An unexpected journey: Experimental insights into magma and volatile transport beneath Erebus volcano, Antarctica



Kayla Iacovino University of Cambridge Department of Geography Darwin College

A thesis submitted for the degree of Doctor of Philosophy

February 2014

## DECLARATION OF ORIGINALITY

I certify that this dissertation is the result of my own work and includes nothing that is the outcome of work done in collaboration, except where specifically indicated in the text. I confirm that it does not exceed the word limit as mandated by the degree committee of the Department of Geography and does not contain work that has been submitted for another degree, diploma, or other qualification at any other university.

Kayla Iacovino

"If you wish to make a phonolite from scratch, you must first invent the universe."

### Dedication

It's been a long (and unexpected) journey. I've learned about geology, fieldwork, friendship. Science, life, and love. I am so different from the person I was when I started this PhD. I suppose all of us are. This section, which could never be long and extensive enough, is dedicated to just a handful of the people that helped me get here and to those who will no doubt continue to be an inspiration to me.

First and foremost, I would like to acknowledge my loving boyfriend, Andrew Britton, and my cat Jazzmyn, both of whom travelled across the world for me many times over, provided support every day, and stuck with me through the thick and thin.

I was given the gifts of encouragement and strength from so many long Skype conversations with my mother, Susan Kayler, and my best friend, Emily Allender. My father, Mark Iacovino, never let me down and always provided a place to go or a loving hand when I needed it most. My brother, Matt Larson, inspires me everyday with the amazing things he does in life, and he has taught me what is possible in this world.

My experience here would never have been complete without much gallivanting around the globe done in the name of science. Where would I be without Nial Peters, Tehnuka Ilanko, Kelby Hicks, and Yves Moussallam (that latter of whom I learned a lot from, albeit the hard way)? If I were religious, I would thank God on my knees that Clive Oppenheimer and James Hammond never got me arrested in North Korea. Coming home would never have been complete were it not for Talfan Barnie, with whom I spent many long nights searching for the last open pub in Cambridge and musing on the finer points in life (beer and science).

My supervisor, Clive Oppenheimer, taught me that some people really never grow up (even after they have a baby) and that you should always be ready for the next opportunity, which can present itself at a moment's notice. Phil Kyle taught me that some people really, *really* never grow up, and that you should always be ready for that next handful of cow dung, which can present itself at a moment's notice. Bruno Scaillet taught me to keep my chin up in the face of harsh experimental realities (exploding experiments).

Last, and certainly not least, I want to thank Gordon Moore. Although Gordon didn't supervise me in any official capacity during my PhD, I give him credit for sculpting my malleable undergraduate brain into something that was ready to take on the challenges I've faced since leaving Arizona. I can't imagine navigating academia without his teachings on science, experiments, life, wine, Italian politics, and more wine. Gordon will always be the person I look to as the shining example of a good researcher and a good person.

### Abstract

Erebus is a well-studied open-vent volcano located on Ross Island, Antarctica (77° 32' S, 167° 10' E). The volcano is the focus of ongoing research aimed at combining petrologic data and experiments with surface gas observations in order to interpret degassing histories and the role of volatiles in magma differentiation, redox evolution, and eruptive style. This research focus has been driven in part by an abundance of studies on various aspects of the Erebus system, such as physical volcanology, gas chemistry, petrology, melt inclusion research, seismic, and more. Despite this large data set, however, interpretations of Erebus rocks, particularly mafic and intermediate lavas, which are thought to originate from deep within the magmatic plumbing system, have been hindered due to a lack of experimental data.

Experimental petrology is a common tool used to understand volcanic plumbing systems and to tie observations made at the Earth's surface to the deep processes responsible for driving volcanic activity. Experimental petrologists essentially recreate natural magma chambers in miniature by subjecting lavas to conditions of pressure, temperature, and volatile chemistry (P-T-X) relevant to a natural underground volcanic system. Because many important parameters can be constrained in the laboratory, the comparison of experimental products with naturally erupted ones allows for an understanding of the formation conditions of the rocks and gases we see at the surface.

In this thesis, I have employed experimental and analytical petrological techniques to investigate the magmatic plumbing system of Erebus volcano. Broadly, the research is focused on volatiles (namely  $H_2O$ ,  $CO_2$ , and S species) in the Erebus system: their abundances, solubilities, interactions, evolution, and ultimate contributions to degassing. Specifically, three key themes have been investigated, each employing their own experimental and analytical techniques. Firstly, the mixed volatile  $H_2O-CO_2$  solubility in Erebus phonotephrite has been investigated under P-T-X conditions representative of the deep plumbing system of Erebus. Understanding the deep system is crucial because the constant supply of deeply derived  $CO_2$ -rich gases combined with a sustained energy and mass input into the lava lake suggests a direct link between the phonolite lava lake and the volcano's ultimate mantle source via a deep mafic plumbing system.

Secondly, I have mapped the phase equilibria and evolution of primitive, intermediate, and evolved Erebus lavas. The chemistries of these experimental products span the full range of lavas on Ross Island and help to constrain magmatic evolution from basanite to phonolite as well as to elucidate the geometry of the deep Ross Island plumbing system.

Finally, lower-pressure experiments representing the shallow plumbing system at Erebus have been performed in order to understand the transport properties of sulfur in alkaline magma. Experiments were performed on natural Erebus basanite and phonolite, which represent the most primitive and evolved lavas from Erebus. A distinct cocktail of C-O-H-S fluid was equilibrated with each experiment, and a wide range of experimental oxygen fugacities was explored.

Overall, experiments from this work are the first to place constraints on the entire magma plumbing system of Erebus volcano. In addition, experimental results foster a new understanding of non-ideal gas behavior at high pressure, the affinity of  $CO_2$  to deeply sourced rift magmas, and the effect of alkalis on fluid transport capabilities in melts.

# Nomenclature

#### **Repeated Symbols**

- $\epsilon$  Absorption coefficient
- $\gamma i$  Fugacity coefficient of component i
- $\omega$  Acentric factor
- a Empirical coefficient in Redlich-Kwong equation of state (bar·cm<sup>6</sup>·K<sup>1/2</sup>/mole<sup>2</sup>)
- b Empirical coefficient in Redlich-Kwong equation of state  $(cm^3/mol)$
- fi Fugacity of component i
- $K_D$  Partition coefficient of some component between the superscripted phases
- $K_F$  Equilibrium constant of formation
- m Mass
- P Pressure
- $P_i$  Partial pressure of component i
- $P_{tot}$  Total pressure
- R Gas constant (= 83.12 cm<sup>3</sup> · bar/deg·mol unless otherwise indicated)
- T Temperature
- V Volume

### Xi Mole fraction of component i

#### Superscripts

- fl Fluid
- m Melt
- $pure \ \ \mbox{Property of a pure species at } P \mbox{ and } T \mbox{ of interest}$

### Subscripts

- c Refers to variable at critical point
- i Refers to component i
- j Refers to component j

# Contents

Co	Contents ix			ix
List of Figures xiii				xiii
1	Intr	Introduction		
	1.1	Releva	ant Volcanological Background	1
	1.2	The C	Chemistry of Ross Island Lavas	9
		1.2.1	Mineralogy of DVDP and EL rocks	12
		1.2.2	Ross Island Melt Inclusions	13
	1.3	Exper	imental Petrology Background	16
	1.4	Resear	rch Rationale and Objectives	19
		1.4.1	Mixed volatile solubility in Erebus magma	19
		1.4.2	Phase Equilibria of Intermediate and Primitive Erebus Lavas	21
		1.4.3	C-O-H-S Fluids in Erebus Magma	23
		1.4.4	This Thesis, Overall	25
	1.5	Comm	nents on Previously Published or Submitted Materials	26
<b>2</b>	Nat	ural S	ample Selection and Preparation of Starting Materials	29
	2.1	Startin	ng Materials	29
		2.1.1	Phonotephrite AW-82038	29
		2.1.2	Basanite KI-04	33
		2.1.3	Phonolite ERE-97018	35
3	$\mathbf{H}_{2}\mathbf{C}$	$\mathbf{D}$ - $\mathbf{CO}_2$	Solubility in Erebus Phonotephrite Magma	36
	3.1	Abstra	act	36

	3.2	Introd	luction	37
		3.2.1	The role of alkalis in controlling volatile solubility	37
		3.2.2	Disagreement between solubility models for mafic alkaline	
			melts	38
	3.3	Exper	imental methods	41
		3.3.1	Preparation of experimental capsules	41
	3.4	Analy	tical techniques	42
		3.4.1	$H_2O-CO_2$ fluid manometry	42
		3.4.2	Infrared spectroscopy	44
		3.4.3	Electron microprobe	47
		3.4.4	Establishment of equilibrium	47
	3.5	Result	ts	50
		3.5.1	Iron oxidation state and experimental oxygen fugacity	50
		3.5.2	$H_2O-CO_2$ solubility in phonotephrite $\ldots \ldots \ldots \ldots \ldots$	51
		3.5.3	Thermodynamic modeling of mixed-volatile solubility data	
			and comparison with other solubility models	51
		3.5.4	Determination of empirical solubility relationships	55
	3.6	Discus	ssion	58
		3.6.1	Saturation pressures and fluid compositions of primitive Ere-	
			bus magmas	58
		3.6.2	Determining the source of volatiles released in explosive erup-	
			tions through the Erebus lava lake	59
	3.7	Concl	usions $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	62
4	Pha	ise Eq	uilibrium Constraints on the Deep and Intermediate	<b>;</b>
	Mag	gma P	lumbing Beneath Ross Island	65
	4.1	Abstra	act	65
	4.2	Exper	imental Overview	66
	4.3	Exper	imental Techniques	67
		4.3.1	Preparation of Experimental Capsules	67
	4.4	Analy	tical Techniques	69
		4.4.1	SEM and Electron Microprobe	69
		4.4.2	Visual analysis of samples and measure of crystallinity	72

		4.4.3	Mapping FTIR Spectroscopy	3
		4.4.4	Calculation of Dissolved Volatiles in Highly Crystalline Sam-	
			ples	7
		4.4.5	Establishment of Equilibrium	9
		4.4.6	Oxygen Fugacity 8	2
	4.5	Result	ts	5
		4.5.1	Textural and Mineralogical Observations 8	5
		4.5.2	Experimental Phase Compositions	6
			4.5.2.1 Oxides	6
			4.5.2.2 Olivine	6
			4.5.2.3 Clinopyroxene	1
			4.5.2.4 Kaersutite Amphibole	1
			4.5.2.5 Plagioclase Feldspar	5
			4.5.2.6 Glass Compositions	5
		4.5.3	Experimental Phase Relations	4
	4.6	Discus	ssion $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $10$	6
		4.6.1	Phase Equilibrium Constraints on the Natural Erebus System10	6
		4.6.2	Comparison with Other Volcanic Systems	8
		4.6.3	One Source, Two Lavas: Pre-eruptive Histories of EL and	
			DVDP Rocks	9
		4.6.4	The Case for $CO_2$ -dominated volcanism at Erebus 11	2
	4.7	Concl	usions	8
<b>5</b>	Sul	fur De	egassing at Erebus: Contributions from Basanite and	
	Pho	onolite	Melts 12	0
	5.1	Abstr	act $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $12$	0
	5.2	Exper	imental Overview $\ldots \ldots 12$	1
		5.2.1	Why Does Sulfur Degas?	1
	5.3	Exper	imental Methods $\ldots \ldots 12$	2
		5.3.1	Starting Material	2
		5.3.2	Preparation of Experimental Capsules	2
	5.4	Analy	sis $\ldots \ldots 12$	5
		5.4.1	Major Element Chemistry of Run Products	5

