on Earth. The specific results and implications of each study are briefly addressed below. Overall, this research has both advanced the understanding of the role of volcanic / hydrothermal systems to the long-term carbon cycle, has provided a new means of further assessing this contribution in the future, and provided a new method for assessing hazard through continuous measurement of fluxes over large active regions.

In Chapters 2 and 3, eddy covariance (EC) was successfully used to measure carbon dioxide fluxes over large (km$^2$) areas in volcanic / hydrothermal terrain for the first time. Average surface fluxes in both studies (Yellowstone and Solfatara Volcano) measured using the chamber technique were consistent with fluxes measured using eddy covariance. Furthermore, at Solfatara fluxes measured using EC were found to vary with
atmospheric pressure as did the hourly measurements of surface flux using the chamber technique over a period of three weeks. These results suggest that EC can be successfully implemented for monitoring carbon dioxide fluxes over large land areas and could potentially be used as a predictor of volcanic hazard. At Solfatara, two likely scenarios for eruption or magma movement were assessed for CO\textsubscript{2} loss based on solubility, and these first-order models suggest that the emplacement or eruption of magma would result in increases in flux that exceed the maximum daily variability at Solfatara due to changing meteorological conditions. Since this work began eddy covariance has been recognized by the volcanological community as a viable and useful technique that complements established methods of measuring fluxes from volcanic regions.

In Chapter 4, the results of measurement of carbon dioxide flux over multiple regions of Yellowstone were presented and compared to a geological model of degassing based on solubility. Both methods of assessing the total carbon dioxide output from the Yellowstone volcanic / hydrothermal system suggest that Yellowstone is a significant contributor to global estimates of volcanic and hydrothermal degassing. This work also demonstrates that assessing the carbon dioxide emissions from large and heterogeneous volcanic systems such as Yellowstone is non-trivial and will take many years to validate. Ultimately, until remote methods are developed to assess the carbon dioxide emissions over large volcanic and hydrothermal regions, individual estimates of degassing will inherently contain significant error. However, studies such as this one demonstrate that CO\textsubscript{2} emissions from large systems can be estimated within an order of magnitude. As techniques for measuring emissions improve and as spatially and temporally
representative estimates are obtained, the understanding of the processes controlling emissions will also improve, which will in turn advance our capability to predict hazard in active regions and assess the contribution of volcanic environments to global carbon cycling.
VITA

Cynthia A. Werner

Cynthia A. Werner was born in Town and Country, Missouri on July 14, 1970. She is the daughter of Richard Karl and Patricia Lee Werner. She attended the University of Missouri, Columbia from 1988 to 1994, spending one year at the Universität des Saarlandes, Saarbrücken, Germany. She received a B.S. in Geology, a B.A. in German, and a minor in Mathematics in 1994. She spent a summer working at the U.S. Geological Survey in Lawrence, Kansas as part of the National Association of Geology Teachers summer intern program. In Fall 1994, she took a position at Los Alamos National Laboratory (LANL) researching the distributions of U and Th in the Upper Bandelier Tuff as part of the U.S. Department of Energy (DOE), Science and Engineering Research program. In 1995 she began working as a graduate research assistant with Fraser Goff and Jamie Gardner at LANL on projects related to volcanic gas geochemistry and seismic hazards prediction. In 1996 she came to The Pennsylvania State University to work with Dr. Susan L. Brantley. She completed a M.S. in Geosciences 1999 entitled ‘CO$_2$ Emissions in Yellowstone National Park, U.S.A.: Statistical Sampling, Total Degassing, and Transport Mechanisms’. Cindy was awarded a NASA Earth System Science Graduate Research Fellowship in 1997, and a U.S. DOE, Global Change in Education, Graduate Research Fellowship in 2000. She has published her work on volcanic geochemistry in the *Journal of Geophysical Research, Geophysical Research Letters*, The New Mexico Geological Society 1996 Guidebook, and technical reports at LANL.