		5.4.2	S Speciation via Wavelength Shifts of SK $\alpha$ X-rays	126
		5.4.3	Dissolved Volatile Contents via FTIR Spectroscopy	127
		5.4.4	Modeling of the Experimental Fluid Phase Compositions	129
	5.5	Result	s	132
		5.5.1	Crystalline Phase Assemblages	132
		5.5.2	Glass Compositions	139
		5.5.3	Fluid Phase Compositions	139
		5.5.4	Fluid/Melt Partitioning of Sulfur	143
		5.5.5	Sulfur Speciation	145
	5.6	Discus	ion	149
		5.6.1	Sulfur Carrying Capacity of Basanite and Phonolite Melts .	149
		5.6.2	Implications for Degassing at Erebus	154
	57	Conclu	isions	156
	<b>D.</b> 7	Conten		
0	0.7 T	<b>T</b>		100
6	The	Last	Stage: Modeling degassing at Erebus from the inside	
6	The out	Last	Stage: Modeling degassing at Erebus from the inside 1	158
6	5.7 The out 6.1	Last	Stage: Modeling degassing at Erebus from the inside         1         cation of the Thermodynamic Model to Natural Systems	<b>158</b> 159
6	<b>The</b> <b>out</b> 6.1	Last Applic 6.1.1	Stage: Modeling degassing at Erebus from the inside         1         cation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases	<b>L58</b> 159 161
6	<b>The</b> <b>out</b> 6.1	Last Applic 6.1.1 6.1.2	Stage: Modeling degassing at Erebus from the inside         1         cation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations	<b>158</b> 159 161 164
6	5.7 The out 6.1 6.2	Last Applic 6.1.1 6.1.2 Interp	Stage: Modeling degassing at Erebus from the inside         1         cation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations	<b>158</b> 159 161 164 167
6	<ul> <li>5.7</li> <li>The out</li> <li>6.1</li> <li>6.2</li> </ul>	Last Applic 6.1.1 6.1.2 Interp 6.2.1	Stage: Modeling degassing at Erebus from the inside         1         eation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations         Modeling an Idealized Gas Mixture	<b>158</b> 159 161 164 167 168
6	<ul> <li>5.7</li> <li>The out</li> <li>6.1</li> <li>6.2</li> </ul>	Last Applic 6.1.1 6.1.2 Interp 6.2.1 6.2.2	Stage: Modeling degassing at Erebus from the inside         1         eation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations         Modeling an Idealized Gas Mixture         Other considerations	<b>L58</b> 159 161 164 167 168 172
6	<ul> <li>5.7</li> <li>The out</li> <li>6.1</li> <li>6.2</li> <li>6.3</li> </ul>	Last Applic 6.1.1 6.1.2 Interp 6.2.1 6.2.2 Future	Stage: Modeling degassing at Erebus from the inside         1         cation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations         Modeling an Idealized Gas Mixture         Other considerations         e work	<b>158</b> 159 161 164 167 168 172 174
6	<ul> <li>5.7</li> <li>The out</li> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> </ul>	Last Applic 6.1.1 6.1.2 Interp 6.2.1 6.2.2 Future Summ	Stage: Modeling degassing at Erebus from the inside         1         eation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations         Modeling an Idealized Gas Mixture         Other considerations         e work         ary of this Thesis	<b>158</b> 159 161 164 167 168 172 174 175
6	<ul> <li>5.7</li> <li>The out</li> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>Apped</li> </ul>	Last Applic 6.1.1 6.1.2 Interp 6.2.1 6.2.2 Future Summ endix.A	Stage: Modeling degassing at Erebus from the inside         1         eation of the Thermodynamic Model to Natural Systems         Ideal Mixing of Non-ideal Gases         Details of Equilibrium Fluid Phase Calculations         retations         Modeling an Idealized Gas Mixture         Other considerations         e work         ary of this Thesis	158 159 161 164 167 168 172 174 175 178

# List of Figures

1.1	Erebus volcano viewed from the Ross Sea in November, 2010	2
1.2	The persistently active phonolitic lava lake in the Erebus summit crater	
	in December, 2010. A slug of gas can be seen bursting through the lake	
	crust, exposing the hot lake interior. The long axis of the lake is ${\sim}40$ m.	
	Photo credit: Clive Oppenheimer	3
1.3	Satellite image mosaic of Ross Island, Antarctica, showing the loca-	
	tions of individual volcanoes constituting the island. Images of Ross	
	Island are from the ASTER instrument aboard the Terra satellite (USGS,	
	2001/2000); inset of Antarctica is from LIMA (Bindschadler et al., 2008)	5
1.4	Map of the Erebus Volcanic Province showing: a) the Antarctic continent	
	with black dashed lines indicated the bounding faults of the WARS; b)	
	the coast of Victoria Land, showing the distribution of volcanic provinces	
	within the McMurdo Volcanic Group: Hallett (HP), Melbourne (MP),	
	and Erebus (EP). VLB is the Victoria Land Basin; and c) detailed map	
	of the EP, with locations of most recently active volcanoes. Figure from	
	Cooper et al. (2007)	6
1.5	Roughly NE-SW cross section of Erebus showing the three stages of evo-	
	lution. Figure from Esser et al. (2004)	7

1.6	$^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ apparent ages of Erebus Lineage rocks plotted versus their	
	Mg number $[100(MgO/MgO+FeO^*))]$ , where decreasing Mg# represents	
	increasing differentiation, showing a general younging trend with differ-	
	entiation. Argon age data are from Esser et al. (2004); chemical data are	
	from Kyle et al. (1992). The Dellbridge Island and Trachyte successions	
	are shown for comparison and are notably different than the EL lavas.	
	Figure from Esser et al. $(2004)$	8
1.7	Harker diagrams illustrating the evolution of DVDP Lineage (Red dia-	
	monds; Kyle, 1981) and Erebus Lineage (EL; blue triangles; Kyle et al.,	
	1992) whole rock compositions, with major element totals normalized to	
	100%	10
1.8	The two most prevalent lava lineages on Ross Island, showing the evo-	
	lution from basanite to phonolite as modeled by mass balance and trace	
	element chemistry (Kyle et al., 1992). The main mineralogical distinc-	
	tion between the two suites is the presence or lack of kaersutite amphi-	
	bole. Numbers represent the percent of fractionation. Ol: olivine; Cpx:	
	clinopyroxene; Kaer: kaersutite; Mt: opaque oxides; Feld: feldspar; Ne:	
	nephelene; Ap: apatite. Figure adapted from Kyle et al. (1992) $\ldots$	11
1.9	Photomicrographs of selected melt inclusions from Eschenbacher	
	(1998). A) DVDP 3-283c basanite; B) AW82033I phonotephrite;	
	C) 97010c tephriphonolite; D) EA1h phonolite. Figure from Es-	
	chenbacher (1998)	15
1.10	Major element (a) and volatile compositions (b) of melt inclusions	
	from Erebus lavas, which illustrate the complete fractional crys-	
	tallization sequence from primitive basanite to evolved phonolite.	
	Major element chemistry analyzed with EMP; volatiles analyzed	
	via transmission FTIR. Data from Eschenbacher (1998). $\ldots$ .	17
1.11	Both types of high-pressure, high-temperature experimental apparatuses	
	used for this work. The IHPV (left) is "Gros Bleu" at the Université	
	d'Orléans, France. The piston cylinder (right) is "Daisy" at Arizona State	
	University.	18

2.1	Map of Ross Island showing the sample locations of the three starting	
	materials used in this work (yellow dots). Red dots show the locations of	
	other lavas sampled during this work but not used in experiments. More	
	detailed location and compositional data for those samples can be found	
	in Appendix A	30
2.2	Compositional variation of the three chosen starting material lavas (large	
	black diamonds), the modeled parent lava DVDP2-105.53 (large purple	
	diamond), and a suite of olivine-hosted melt inclusions (except in the case	
	of phonolites whose inclusions are anorthoclase-hosted) from the Erebus	
	Lineage. Melt inclusion data from Oppenheimer et al. (2011a). Bulk rock	
	analyses of parent lava and AW-82038 from Kyle et al. $(1992)$ . Analysis	
	of ERE-97018 from Kelly et al. (2008). Analysis of KI-04 from this study.	
	Gray curve indicates the liquid line of descent from primitive basanite to	
	evolved phonolite.	31
2.3	a.) Photograph taken from Observation Hill with the Fortress Rocks	
	outcrop visible in the midground (outlined in red). Mt. Erebus is in the	
	background, and part of McMurdo Station is in the foreground. (Photo	
	credit: Nial Peters) b.) Photograph of the boulder from which sample	
	KI-04 was taken.	34
3.1	Modeled H <sub>2</sub> O and CO <sub>2</sub> solubility in phonotephrite AW-82038 at 1190 $^{\circ}\mathrm{C}$	
	using: (a) SiO <sub>2</sub> -corrected VolatileCalc (Newman & Lowenstern, 2002)	
	and SOLEX (Witham et al., 2012), blue dashed curves; (b) Papale et al.	
	(2006), red curves; and (c) Lesne et al. (2011b,c) for alkali basalt from	
	Etna, black curves. Isobars are plotted for pressures of 100, 300, 500,	
	and 700 MPa for Papale et al. (2006) and Lesne et al. (2011b,c) and	
	for pressures of 100 and 300 MPa for VolatileCalc/SOLEX as the latter	
	models are not calibrated for pressures above 400 MPa	40
3.2	Representative FTIR spectra of experimental samples, plotted with offset $% \mathcal{F} = \mathcal{F} = \mathcal{F} + $	
	scales on the y-axes. Note how the carbonate peaks merge in samples with	
	high total dissolved volatile concentrations (AW 44C-2). In samples with	
	unresolved carbonate peaks, the carbonate abundance was determined	
	by peak height at 1420 cm <sup>-1</sup>	49

3.3	Plots showing the relationship between the fugacity of the volatile com-	
	ponent in the fluid phase (in bars) versus the amount of that volatile	
	component dissolved in the melt (in $wt\%$ ). Fugacities calculated with	
	the modified Redlich-Kwong equation of state. Lines represent power	
	regressions of the data with an $R^2$ of 0.94 and 0.44 for $H_2O$ and $CO_2$ ,	
	respectively.	52
3.4	Thermodynamically calculated, fully ideal model of $H_2O$ and $CO_2$ satu-	
	ration in Erebus phonotephrite modeled using the relationship between	
	fugacity of the volatile component and the concentration of that volatile	
	dissolved in the melt. Because of the poor fit of our $CO_2$ data to a	
	power law regression, the pure- $CO_2$ experiments of Lesne et al. (2011b)	
	were used to create these isobars. This modeling approach does not work	
	well for our high P experiments given their enhanced $CO_2$ dissolution at	
	moderate to high $X_{H2O}^{fluid}$	54
3.5	$H_2O-CO_2$ solubility data from this study compared with the predicted	
	solubility curves (isobars) of (Lesne et al., 2011b,c, upper) and (Papale	
	et al., 2006, lower). Curves of Lesne et al. (2011b,c) calculated for alkali	
	basalt from Etna at 1200 °C. Those of Papale et al. (2006) calculated for	
	the Erebus phonotephrite used in this study with an $fO_2$ of NNO+1, the	
	intrinsic $fO_2$ of our experimental apparatus. Lesne et al. (2011b,c) over-	
	estimates saturation pressures for our experiments at low $X_{H_2O}^{fluid}$ , while	
	Papale et al. (2006) overestimates saturation pressures significantly for	
	400 and 500 MPa experiments. The shape of the Papale et al. $(2006)$	
	curves better matches the distribution of our data at moderate to high	
	$\mathbf{X}^{fluid}_{H_2O}$ , possibly owing to the fact that this model is fully non-ideal	55
3.6	Empirically determined $H_2O-CO_2$ fluid saturation isobars for Erebus	
	phonotephrite. Isobars were fitted through our experimental data us-	
	ing a third-order polynomial. 400 MPa runs are shown as red diamonds,	
	$500~\mathrm{MPa}$ runs as blue diamonds, $600~\mathrm{MPa}$ runs as green diamonds, and	
	700 MPa runs as yellow diamonds	56

3.7	Volatile contents in olivine-hosted basanite and phonotephrite melt in-	
	clusions from Erebus volcano (Oppenheimer et al., 2011a) superimposed	
	on my empirically determined, non-ideal $H_2O-CO_2$ solubility curves and	
	is opleths for Erebus phonotephrite at 400, 500, 600, and 700 MPa and at	
	$X_{H_2O}^{fluid} = 0.01, 0.05, 0.1, \text{ and } 0.2.$ Red diamonds represent DVDP 3-295;	
	blue triangles represent AW-82033. Primary basanite DVDP 3-295 be-	
	came saturated and began degassing at about 600 MPa, and phonotephrite	
	AW-82033 began degassing at about 300 MPa	60
4.1	Normal SEM image selected for analysis (left), the same image	
	thresholded to isolate crystals and melt (middle), and the image	
	thresholded to isolate only oxide crystals (right)	73
4.2	Graduated color map of the peak height of the 3500 $\rm cm^{-1}$ (total H <sub>2</sub> O)	
	infrared band in sample KI-10 based on 36 separate FTIR analyses over-	
	lain on an optical image of the sample. Variations in peak height are	
	a result of variations in sample thickness (e.g. at the edge of the glass	
	chip) and the presence of holes or crystalline phases within the IR beam.	
	Use of FTIR maps illustrates the homogeneity of dissolved volatiles in	
	crystalline samples and elucidates the locations best suited for analysis	74
4.3	Calculated dissolved volatile contents of experimental charges via: a)	
	the "by difference" method; and b) mass balance, both compared with	
	measured values via FTIR. The solid blue line is a linear best fit to	
	AW-82038 phonotephrite samples (blue squares), the dashed red line is $% \left( {{\left[ {{{\rm{AW-82038}}} \right]_{\rm{AW-12}}}} \right)$	
	a linear best fit to KI-04 basanite samples (red diamonds), and the gray	
	line is a 1:1	79
4.4	Histogram showing the distributions of Fe-Mg crystal-melt distribution	
	coefficients ( $K_D$ for experimental (black) and natural (gray; data from	
	Kyle, 1981) olivines	87

4.5	Ternary diagram showing compositions of experimental (symbols) and	
	natural (fields) olivine (green) and clinopyroxene (yellow). Clinopyrox-	
	enes are plotted in terms of recalculated end-member compositions en-	
	statite, ferrosillite, wollastonite. Olivine is plotted along the baseline of	
	the ternary in terms of recalculated end-members forsterite (Mg) and	
	fayalite (Fe).	92
4.6	Chemical compositions of experimental olivines in terms of Fo content	
	versus the calculated equilibrium $XH_2O^{fluid}$ . Isobars are shown for 250,	
	300, and $400$ MPa. The Fo content of natural KI-04 olivines is indicated	
	by the horizontal red line	93
4.7	Chemical compositions of experimental (filled diamonds) and natural	
	(open diamonds) kaersutite amphibole, plotted in terms of magnesium	
	number versus Na+K (a) and versus $Al_2O_3$ (b). Natural kaersutites are	
	from intermediate and evolved DVDP lavas from Kyle (1981)	94
4.8	Ternary diagram showing the compositions of experimental plagioclase	
	crystals (purple squares) and natural plagioclase from EL lavas (open	
	fields, data from Kyle et al., 1992)	96
4.9	Harker variation diagrams (SiO <sub>2</sub> vs major oxides) showing compositions	
	of experimental residual glasses (KI-04 as red squares; AW-82038 as blue $$	
	diamonds) at op compositions from olivine-hosted melt inclusions in EL	
	lavas (green fields; data from Eschenbacher, 1998 and Oppenheimer et al.,	
	2011a). The parent basanite composition is shown as a black dot, and	
	compositions of starting materials used in this study are shown as pale	
	red (basanite KI-04) and pale blue (phonotephrite AW-82038) dots	98

- 4.11 Conventional phase diagrams for experiments with AW-82038 phonotephrite at fixed pressures of 200 MPa (a) and 300 MPa (b) in terms of the equilibrium fluid composition (calculated by gravimetery) and temperature. Numbers next to symbols represent the volume percentage of melt in the charge. Apatite was only observed in the most water-rich charges, but the steadily decreasing  $P_2O_5$  content in residual glasses suggests that it did crystallize in drier charges but that crystals were too small for microprobe analysis. . . . . . . 101
- 4.12 Experimental phase relations in terms of wt% H<sub>2</sub>O dissolved in the residual melt versus pressure for: a) AW-82038 phonotephrite experiments (blue circles); and b) high-temperature (1050-1150 °C) KI-04 basanite experiments (red diamonds). Shaded regions indicate where the natural phase assemblages were best reproduced. Figure c) shows the phase relations for KI-04 basanite experiments conducted at 1100 °C in terms of the equilibrium fluid composition versus pressure. Numbers next to symbols represent the volume percentage of melt (or melt+quench) in the charge.

4.13 Composite phase diagrams showing the stability of various phases in terms of wt% H<sub>2</sub>O dissolved in the residual melt versus temperature. Note that experiments conducted at all investigated pressures (200, 300, and 400 MPa) are plotted in order to illustrate the phase relations in general. Blue circles (top) are for AW-82038 phonotephrite experiments; red diamonds (bottom) are for KI-04 basanite experiments. . . . . . . 103 4.14 Cross section schematic of the magmatic plumbing system beneath Ross Island showing both the main EL (Erebus Lineage) conduit and the offshoot DVDP (Dry Valley Drilling Project lineage) conduit. Figure is 4.15 The relationship between the  $H_2O$  content of the glass and the crystal content in AW-82038 experimental charges. An increase in  $H_2O$  lowers the liquidus temperature of the melt, thus resulting in a lower volume %of crystals. Sample AW-19B was considered an outlier and is not plotted on this graph. With the one outlier excluded, straight lines were fit to the data. Because the AW-82038 starting material charges (this figure) have poor straigh line fits to the data compared with those for KI-04 starting material, the average slope from KI-04 charges were used. Still, AW-82038 charges generally exhibit the expected inverse relationship between 4.16 The relationship between the  $H_2O$  content of the glass and the crystal content in KI-04 experimental charges. An increase in H<sub>2</sub>O lowers the liquidus temperature of the melt, thus resulting in a lower volume % of crystals. Samples KI-09 and KI-15 are outliers of these linear trends and were omitted from this graph. With outliers excluded, straight lines were fit to the data. These relationships were then used to model dehydration-5.1Phase assemblages of ERE-97018 phonolite (upper) and KI-04 basanite (lower) experiments plotted in terms of oxygen fugacity relative to the NNO buffer versus the amount of sulfur in the system (as the wt% of sulfur added to the experimental capsule). Gray vertical line represents the iron-wüstite buffer.  $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$  134

5.2	Immiscible sulfide liquid (ISL) phases in sample ERE_S11 as seen in
	reflected light (top) and electron backscatter (bottom). Bright ISL phases
	contain $\sim 80 \text{ wt\%}$ silver. Dark ISL phases have a composition similar to
	pyrrhotites in other samples
5.3	Harker variation diagrams illustrating the evolution of experimental melts
	in ERE-97018 samples. Open square represents the composition of the
	starting material. Light blue bars spanning the width of each figure
	represent $\pm 1$ standard deviation of the starting material analysis 141
5.4	Harker variation diagrams illustrating the evolution of experimental melts
	in KI-04 samples. Open square represents the composition of the start-
	ing material. Pink bars spanning the width of each figure represent $\pm 1$
	standard deviation of the starting material analysis
5.5	Partition coefficients $(\mathbf{K}_D^{fl/m})$ of sulfur in phonolite and basanite experi-
	ments as a function of XFeOtot
5.6	Partition coefficients $(\mathbf{K}_D^{fl/m})$ of sulfur in basanite experiments as a func-
	tion of melt silica content. $\ldots \ldots 147$
5.7	Proportion of sulfate relative to total sulfur in our glasses as measured by
	EMP with $\Delta\lambda(SK\alpha)$ . Phonolite ERE-97018 samples were likely oxidized
	during analysis (see text). Curves are empirical fits to EMP (Jugo et al.,
	2005; Wallace & Carmichael, 1994) and XANES data (Jugo et al., 2010). 150
5.8	Sulfur concentration in experimental melts as a function of sulfur fugacity.
	Points are grouped by $PH_2$ , which serves here as a proxy for oxygen fugacity. 152
5.9	Sulfur contents dissolved in melt inclusions from Erebus measured by
	electron microprobe. The degree of fractionation was determined by cor-
	relation of the melt inclusion silica content with the fractionation model
	compositions of (Kyle et al., 1992). Figure from Eschenbacher $(1998)$
	(data also published in Oppenheimer et al., 2011a)
5.10	The volume of Erebus phonolite magma per day required to produce an
	$SO_2$ flux of 61 Mg day <sup>-1</sup> as a function of sulfur $K_D^{fl/m}$ based on 5.14. The
	full range of sulfur $\mathcal{K}_D^{fl/m}$ values from 0–100 is shown on in (a). A $\mathcal{K}_D^{fl/m}$
	range of 10–100, assumed here to be a reasonable range of estimates for
	Erebus, is shown in (b). $\ldots \ldots 157$

6.1	Ternary diagram showing the calculated compositions of equilibrium flu-
	ids (dots) and fluids from degassed melt inclusions (squares). The nor-
	malized surface gas composition is also shown (large red dot). Each dot
	represents the equilibrium fluid calculated for a single melt inclusion or
	glass analysis. The names correspond to those in Table 6.1
6.2	Bright features that appear to be flames coinciding with a bubble burst in
	the Erebus lava lake in December, 2010. The long axis of the lake is $\sim 40$
	m, and the bubble diameter is ${\sim}5$ m. Photo credit: Clive Oppenheimer 170
6.3	All outputs from my simple gas mixing model that satisfy Equation 6.9.
	Fluids are stacked based on depth of origin from the most shallow (top)
	to deepest (bottom)
6.4	Ice tower "Harry's Dream" located ${\sim}1~{\rm km}$ north of the Erebus crater, seen
	actively degassing in December, 2010. Laura Jones and Jed Frechette for
	scale
App	endix A.1 International Geo Sample Numbers (IGSNs) and QR
	codes for samples collected during the G-081 Antarctic Expedition
	in 2010

# Chapter 1

# Introduction

### 1.1 Relevant Volcanological Background

Erebus is a well-studied open-vent volcano located on Ross Island, Antarctica  $(77^{\circ})$ 32' S, 167° 10' E; Figure 1.1). The persistently active lava lake in its 3794 mhigh summit crater (Figure 1.2), which has likely prevailed since the volcano was discovered in 1841, represents a window into the shallow regions of the alkaline intraplate volcanic plumbing system. Since the 1970s, Erebus and its lava lake have been monitored each year during the austral summer (typically November-January) using a multitude of instrumentation. Modern monitoring employs techniques such as open-path Fourier transform infrared (OP-FTIR) and Differential Optical Absorption spectroscopy (DOAS) to measure gas compositions and flux (Oppenheimer & Kyle, 2008a; Oppenheimer et al., 2011a; Wardell et al., 2004), infrasound microphones (Jones et al., 2008), ground-based thermal cameras to understand lava lake dynamics (Calkins et al., 2008; Peters et al., 2014), passive seismology (Aster et al., 2008), and ground-based terrestrial laser scanners (TLS; Jones et al., 2011). Two recent studies on Erebus employing experimental petrological work (Moussallam et al., 2013) and seismic tomography (Zandomeneghi et al., 2013) have placed tight constraints on the physical and petrological properties of the shallow plumbing system and phonolitic lava lake including geometry, temperature, pressure, and oxygen fugacity. These works have the potential to refine the results of numerical models developed for the shallow Erebus system, such as those of Burgisser et al. (2012) and Molina et al. (2012). Little is known, however, about the deep plumbing system beneath Erebus (>8 km depth). Understanding the deep system at Erebus is crucial because the constant supply of deeply derived  $CO_2$ -rich gases combined with a sustained energy and mass input into the lava lake suggests a direct link between the phonolitic lava lake and the volcano's ultimate mantle source via a deep mafic plumbing system (Kyle et al., 1992; Oppenheimer & Kyle, 2008a; Oppenheimer et al., 2011a)



Figure 1.1: Erebus volcano viewed from the Ross Sea in November, 2010.

Ross Island sits atop the West Antarctic Rift System (WARS), a 750-1000 km wide by 3000 km long region of thinned lithosphere (Figure 1.3 & 1.4). WARS extension began in the Jurassic, and extension is ongoing today within the Terror Rift, which extends NNW from Ross Island (Behrendt et al., 1991). Volcanism in the Erebus Volcanic Province, which includes Mts. Erebus, Discovery, and Morning, is thought to be caused by the upwelling of a plume of mantle material (Gupta et al., 2009; Kyle et al., 1992) and subsequent generation of basanitic magma through partial melting of the mantle source rock. Subsidiary volcanic centers and cones on Ross Island, namely Mt. Terror, Mt. Bird, and Hut Point Peninsula,



Figure 1.2: The persistently active phonolitic lava lake in the Erebus summit crater in December, 2010. A slug of gas can be seen bursting through the lake crust, exposing the hot lake interior. The long axis of the lake is  $\sim 40$  m. Photo credit: Clive Oppenheimer.

are distributed radially around Erebus approximately 120° from each other. This symmetrical distribution is hypothesized to be the result of radial fractures created by the pressure of updoming material on the crust directly beneath Mount Erebus (Kyle & Cole, 1974; Kyle et al., 1992).

Rare Earth element (REE) contents and Pb isotope data have been used to infer the petrogenesis of primitive Ross Island basanites (Kyle, 1981; Kyle & Rankin, 1976; Sun & Hanson, 1975). All of these studies conclude that the basanites were likely derived by partial melting of a garnet-bearing peridotitic mantle enriched in REE, although there is insufficient evidence to suggest whether or not metasomatism of the mantle played an important role in petrogenesis. It is noteworthy that mantle metasomatism by C-O-H fluids has been invoked to explain the formation of other basanites (Galer & O'nions, 1989; Menzies et al., 1985) and primitive rocks in similar tectonic settings (Furman & Graham, 1999; Späth et al., 2001). The degree of partial melting beneath Ross Island is expected to be quite low, with both Kyle & Rankin (1976) and Kyle (1981) suggesting 1–2%. This model has been largely supported by experimental studies (Eggler, 1974; Green, 1973; Mysen, 1977), which also suggest that  $CO_2$  is a necessary phase during melting. Experiments on basanite melts (Green, 1973; Merrill & Wyllie, 1975) show that garnet is only stable over 20 kb pressure, indicating that the mantle source for Erebus basanites could be as deep as ~60 km or more.

Recent experimental investigations (Gerke et al., 2005; Moussallam et al., 2013), melt inclusion studies (Oppenheimer et al., 2011a), and in-situ monitoring of the Erebus lava lake and its degassing behavior (Boichu et al., 2010; Johnson et al., 2008; Oppenheimer & Kyle, 2008a; Sweeney et al., 2008; Wright & Pilger, 2008) have shown that Erebus is a stable, yet complex system. Sustained degassing and heat output from the continuously active lava lake implies a constant heat and magma flux from below and, presumably, a persistent energy source fueling the shallow system from great depths. Preliminary analyses of melt inclusion volatile contents indicate that a parental basanite magma, perhaps the body supplying energy to the system, may pond near the crust/mantle boundary. Seismic and gravitational investigations on and around Ross Island suggest that this boundary is ~20 km deep (Cooper et al., 1994; Finotello et al., 2011; Newhall & Dzurisin, 1989).

The evolution of the Erebus cone itself is inferred to have taken place in three stages of eruptive activity: a shield building phase (>1.3-1 Ma), a proto-Erebus cone building phase (1000-250 ka), and the modern-Erebus cone building phase (250 ka to present; Esser et al., 2004). Figure 1.5 is a roughly NE-SW cross section of the Erebus cone depicting these three eruptive phases. As Erebus has evolved, so has the chemistry of its lava, with older rocks typically being more primitive and younger rocks being more evolved, as demonstrated in Figure 1.6. In total, Erebus required approximately 1 million years to evolve from a basanitic to phonolitic magmatic system, with very few deviations (Esser et al., 2004).



Figure 1.3: Satellite image mosaic of Ross Island, Antarctica, showing the locations of individual volcanoes constituting the island. Images of Ross Island are from the ASTER instrument aboard the Terra satellite (USGS, 2001/2000); inset of Antarctica is from LIMA (Bindschadler et al., 2008)



Figure 1.4: Map of the Erebus Volcanic Province showing: a) the Antarctic continent with black dashed lines indicated the bounding faults of the WARS; b) the coast of Victoria Land, showing the distribution of volcanic provinces within the McMurdo Volcanic Group: Hallett (HP), Melbourne (MP), and Erebus (EP). VLB is the Victoria Land Basin; and c) detailed map of the EP, with locations of most recently active volcanoes. Figure from Cooper et al. (2007).





Figure 1.5: Roughly NE-SW cross section of Erebus showing the three stages of evolution. Figure from Esser et al. (2004).



Figure 1.6:  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  apparent ages of Erebus Lineage rocks plotted versus their Mg number [100(MgO/MgO+FeO\*))], where decreasing Mg# represents increasing differentiation, showing a general younging trend with differentiation. Argon age data are from Esser et al. (2004); chemical data are from Kyle et al. (1992). The Dellbridge Island and Trachyte successions are shown for comparison and are notably different than the EL lavas. Figure from Esser et al. (2004).

### 1.2 The Chemistry of Ross Island Lavas

The majority of lavas on Ross Island are represented by two strongly undersaturated sodic differentiation lineages: the Erebus Lineage (EL), made up of lavas erupted from Erebus volcano; and the Dry Valley Drilling Project (DVDP) lineage, made up of lavas on Hut Point Peninsula and sampled via drill coring (see Figure 1.3). The more sparse Enriched-Iron Series (EFS) lavas are less silica undersaturated and constitute only a small volume of Ross Island rocks. The whole rock chemistries of the DVDP and EL suites are similar (Figure 1.7). Major element mass balance and trace element modeling (Kyle, 1981; Kyle et al., 1992) is consistent with similar fractional crystallization trends for both lineages (Figure 1.8), with a few key mineralogical distinctions between the two (namely, the presence or lack of kaersutite in DVDP and EL suites, respectively). While basanites have not been recovered on Erebus itself, modeling indicates that the phonolitic EL magma that resides in Erebus's active lava lake can be derived via fractional crystallization from a parental basanitic magma similar to primitive DVDP basanite (specifically, sample DVDP 2-105.53 from Kyle et al., 1992). Erebus lava compositions are consistent with the fractionation of 16% olivine, 52% clinopyroxene, 14% Fe-Ti oxides, 11% feldspar, 3% nepheline, and 3% apatite (in wt%) from a parental basanite melt yielding a 23.5% residual anorthoclase phonolite.

Phonolite has been the only historically erupted lava from Erebus, (Kelly et al., 2008) and so information concerning the less evolved melts comes in the form of petrological observations of previously erupted products. A remarkably complete apparent fractional crystallization sequence of lavas from primitive basanite to evolved phonolite can be seen in outcrop on Erebus and Ross Island, the petrology of which is well documented by Kyle (1981) and Kyle et al. (1992). Melt inclusions from these rocks have given clues as to where these magmas differentiate within the magmatic plumbing system (Oppenheimer et al., 2011a), but the lack of experimental data on the Erebus system or similar rocks has made the precise interpretation of these melt inclusions difficult. The deepest part of the magmatic system, where basanitic magma resides, is located close to the crust-mantle boundary with some uncertainty as to whether basanite ponds just above



Figure 1.7: Harker diagrams illustrating the evolution of DVDP Lineage (Red diamonds; Kyle, 1981) and Erebus Lineage (EL; blue triangles; Kyle et al., 1992) whole rock compositions, with major element totals normalized to 100%.



Figure 1.8: The two most prevalent lava lineages on Ross Island, showing the evolution from basanite to phonolite as modeled by mass balance and trace element chemistry (Kyle et al., 1992). The main mineralogical distinction between the two suites is the presence or lack of kaersuite amphibole. Numbers represent the percent of fractionation. Ol: olivine; Cpx: clinopyroxene; Kaer: kaersuite; Mt: opaque oxides; Feld: feldspar; Ne: nephelene; Ap: apatite. Figure adapted from Kyle et al. (1992)

or just below the Moho (located 19-27 km below Ross Island; Finotello et al., 2011).

#### 1.2.1 Mineralogy of DVDP and EL rocks

The mineralogy of Erebus Lineage (EL) and Dry Valley Drilling Project (DVDP) lineage rocks from Ross Island have been extensively documented by Kyle et al. (1992) and Kyle (1981), respectively. The observations of those studies will be summarized here.

In the EL rocks, olivine is ubiquitous in all lavas and appears as 1-5 mm euhedral and subhedral phenocrysts. The forsterite content of EL olivine's ranges from  $Fo_{88}$  in basanites to  $Fo_{51}$  in phonolites. Olivine xenocrysts are rare and occur only in the most primitive lavas. In DVDP lavas, olivine occurs only in basanites as euhedral to subhedral phenocrysts and in the groundmass. In all other DVDP lavas, only xenocrysts of olivine are found.

Clinopyroxene is ubiquitous in all EL and DVDP lavas and occurs as euhedral to subhedral phenocrysts. Pyroxenes with green cores, which show irregular rims possibly due to resorption, are occasionally found in DVDP lavas. In the EL lavas, pyroxenes show oscillatory zoning in basanites and intermediate lavas and no zoning in phonolites.

Kaersutites do not appear in EL lavas but are an important phase in all DVDP lavas except the basanites where it is rare. In some phonotephrites, kaersutites range from euhedral grains to those showing strong resorption and oxidation. It was postulated by Kyle (1981), based on previous experimental work, that temperature and PH<sub>2</sub>O likely exert a strong control on the appearance or lack of kaersutite in DVDP and EL lineages, respectively.

Opaque oxides are common in both lava suites and are typically titanomagnetite as phenocrysts and in the groundmass plus rare ilmenite phenocrysts. Using magnetite-ilmenite pairs, temperatures and oxygen fugacities were estimated for many EL and DVDP lavas (these data will be used in Chapter 6).

Feldspar is the modally dominant phenocryst phase in EL lavas (up to 40% of the mode in anorthoclase phonolites), but occurs only as microphenocrysts or in the groundmass of DVDP lavas. In EL lavas, the compositions of felspars range from  $An_{72}$  in basanites to  $Or_{54}$  in the groundmass of more evolved lavas. Feldspars in DVDP lavas are mainly labradorite ( $An_{50}$  to  $An_{60}$ ).

Feldspathoids only occur in EL lavas (as nephelene), which contain up to 24% normative Ne. Microphenocrysts of apatite are common in most rocks of both lineages and is often found as inclusions in kaersutite and magnetite in DVDP rocks. Pyrrhotite is present in all rocks from both lineages and occurs as small round blebs, possibly indicating the presence of an immiscible sulfide liquid in Ross Island magmas.

#### 1.2.2 Ross Island Melt Inclusions

A large and complete suite of melt inclusions spanning the entire compositional range of lavas on Ross Island were analyzed for major elements via electron microprobe and dissolved volatiles via FTIR by Eschenbacher (1998) as a Master's thesis and later published by Oppenheimer et al. (2011a). All of the glass chemistry and volatile content data from Eschenbacher (1998) are given in Appendix A. Rock samples were taken on the Erebus summit (for phonolites) and around Ross Island (for all other compositions) and included hyaloclastites from drill core, palagonite breccias, lava flow tops, pillow breccias, phonolite bombs, and single anorthoclase crystals (Table 1.1). Only samples determined to have undergone rapid quenching were chosen for melt inclusion analysis in order to avoid postentrapment alterations such as diffusive hydrogen loss. More details of the rock samples and analysis methods can be found in Eschenbacher (1998).

All melt inclusions analyzed by Eschenbacher (1998) were hosted in olivine phenocrysts, except for those from phonolites, whose olivine-hosted melt inclu-
Sample	Location	Composition	Occurance
DVDP 3-283	Hut Point	Basanite	Drill core/hyaloclastite
AW82033	Turks Head	Basanite	Palagonite breccia
7713	Turks Head	Phonotephrite	Palagonite breccia
97006	Turks Head	Tephriphonolite	Lava flow top
97009	Inaccessible Is.	Tephriphonolite	Palagonite breccia
97010	Tent Island	Tephriphonolite	Pillow breccia
97011	Tent Island	Phonotephrite	Pillow breccia
97018	Erebus summit	Phonolite	Bomb
EA1	Erebus summit	Phonolite	Single anorthoclase crystal
Table adapted	l from Eschenbacher (	(1998)	

Table 1.1: Sample locations and rock types from the melt inclusion study of Eschenbacher (1998)

sions were too small to be reliably analyzed. For phonolites, anorthoclase-hosted melt inclusions were analyzed. Olivine-hosted inclusions range in size from  $<20-350 \ \mu\text{m}$ , are brown to transparent in color, and have ovoid to negative crystal form often with cuspate boundaries. In anorthoclase crystals, inclusions are typically very large, ranging in size from <10 to  $>600 \ \mu\text{m}$  and occur as both irregular and negative crystal forms. Vapor bubbles are common within inclusions but typically make up less than 1 vol% of the inclusion (Figure 1.9).

Electron microprobe was used to analyze major element chemistry of melt inclusion glasses as well as sulfur, fluorine, and chlorine. The error for Cl and S measurements is estimated to be approximately  $\pm 200$  ppm, and F measurements have estimated errors on the order of  $\pm 1000$  ppm. Transmission FTIR spectroscopy was used to analyze dissolved H<sub>2</sub>O and CO<sub>2</sub> contents in doubly polished melt inclusion glasses. Backgrounds were drawn by hand using a French curve. Water was determined using 3350 cm<sup>-1</sup> peak (OH and molecular water), and carbon dioxide was determined using the average of the 1500 and 1400 cm<sup>-1</sup> peaks (carbonate doublet). Molar absorption coefficients for each composition were chosen from those reported for similar compositions in the literature. All absorption coefficients for carbonate were calculated using the method of Dixon & Pan (1995). Uncertainties in H<sub>2</sub>O and CO<sub>2</sub> analyses for most samples is  $\pm 11-12\%$  and  $\pm 15-50\%$ , respec-



Figure 1.9: Photomicrographs of selected melt inclusions from Eschenbacher (1998). A) DVDP 3-283c basanite; B) AW82033I phonotephrite; C) 97010c tephriphonolite; D) EA1h phonolite. Figure from Eschenbacher (1998)

tively. Secondary ion mass spectrometry was used as a secondary measure of  $H_2O$  in some samples, and results were in agreement with those from FTIR. Major element compositions (in terms of total alkalis and silica) and  $H_2O-CO_2$  contents of melt inclusions glasses are shown in Figure 1.10.

## 1.3 Experimental Petrology Background

The majority of our observations of volcanoes come from active volcanic monitoring (measurements of gas chemistry and flux, seismic monitoring, etc.) or from mineralogical and petrological studies of eruptive products representative of past volcanic activity. In order to understand the significance of a sample of lava or gas, it is often necessary to understand its origins: where in the magmatic plumbing system did this sample originate? What was the pressure? The temperature? The redox state? In the laboratory, we can subject the rocks we find on the surface to known P-T- $fO_2$  conditions. In this way, we can constrain which conditions are necessary to produce the observed mineralogies and chemistries (and their proportions) in a natural system.

For the past several decades, experimental petrology has laid the groundwork for modeling pre-eruptive magmatic processes (see Rutherford, 1993). Many of the parameters of interest (e.g. volatile solubility, crystal phase stability) are dependent not only on P-T- $fO_2$  but also on melt chemistry (Asimow & Ghiorso, 1998; Giordano et al., 2008; Moore, 2008; Papale et al., 2006; Witham et al., 2012). Because of this, data from a wide range of magma compositions is necessary to model these compositionally dependent variables. The best approach to modeling a *specific* volcanic system is thus experimental data gathered using materials from the system of interest.

At Erebus volcano, there is no shortage of observational data (see Section 1.1). The silica-undersaturated and peralkaline lavas of Ross Island represent lava chemistries not common on Earth's surface, however, meaning that experimental studies on such systems are equally rare. It is not surprising, then, that a lack of experimental data has hindered the interpretation of rock and gas samples from



Figure 1.10: Major element (a) and volatile compositions (b) of melt inclusions from Erebus lavas, which illustrate the complete fractional crystallization sequence from primitive basanite to evolved phonolite. Major element chemistry analyzed with EMP; volatiles analyzed via transmission FTIR. Data from Eschenbacher (1998).17

Erebus (namely, a large suite of melt inclusions spanning the entire compositional range of lavas on Ross Island, Oppenheimer et al., 2011a). This thesis presents some of the first experimental data on Ross Island rocks. Specifically, the goals of this project have included: a better understanding of degassing throughout the Erebus system; the identification of storage conditions of Erebus rocks (with particular focus on deep and intermediate regions of the plumbing system); and the contributions of deep magma and fluid to the degassing measured at the surface. It hoped that, beyond placing constraints on the Erebus system, these data might also contribute to compositionally dependent models (e.g. Duan, 2014; Papale et al., 2006) applicable to understanding volcanoes around the world.



Figure 1.11: Both types of high-pressure, high-temperature experimental apparatuses used for this work. The IHPV (left) is "Gros Bleu" at the Université d'Orléans, France. The piston cylinder (right) is "Daisy" at Arizona State University.

In this work, I have utilized two types of commonly used high-pressure high-

temperature experimental apparatuses, both of which are shown in Figure 1.11. For mixed volatile solubility experiments exploring the deepest part of the Erebus system (Chapter 3), non-end loaded piston cylinders at Arizona State University, capable of reaching pressures between  $\sim 4000-10000$  bars, were used. High pressure is attained through the use of a hydraulic ram situated below the sample applying an upward force. The pressure plate, which houses the sample, is pressed against a static upper plate. Because force is only applied in a single direction, this piston cylinder design is referred to as "non-end loaded". Control of the oxygen fugacity in piston cylinder experiments is achieved through the use of solid buffers (e.g. nickel and nickel oxide powders). For the experiments in Chapter 3, no buffer was used, and so the oxygen fugacity of the experiments corresponds to that intrinsic to the system (NNO-1). For phase equilibria and sulfur-bearing experiments (Chapters 4 & 5), internally heated pressure vessels (IHPV's) at the Université d'Orléans were used. These IHPVs can sustain pressures from near atmospheric (a few 10s of bars) to 4000 bars. The pressure medium in the IHPVs used in this work is an  $Ar-H_2$  gas mixture, where the proportions of Ar and  $H_2$  are controlled in order to control the oxygen fugacity.

## 1.4 Research Rationale and Objectives

#### 1.4.1 Mixed volatile solubility in Erebus magma

Dissolved volatiles, notably  $H_2O$  and  $CO_2$ , strongly affect the physical properties of magmas, including density and viscosity, thereby influencing magma ascent and eruptive behavior (Lange, 1994). Additionally, volcanoes play a key role in carbon exchange between the deep Earth and the atmosphere (Dasgupta, 2013). For these reasons, experimental studies determining the solubilities of pure  $H_2O$ (e.g., Behrens & Jantos, 2001; Botcharnikov et al., 2006; Carroll & Blank, 1997; Lesne et al., 2011c; Moore et al., 1998), pure  $CO_2$  (e.g., Botcharnikov et al., 2006; Brooker et al., 2001; Jendrzejewski et al., 1997; Lesne et al., 2011b; Morizet et al., 2002; Thibault & Holloway, 1994), and to a lesser extent mixed  $H_2O$ – $CO_2$  systems (e.g., Behrens et al., 2004; Botcharnikov et al., 2006, 2007; Dixon et al., 1995; Jakobsson, 1997; Lesne et al., 2011a; Vetere et al., 2011) have been conducted for silicate melts over a range of compositions and experimental P–T conditions.

One of the most well studied aspects of Erebus volcano is the composition and flux of the volcanic plume constantly emanating from the phonolitic lava lake. Infrared and ultraviolet spectrometers are regularly deployed at the crater rim to quantify the gas output from the lake. These studies have indicated significant variability in gas flux and chemistry on short time scales that appears linked to aspects of magma differentiation, redox evolution, magma flow in the feeder conduit, and eruptive regime (i.e., passive vs. explosive degassing; Boichu et al., 2010; Burgisser et al., 2012; Oppenheimer & Kyle, 2008a; Oppenheimer et al., 2009, 2011a).

Additional information about the volatile budget of the volcano comes in the form of an extensive suite of melt inclusions, which spans the entire compositional range of Erebus lavas (Figure 1.10). Melt inclusion data are a common tool used to infer deep, pre-eruptive magmatic processes. Specifically, the concentrations of dissolved volatiles (namely  $H_2O$ ,  $CO_2$ , and to a lesser extent F, Cl, and S species) give information about the pre-eruptive volatile content of a magma. If it is assumed that the melts in these inclusions were saturated and at equilibrium at the time of entrapment and the solubility laws for that melt composition are known, one can determine the minimum saturation pressure of the melt inclusions. These data can then be used to infer depths of melt inclusion entrapment and degassing.

The solubility of  $H_2O$  and  $CO_2$  can be strongly dependent upon melt composition (Dixon, 1997; Papale et al., 2006), and therefore, the analysis of melt inclusions requires knowledge of the specific solubility behavior in a given silicate melt. Solubility models are built upon empirical solubility data drawn from the literature and enable the estimation of the saturation pressures of volatiles in melts based upon their composition, pressure, and temperature.

Very few experimental solubility data for mafic alkali-rich melts have been reported in the literature, however, hindering the reliable interpretation of basanite and phonotephrite melt inclusions. Low-pressure experiments have been performed with pure  $H_2O$  in basanite (20–140 MPa; Cocheo, 1993), with pure  $CO_2$  in alkali basalts (20–200 MPa; Lesne et al., 2011b), and with mixed  $H_2O-CO_2$  fluids in ultrapotassic melts (50–500 MPa; Behrens et al., 2009).

Erebus volcano is the focus of ongoing research aimed at combining petrologic data and experiments with surface gas observations in order to interpret degassing histories and their role in magma differentiation, redox evolution, and eruptive style (e.g., Burgisser et al., 2012; Oppenheimer et al., 2011a). This task is made more challenging by the need to account for the differentiation of parental basanites through intermediate compositions to the evolved phonolitic lava that is erupted in the volcano's persistent lava lake. Given that melt inclusions from Erebus magmas record significant mixed-volatile contents (up to  $1.75 \text{ wt}\% \text{ H}_2\text{O}$ ,  $0.72 \text{ wt}\% \text{ CO}_2$ ; Figure 1.10; Oppenheimer et al., 2011a), reliable data for the H<sub>2</sub>O–CO<sub>2</sub> solubility properties in Erebus compositions at relevant pressure and temperature conditions are needed for the robust interpretation of melt inclusion analyses and to model degassing processes beneath the volcano.

To this end, I have conducted high-pressure volatile solubility experiments on an Erebus phonotephrite, the results of which are reported in Chapter 3. The aims of this work include the interpretation of volatile contents in Erebus melt inclusions in order to shed light on deep magmatic processes associated with the evolution and eruptive behavior of the volcano. In addition, experiments conducted with Erebus melts will test the hypothesis that alkali-rich magmas can dissolve more  $CO_2$  than their less alkaline counterparts. The findings complement recent studies by Lesne et al. (2011b,c) and show that existing  $H_2O-CO_2$  solubility models fail to reproduce my experimentally determined  $H_2O-CO_2$  data set.

## 1.4.2 Phase Equilibria of Intermediate and Primitive Erebus Lavas

The study of a lava's mineralogy is one of the main avenues by which we can begin to understand the origins of that lava. Factors such as mineral and glass chemistry, crystal shape and size, and modal abundance of crystalline phases provide clues as to the formation conditions of the rock such as the pressure, temperature, redox state, and even presence of dissolved volatiles. Without experimental data on a particular system of interest, however, it is difficult to place anything more than broad constraints on these parameters. To this end, experimental studies on the phase equilibria of igneous rocks have been widely used to constrain pre-eruptive processes at volcanic systems (Andújar et al., 2010; Barclay et al., 1998; Di Carlo et al., 2010; Freise et al., 2003; Martí et al., 2008; Moore & Carmichael, 1998; Rutherford et al., 1985).

On Ross Island, magma evolution via fractional crystallization is hypothesized to be the process underpinning the trends in chemical variation seen throughout the silica-undersaturated, alkaline lava suites. Mass balance models are consistent with the two volumetrically dominant lava suites, the Erebus Lineage and DVDP lineage, being derived from the same parental basanitic magma (Kyle, 1981; Kyle et al., 1992). Key mineralogical distinctions between the two suites, however, suggest differing conditions during evolution. For example, the presence of kaersuite amphibole in DVDP lavas and not in the EL lavas suggests a lower temperature and higher  $PH_2O$  in DVDP lavas relative to the EL. The lineages are defined by their location on the surface: EL lavas are those found only on the Erebus cone itself, and DVDP lineage lavas are samples taken from drill core and in outcrop on Hut Point Peninsula. It is likely that these two lineages followed different pathways through the country rock, thus differences in formation conditions are largely spatial rather then temporal.

The oxidation state throughout the Erebus plumbing system, in addition to pressure and temperature, likely plays an important role in establishing phase equilibria. OP-FTIR measurements of gas emissions from the Erebus summit crater show two distinct gas signatures, which are inferred to be derived from different depths within the system. The deeper gas signature is more oxidized than the shallow signature, indicating that the oxidation state of Erebus could follow a reducing upwards trend. Coupled chemical-physical modeling of redox evolution in volcanic systems (Burgisser & Scaillet, 2007) has shown that a reducing upwards behavior may be expected in sulfur-bearing volcanic systems, depending on the initial oxygen fugacity of the magma reservoir.

In order to investigate distinctive evolutionary traits from the two suites, phase equilibria experiments have been performed over a range of H<sub>2</sub>O and CO<sub>2</sub> fugacities (XH<sub>2</sub>O of the H<sub>2</sub>O-CO<sub>2</sub> fluid ranging from 0-1) on lavas from both of the dominant Ross Island lava suites. Experiments have been conducted under oxidizing conditions ( $\sim$ NNO+1) to test the hypothesis that deep magmas are subject to high  $fO_2$  compared to the relatively reducing conditions in the phonolitic lava lake ( $\sim$ QFM). One starting material has been chosen from each lineage – KI-04, a DVDP basanite representing the universal basanitic parent magma, and AW-82038, an EL phonotephrite representing a 45% residual melt from a basanitic parent. Phase equilibrium experiments have been tailored to test the hypothesis that both EL and DVDP lavas can be derived from a common basanite parent (represented here by starting material KI-04) and to investigate the conditions necessary to establish the mineralogy of each lineage.

Results of these experiments, presented in Chapter 4, place tight constraints on the storage conditions of primitive and intermediate lavas at Erebus and make a case for Erebus volcano representing an archetype for  $CO_2$ -dominated alkaline rift volcanism.

### 1.4.3 C-O-H-S Fluids in Erebus Magma

Although it is considered a minor species in volcanic systems, sulfur plays an important role in magma evolution, phase equilibria, and degassing. In part, this is due to its interaction with (and dilution of) other major species. Moreover, sulfur is the most common gas actively monitored at degassing volcanoes (Harris et al., 2013; Oppenheimer et al., 2011b; Sweeney et al., 2008). Its characteristic absorption cross-section in the ultraviolet combined with its negligible abundance in Earth's atmosphere make it the species most easily measured via remote sensing, and is therefore commonly used as a proxy for volcanic gas flux on the whole.  $SO_2$  flux is thus often used as a key parameter in volcanic monitoring and eruption forecasting.

Sulfur and sulfate-water aerosols are also a significant driver of local and global climate forcing. Given that volcanic degassing makes a significant contribution to atmospheric sulfur (Berresheim & Jaeschke, 1983; Graf et al., 1997; Halmer et al., 2002; Oppenheimer et al., 2011b; Schnetzer, 1993; Stoiber et al., 1987; Williams et al., 1992) it is important to understand the mechanisms that control sulfur exsolution and degassing in magmatic systems.

Few studies have investigated magmatic systems containing H-O-S fluids – that is, silicate melt plus a fluid containing H<sub>2</sub>O and S species (Botcharnikov et al., 2004; Carroll & Rutherford, 1985; Clémente et al., 2004; Keppler, 2010). Due to the added complexity, even fewer investigations have been made in the C-H-O-S system – silicate melt plus a fluid containing H<sub>2</sub>O, CO<sub>2</sub>, S species and other minor species (e.g. CO, CH<sub>4</sub>; Scaillet et al., 2005; Witham et al., 2012). Furthermore, because of the difficulty in performing S-bearing experiments with mafic melts, most of these studies have focused on felsic compositions (Moune et al., 2009). At P-T- $fO_2$  conditions relevant to most magmatic systems, it is generally valid to assume minor contributions from CO and CH<sub>4</sub>, and so I assume that the partial pressures of these species are negligible. Still, the addition of carbon to the system adds a degree of freedom and therefore increases uncertainties in the calculations of the thermodynamic properties of the fluid.

Erebus is known to be a remarkably C-rich system, with carbon placing strong controls on phase equilibria, crystal fractionation, degassing, and magmatic  $fO_2$ . Based on the analysis of a suite of Erebus melt inclusions, for example, Oppenheimer et al. (2011a) suggest that the flux of an extremely CO<sub>2</sub>-rich fluid is responsible for dehydration-driven crystallization at various depths within the Erebus plumbing system and is consistent with the CO<sub>2</sub>-rich gas emissions measured at the surface. The experimental study of Moussallam et al. (2013) additionally concluded that a CO<sub>2</sub>-rich fluid is necessary to explain the phase assemblages observed in Erebus phonolites. Throughout this thesis, I have investigated the role of CO<sub>2</sub> in primitive and intermediate Erebus magmas, and my results agree with previous studies that a CO<sub>2</sub>-rich fluid is required to produce the mineral assemblages and melt inclusions in Erebus lavas. Because of the strong influence of carbon in the Erebus system, some of the sulfur-bearing experiments in this study contain C-rich fluids that more closely approximate the natural system.

To investigate the behavior of sulfur in Erebus melts, experiments have been conducted to equilibrate Erebus phonolite and basanite with C-O-H-S and H-O-S fluids. This work will test the hypothesis that sulfur gas fluxes from Erebus can be accounted for by the degassing of small batches of phonolitic melt within the lava lake. The melt sulfur contents (both at and below sulfide saturation), sulfur fluid/melt partitioning, and equilibrium fluid phase compositions have been determined for both melt compositions at 1000 bars over a wide range of oxygen fugacities. Using the results of these experiments, presented in Chapter 5, and knowledge on the behavior of S in melts from the literature, I place broad constraints on sulfur degassing at Erebus volcano. As no such experimental data constraining both melt sulfur speciation and equilibrium fluid compositions for mafic melts currently exist in the literature, my results have important implications for the compositional dependence of S solubility and partitioning in silicate melts.

### 1.4.4 This Thesis, Overall

Broadly, the aims of this thesis have been to place the first experimental constraints on the intermediate and deep plumbing system of Erebus volcano with respect to: volatile transport and degassing, magma evolution and storage conditions, and the contributions of intermediate and primitive magmas to surface behavior and explosivity. Ultimately, results from each of the three key studies outlined above have been used to parameterize a thermodynamic approach to modeling degassing throughout the Erebus plumbing system (Chapter 6). When combined with other recent studies, which have characterized the shallow system, my data allow for the first experimentally constrained model of the entire Erebus system, from mantle to surface.

## 1.5 Comments on Previously Published or Submitted Materials

Chapters 3 & 4 are both based on manuscripts that have been published or submitted for publication in journals and have involved co-authorship. I am first author on both of these works, and the role of the co-authors extends no further than typical levels of support from supervisors and colleagues. These works are not presented as verbatim copies of published (or submitted) work, as some sections have been removed, altered, or added. Specifically, the introduction and experimental methods sections from the two journal articles have been altered and used in the Introduction and Natural Sample Selection and Preparation of Starting Materials chapters of this thesis.

Chapter 3,  $H_2O-CO_2$  Solubility in Erebus Phonotephrite Magma, has been published in Contributions to Mineralogy and Petrology, vol. 166, no. 3, pp. 845-860 under the name "H<sub>2</sub>O-CO<sub>2</sub> solubility in mafic alkaline magma: applications to volatile sources and degassing behavior at Erebus volcano, Antarctica". Co-authors on this paper include: Gordon Moore, who served as undergraduate advisor to myself during my tenure at Arizona State University and trained me on the experimental procedures and analytical techniques as well as advising on the content of the manuscript; Kurt Roggensack, who served as a co-advisor along with Gordon Moore and performed some of the FTIR measurements; Philip Kyle, an expert in Erebus volcanology and petrology who provided the starting material rock powders for this work and commented on the content of the manuscript; and Clive Oppenheimer, my PhD supervisor, who provided the initial inspiration for the work and commented on the content of the manuscript. Stan Klonowski performed all manometry measurements. Matthijs van Soest provided use of and training on his surface mapping microscope at Arizona State University. Amber Gullikson and Erika Beam performed a small number of the experiments that contributed to this work. Experiments and analysis (except that listed previously), creation of the figures, and writing of the manuscript were all done by me. Peerreview from Jackie Dixon, Jacob Lowenstern, Richard Brooker, and one other anonymous reviewer contributed to the final version of the manuscript and helped to refine the arguments presented.

Chapter 4, Phase Equilibrium Constraints on the Deep and Intermediate Magma Plumbing Beneath Ross Island, has been submitted for publication in the Journal of Petrology under the name "Erebus volcano as an archetype for CO<sub>2</sub>-dominated rift volcanism: Experimental constraints on the magma plumbing system of Ross Island, Antarctica". Co-authors on this paper include: Clive Oppenheimer, my PhD supervisor who provided the initial inspiration for the work, assisted in fieldwork in Antarctica in 2010, and advised on the content of the manuscript; Bruno Scaillet, who acted as my PhD co-supervisor, trained me on the experimental equipment in Orléans, helped in the interpretation of experimental results and data, and advised on the content of the manuscript; and Philip Kyle who served in the same capacity as with Chapter 3 in addition to coordinating fieldwork in Antarctica. Jacob Lowenstern provided access to and training on his mapping FTIR spectrometer at the USGS in Menlo Park, California. Marina Alletti, Juan Andújar, and Rémi Champallier gave helpful advice on performing experiments. Ida Di Carlo provided access to and training on the SEM at the Université d'Orléans. Nial Peters developed the vast majority of the FTIR spectra background fitting code. Bill McIntosh assisted in sample collection on Ross Island. Iris Buisman, Raul Carampin, and Kenneth Domanik provided assistance with electron microprobe work at the University of Cambridge, Università di Padova, and University of Arizona, respectively. Matthijs van Soest provided access to his surface mapping microscope at Arizona State University. All experiments, analysis, creation of the figures, and writing of the manuscript was done by me.

Chapter 5, Sulfur Degassing at Erebus: Contributions from Basanite and Phonolite Melts, has not been submitted for publication. All experiments (with the exception of one run, kindly performed by Rémi Champallier), analysis, the creation of figures, and writing of the chapter was done by me. Iris Buisman assisted greatly in the use of the microprobe at the University of Cambridge, particularly for the measurement of the SK $\alpha$  radiation. Raul Carampin provided assistance with electron microprobe measurements of sample glasses at the Università di Padova. Louisa Preston gave me access to and training on the FTIR spectrometer at the Open University. Gabriele Giuli provided advice on experimental design and funded the use of the electron microprobe in Padova. Both Clive Oppenheimer and Bruno Scaillet have helped in the refinement of the text of this chapter.

## Chapter 2

# Natural Sample Selection and Preparation of Starting Materials

## 2.1 Starting Materials

Three lavas from Ross Island were chosen for starting materials: AW-82038, a phonotephrite from the Erebus Lineage; KI-04, a basanite from the DVDP Lineage; and ERE-97018, a phonolite bomb erupted from the Erebus lava lake in 1997 and part of the Erebus Lineage. Compositions of these three starting materials are shown in Table 2.1. Other samples were collected from locations on and around Ross Island in 2010. These samples are not used in this experimental study, but for reference, their chemical analyses and location information are presented in Appendix A. Figure 2.1 shows the locations where the starting materials were sampled. Figure 2.2 illustrates the starting material compositions relative to those from a suite of melt inclusions in Erebus Lineage rocks, which gives a representative cross-section through the evolutionary chemical trend of lavas on Ross Island (Oppenheimer et al., 2011a).

### 2.1.1 Phonotephrite AW-82038

Lava AW-82038 is a natural phonotephrite sampled from Turks Head on the flank of Erebus volcano (Figure 2.1 Kyle et al., 1992) and is a member of the Erebus



Figure 2.1: Map of Ross Island showing the sample locations of the three starting materials used in this work (yellow dots). Red dots show the locations of other lavas sampled during this work but not used in experiments. More detailed location and compositional data for those samples can be found in Appendix A.



Figure 2.2: Compositional variation of the three chosen starting material lavas (large black diamonds), the modeled parent lava DVDP2-105.53 (large purple diamond), and a suite of olivine-hosted melt inclusions (except in the case of phonolites whose inclusions are anorthoclase-hosted) from the Erebus Lineage. Melt inclusion data from Oppenheimer et al. (2011a). Bulk rock analyses of parent lava and AW-82038 from Kyle et al. (1992). Analysis of ERE-97018 from Kelly et al. (2008). Analysis of KI-04 from this study. Gray curve indicates the liquid line of descent from primitive basanite to evolved phonolite.

	AW-82038 I	Phonotephrite	KI-04 basar	nite	ERE-97018	Phonolite
	SM	$\mathrm{WR}^1$	SM	$\mathrm{WR}^2$	SM	$\mathrm{WR}^3$
$\mathrm{SiO}_2$	49.94	48.01	43.13	42.13	57.15	56.83
$\mathrm{TiO}_2$	2.65	2.77	4.27	4.169	0.98	1.00
$Al_2O_3$	19.56	18.56	13.82	13.502	19.60	20.03
FeOtot	10.90	9.49	12.45	12.16	5.34	4.86
MnO	_	0.22	0.19	0.1898	0.23	0.23
MgO	2.77	3.18	8.94	8.728	0.93	0.89
CaO	7.93	7.65	11.09	10.833	2.65	2.71
$Na_2O$	5.94	5.99	3.65	3.567	8.06	8.47
$K_2O$	2.68	2.88	1.63	1.595	4.65	4.56
$P_2O_5$	_	1.24	0.83	0.81	0.41	0.41
Total	97.68	98.29	98.61	98.61	98.07	99.61

Table 2.1: Compositions of starting materials used in this work

Note: Analyses normalized to 100% with original analysis totals given. FeOtot is total iron given as FeO; SM: Starting material (after vitrification) analyzed by electron microprobe; WR: Whole-rock analysis of natural sample by XRF.

<sup>1</sup>Analysis from Kyle et al. (1992).

<sup>2</sup>Analysis from this study (see Appendix A).

<sup>3</sup>Analysis from Kelly et al. (2008).

Lineage. The sample plots very near to the phonotephrite/basanite boundary as defined under the TAS classification scheme (Le Bas et al., 1986). The sample is consistent with fractionation of 12% olivine, 35% clinopyroxene, 7% Fe-Ti oxides, and 1% apatite from a basanite parent yielding a 45% residual phonotephrite melt (Kyle et al., 1992) and was chosen because it was possible to quench to a glass with moderate amounts of dissolved  $H_2O$ . Although it is a 45% residual melt, AW-82038 represents one of the more basic EL lavas. Early experiments found a more primitive basanite from Ross Island (Hut Point Peninsula sample DVDP 2-105.53; Kyle, 1981) difficult to quench consistently to a crystal-free hydrous glass, thus making quantitative analysis of the dissolved volatile content by Fourier transform infrared (FTIR) spectroscopy difficult. Natural AW-82038 phonotephrites, also referred to as Ne Hawaiite in Kyle et al. (1992), are either finely or coarsely porphyritic (up to 20 vol% and 20-50 vol% phenocrysts, respectively) with a phenocryst assemblage of plagioclase, olivine, clinopyroxene, opaque oxides, apatite, and rare accessory nepheline. The sample used in this work is finely porphyritic, with <8% phenocrysts. This starting material was used in all H<sub>2</sub>O-CO<sub>2</sub> experiments (Chapter 3) and as one of two starting materials in phase equilibria experiments (Chapter 4).

Large rock samples (2–5 kg) of AW-82038 were broken into smaller pieces by hand and then crushed in a swing mill for 1–2 min down to a grain size of ~5  $\mu$ m. No fractionation of phenocrysts occurs as the entire sample was used during grinding (Kyle et al., 1992). This starting material was then crushed by hand via mortar and pestle to an even finer powder and held in a Pt crucible in a oneatmosphere gas-mixing furnace at 1300 °C under a stream of nearly pure CO<sub>2</sub> (corresponding to an  $fO_2$  near the Ni–NiO buffer) for ~30 min. The crucible was then drop-quenched in water. The resulting glassy sample was extracted, crushed, and re-melted under identical conditions to ensure a homogeneous mixture. A small amount of this starting material glass was polished and analyzed by electron microprobe to ensure that no significant compositional variation (i.e., alkali loss) had occurred during vitrification (see Table 2.1).

### 2.1.2 Basanite KI-04

KI-04 is a basanite (SiO<sub>2</sub> = 41.91 wt%; MgO = 8.68 wt%) representative of primitive lavas from the DVDP lineage and was collected on Hut Point Peninsula in 2010 (Figure 2.1). The sample was collected from a large dense boulder at the base of the Fortress Rocks outcrop (Figure 2.3). Phenocrysts constitute around 12 vol% of KI-04 basanite and include olivine (6 vol%), plagioclase feldspar (2 vol%), augite (2 vol%), apatite (1 vol%), and titanomagnetite (<1 vol%). Although kaersutite amphibole is common in almost all DVDP lavas, it is rare in DVDP basanites and is absent in KI-04. Crystal distribution is relatively homogeneous throughout the sample. Sample KI-04 was used as one of two starting materials in both phase equilibria (Chapter 4) and sulfur solubility experiments (Chapter 5).

KI-04 lava samples were crushed to a powder and melted in a Pt crucible in a one-atmosphere furnace at 1300 °C. Because the gas-mixing furnace setup used



Figure 2.3: a.) Photograph taken from Observation Hill with the Fortress Rocks outcrop visible in the midground (outlined in red). Mt. Erebus is in the background, and part of McMurdo Station is in the foreground. (Photo credit: Nial Peters) b.) Photograph of the boulder from which sample KI-04 was taken.

to vitrify AW-82038 became unavailable, sample KI-04 was held in furnace for 1 h in air (i.e., extremely oxidizing conditions) and then removed from the furnace with tongs and immediately placed into cold water to quench. The resulting glassy samples were extracted from their crucibles, re-crushed, and re-melted under identical conditions to ensure a homogeneous and crystal-free glass. A portion of each starting material was polished and analyzed by electron microprobe to verify that no compositional changes occurred during vitrification (see Table 2.1). Some vitrified KI-04 starting material was then mixed with elemental S to obtain batches of KI-04 (S-free, 2500 ppm S, 1 wt% S) starting material for use in sulfur solubility experiments.

### 2.1.3 Phonolite ERE-97018

The final starting material used in this study is ERE-97018, a phonolite bomb erupted in 1997 and collected on the crater rim (Kelly et al., 2008). This sample represents the most evolved lava found on Erebus and was used as one of two starting materials in sulfur solubility experiments (Chapter 5). The bomb was crushed to a rock powder in a manner similar to AW-82038. Rock powder was then placed within Pt crucibles and held in a one-atmosphere box furnace in air at 1300 °C for  $\sim$ 2 h and then quickly quenched by dropping into cold water. The then crystal-free sample glass was re-powdered and mixed with varying amounts of elemental S to obtain batches of ERE-97018 (125 ppm S, 500 ppm S, 1 wt% S) starting material.

# Chapter 3

# H<sub>2</sub>O-CO<sub>2</sub> Solubility in Erebus Phonotephrite Magma

Published in Contributions to Mineralogy and Petrology, 19 April 2013, vol. 166, no. 3, pp. 845-860 as:

 $H_2O-CO_2$  solubility in mafic alkaline magma: applications to volatile sources and degassing behavior at Erebus volcano, Antarctica

Kayla Iacovino, Gordon Moore, Kurt Roggensack, Clive Oppenheimer, Philip

Kyle

## 3.1 Abstract

I present new equilibrium mixed-volatile (H<sub>2</sub>O–CO<sub>2</sub>) solubility data for a phonotephrite from Erebus volcano, Antarctica. H<sub>2</sub>O–CO<sub>2</sub>-saturated experiments were conducted at 400–700 MPa, 1190 °C, and ~NNO+1 in non-end-loaded piston cylinders. Equilibrium H<sub>2</sub>O–CO<sub>2</sub> fluid compositions were determined using low-temperature vacuum manometry, and the volatile and major element compositions of the glassy run products were determined by Fourier transform infrared spectroscopy and electron microprobe. Results show that the phonotephrite used in this study will dissolve ~0.8 wt% CO<sub>2</sub> at 700 MPa and a fluid composition of XH<sub>2</sub>O ~0.4, in agreement with previous experimental studies on mafic alkaline rocks. Furthermore, the dissolution of CO<sub>2</sub> at moderate to high XH<sub>2</sub>O<sup>fluid</sup> in my experiments exceeds that predicted using lower-pressure experiments on similar melts from the literature, suggesting a departure from Henrian behavior of volatiles in the melt at pressures above 400 MPa. With these data, I place new constraints on the modeling of Erebus melt inclusion and gas emission data and thus the interpretation of its magma plumbing system and the contributions of primitive magmas to passive and explosive degassing from the Erebus phonolite lava lake.

## 3.2 Introduction

### 3.2.1 The role of alkalis in controlling volatile solubility

Alkali-rich magmas typically have higher  $CO_2$  solubilities than their less alkaline counterparts. For example, experimental studies by Brooker et al. (2001) revealed a positive correlation between the concentration of NBOs and the solubility of  $CO_2$  in "simple" compositions (SiO<sub>2</sub>-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>). Lesne et al. (2011b) found a markedly higher CO<sub>2</sub> solubility in alkali basalts compared with less alkaline basaltic melts (up to twice the dissolved  $CO_2$  relative to MORB). Behrens et al. (2009) also found a higher  $CO_2$  capacity in phonotephritic melts, which they explained as a consequence of high K content. This observed behavior can be understood by analogy with the complexing of alkali cations in aqueous solution with  $CO_2$  to form stable alkali carbonate precipitates. It can also be modeled by considering melt polymerization and the proportion of non-bridging oxygen atoms (NBO) to tetrahedral cations (T), known as the "NBO/T" parameter (Mysen, 1990, 1988; Mysen et al., 1982), where  $Si^{4+}$  and  $Al^{3+}$  are tetrahedral cations (network formers) and  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Na^+$  ions are network modifiers that generate NBOs (Mysen, 1990, 1988). Magmas with higher alkali contents will be weakly polymerized compared with less alkaline melts because the large ionization potential of their charge-balancing cations create weaker bridging T-O-T bonds. This weaker polymerization of the melt allows for a higher dissolution of  $CO_2$  through the reaction:

$$CO_2^{melt} + 2NBO^- \Leftrightarrow CO_3^{2-} + O^0 \tag{3.1}$$

where  $O^0$  is a bridging oxygen (Brooker et al., 2001; Dixon, 1997; Eggler &

Rosenhauer, 1978; Fine & Stolper, 1986).

## 3.2.2 Disagreement between solubility models for mafic alkaline melts

Several models exist for interpreting volatile contents in magmas, each with its own advantages and disadvantages. Because of the strong dependence of volatile solubility on intensive variables such as P, T, and melt composition, these models require a strong empirical foundation from a wide range of natural melts to be widely applicable. Nevertheless, such models are not infrequently used outside of the conditions for which they were calibrated (e.g., using a model calibrated for one composition to calculate volatile saturation pressures in another or extrapolating the model beyond its intended P-T range). Below I give a brief history of mixed solubility models, highlight their differences, and discuss the importance of choosing the correct model for a particular application.

The first study to compile a compositional parameterization of mixed-volatile solubility in silicate melts was that of Dixon (1997), which incorporated available data from 100- to 2000-MPa experiments (and additional unpublished data) on MORB and mafic alkalic melts. From these data, Dixon developed the "II" parameter, which relates dissolved  $CO_2$  content to the cation mole fractions of Si, Al, Ca, K, Na, Mg, and Fe, plus an equation relating the mole fraction of H<sub>2</sub>O dissolved in the melt to SiO<sub>2</sub>. This model has been shown to work rather well for tholeiitic to alkalic basalts, but is not suitable for calcic to calc-alkaline compositions (Moore, 2008). Dixon (1997) also showed that the compositional parameter II varies linearly with SiO<sub>2</sub>. This led to the simplification of Dixon's II-based solubility model to one based only on P, T, and SiO<sub>2</sub> concentration: the commonly used VolatileCalc (Newman & Lowenstern, 2002). Despite its simplifications, the VolatileCalc model proved extremely popular in part thanks to its user-friendly environment (VisualBasic macros in Microsoft Excel).

The shortcomings of VolatileCalc due to the simplification of the  $\Pi$  parameter to only one component have been highlighted by many authors including: Moore (2008) in a discussion of the state of the art in volatile solubility experiments and modeling; Lesne et al. (2011b) who presented a refinement of Dixon's II parameter for  $CO_2$  solubility in alkali basalts; and Witham et al. (2012) who coded the work of Dixon (1997) into a computer program, SOLEX, for calculating vapor saturation pressures and degassing paths. For example, Lesne et al. (2011b) found that VolatileCalc overestimates saturation pressures for melts from Vesuvius by 50% on average, since the model does not take into account the large effect of alkalis on  $CO_2$  solubility.

Probably the most comprehensive solubility model is that of Papale et al. (2006), who compiled a database of nearly 1,000 pure and mixed-volatile experiments and developed a non-ideal 29-parameter thermodynamic model calibrated over a wide range of chemical compositions. Despite the extent of the experimental database, the authors noted gaps in the availability of experimental data that limit application of the model (e.g., intermediate-mafic alkalic melts such as those at Erebus).

Saturation curves for Erebus phonotephrite AW-82038 modeled with Volatile-Calc (Newman & Lowenstern, 2002), SOLEX (Witham et al., 2012), Papale et al. (2006), and the experimental model of Lesne et al. (2011b,c) for alkali basalt from Etna are shown in Figure 3.1. Because many studies have already demonstrated the problems associated with the  $SiO_2$  parameterization of VolatileCalc (VC) for alkaline melts, my VC saturation curves have been modeled using a calculated "effective SiO<sub>2</sub>" of 49% from the calculated  $\Pi$  ( $\Pi = 0.3377$ ) for Erebus phonotephrite and match those of SOLEX to within  $\sim 2\%$ . Note the strong disagreement between models for both  $H_2O$  and  $CO_2$  saturation behavior for all pressures. The SOLEX/VC and Lesne et al. (2011b,c) models both assume Henrian behavior (ideal mixing of volatile components) in the melt. The Papale et al. (2006) model, which uses a different thermodynamic approach, makes no *a priori* assumption of ideal mixing in the melt and thus allows for the higher dissolution of  $H_2O$  in the melt at moderate to high  $X_{H_2O}^{fluid}$ . It is important to note that SOLEX and Volatile-Calc are calibrated up to maximum pressures of 400 and 500 MPa, respectively. Given that primitive Erebus melt inclusions are thought to entrap melt at higher



Figure 3.1: Modeled  $H_2O$  and  $CO_2$  solubility in phonotephrite AW-82038 at 1190 °C using: (a) SiO<sub>2</sub>-corrected VolatileCalc (Newman & Lowenstern, 2002) and SOLEX (Witham et al., 2012), blue dashed curves; (b) Papale et al. (2006), red curves; and (c) Lesne et al. (2011b,c) for alkali basalt from Etna, black curves. Isobars are plotted for pressures of 100, 300, 500, and 700 MPa for Papale et al. (2006) and Lesne et al. (2011b,c) and for pressures of 100 and 300 MPa for VolatileCalc/SOLEX as the latter models are not calibrated for pressures above 400 MPa.

pressures (Oppenheimer et al., 2011a), the Papale et al. (2006) and Lesne et al. (2011b,c) models are the only option for interpreting the deep plumbing system at Erebus. Given the lack of experimental data for Erebus magma compositions, however, it is unclear which of the existing models (if any) are appropriate for the interpretation of Erebus melt inclusions. This fact has motivated the following experimental solubility study, which allows us to analyze Erebus melt inclusions

in a context suited directly to their composition, pressure, and temperature.

## 3.3 Experimental methods

### 3.3.1 Preparation of experimental capsules

High-pressure mixed-volatile solubility experiments were carried out in non-endloaded 19-mm piston cylinders at isothermal and isobaric conditions of 1190  $^{\circ}\mathrm{C}$ (superliquidus) and 400–700 MPa at the OmniPressure Lab in Arizona State University. An average of approximately 80 mg of glassy starting material (AW82038; Table 3.1) was loaded into "trash can"-style  $Au_{75}Pd_{25}$  capsules. Liquid  $H_2O$  was added via microsyringe (typically  $\sim 0-2.5$  mg), and CO<sub>2</sub> plus additional H<sub>2</sub>O were added as oxalic acid dihydrate (OAD; typically  $\sim 4-5$  mg). The liquid H<sub>2</sub>O/OAD ratio was varied between runs to achieve either C- or H-rich fluids. The initial experiments contained  $CO_2$ -rich fluid, and used oxalic acid exclusively as a fluid source in an attempt to reproduce the CO<sub>2</sub>-rich melt inclusions in the DVDP basanites (Oppenheimer et al., 2011a). In later experiments, liquid H<sub>2</sub>O was added in order to explore the solubility behavior over a wider range of fluid compositions. All capsules were sealed by arc welding while partially submerged in a cold-water jig to prevent volatile loss. Capsule mass was monitored to detect any weight loss or gain during welding. After welding, capsules were placed in a drying oven at  $\sim 115$  °C for several minutes and subsequently re-weighed to check for H<sub>2</sub>O leakage. Capsules that showed any change in mass during or after welding were discarded. Sample capsules were then placed in 19-mm NaCl-Pyrex-MgO piston cylinder assemblies designed and calibrated to run at moderate pressures (Moore et al., 2008).

The oil pressure and temperature of the piston cylinder were raised simultaneously at a rate of ~60 psi min<sup>-1</sup> (~0.41 · MPa min<sup>-1</sup>) and ~20 °C · min<sup>-1</sup>. Temperature was measured with a W<sub>95</sub>Re<sub>5</sub>–W<sub>74</sub>Re<sub>26</sub> thermocouple (C-type), separated from the capsule by an alumina disk, and no pressure correction was applied. All experiments were run for 24 h and then isobarically quenched to a glass plus fluid phase. Upon completion of the experimental run, capsules were submerged for ~1 h in hydrofluoric acid to dissolve any Pyrex or ceramic adhered to the out-

Sample	P (MPa)	Mass rock	Mass OAD	Mass liquid	Mass post-run
		powder $(mg)$	(mg)	$H_2O~(mg)$	fluid $(mg)^1$
AW3	494	106.2	4.1	—	1.9
AW12	497	100.7	3.9	—	1.52
AW15	503	99.2	3.9	—	2.85
AW19	400	120.9	4.5	_	3.94
AW27	399	123.6	4.5	—	$1.81^{*}$
AW34	561	145	4.5	_	$0.99^{*}$
AW39	506	62	4.4	2.5	7.5
AW40	600	77.2	4.9	2.4	$2.45^{*}$
AW41	592	57.8	4.1	2.6	$2.66^{*}$
AW44	600	53.3	3.8	0.9	$3.67^{*}$
AW45	675	74.4	4.8	2.6	$3.44^{*}$
AW46	699	60.1	3.7	_	$0.93^{*}$
AW48	595	62.3	4.4	_	$1.71^{*}$
AW49	707	76.3	4.8	2.5	$3.37^{*}$
AW50	399	70.3	4.3	2.5	$3.52^{*}$

Table 3.1: Details of experimental capsules

Notes: Mass of rock powder, oxalic acid dihydrate (OAD), and liquid H<sub>2</sub>O all represent amounts loaded into the capsule before experimental run. <sup>1</sup>Mass of H<sub>2</sub>O and CO<sub>2</sub> in fluid phase after experimental run. Asterisk (\*) indicates mass is calculated from mass balance. Mass of the fluid phase in other samples (no asterisk) was measured by low temperature manometry (see text and Table 3.3)

side of the capsule. The capsules were then re-weighed to check for mass loss that occurred during the experiment. Capsules that showed decreased mass after the run were assumed to have leaked and were discarded.

## **3.4** Analytical techniques

### 3.4.1 H<sub>2</sub>O–CO<sub>2</sub> fluid manometry

The equilibrium  $H_2O-CO_2$  fluid composition of each capsule was measured using vacuum manometry at Arizona State University as outlined in Moore et al. (2008). Capsules were placed under vacuum and punctured with a sharpened

Table 3.2: Compositions of starting material, select experimental glasses, Erebus basanites, and similar compositions used in other experimental H<sub>2</sub>O-CO<sub>2</sub> solubility studies for comparison.

Oxide	DVDP 2-	AW-	AW-82038	$AW-3^4$	$AW-50^5$	DVDP 3-	AW-	ETN-1	Alb1
	$105.53^{1}$	$82038^{2}$	Starting			$295^{6}$	82033'	Lesne et_al	Behrens et al
			Material <sup>3</sup>					$(2010)^{8}$	$(2009)^9$
$SiO_2$	42.06	48.01	48.78	49.72	50.82	43.34	45.43	47.95	49.89
$TiO_2$	4.21	2.77	2.59	2.89	2.95	4.32	3.61	1.67	0.89
$Al_2O_3$	13.08	18.56	19.11	19.34	20.32	14.6	17.62	17.32	15.57
FeO*	11.46	9.49	10.65	8.62	6.55	10.7	10.99	10.24	7.82
MnO	0.18	0.22	-	-	-	0.2	0.23	0.17	0.02
MgO	12.12	3.18	2.71	2.84	2.4	6.06	3.64	5.76	5.75
CaO	11.5	7.65	7.75	7.72	7.32	14.23	9.57	10.93	11.4
$Na_2O$	3.03	5.99	5.8	6.18	6.26	3.66	5.11	3.45	1.95
$K_2O$	1.51	2.88	2.62	2.69	2.89	1.59	2.47	1.99	7.52
$P_2O_5$	0.87	1.24	-	-	0.49	0.81	1.33	0.51	
Total	100.01	98.29	97.68	95.86	91.11	96.56	98.53	100	100.82

\*FeO\* is the total iron given as FeO.

<sup>1</sup>Composition of parental basanite (Kyle, et al., 1992)

 <sup>2</sup>Composition used in this study, as analyzed by Kyle, et al (1992) using X-ray fluorescence (XRF)
<sup>3</sup>Electron microprobe analysis of starting material after vitrification in the 1-atm furnace, but before run in the piston cylinder; this study

<sup>4</sup>Electron microprobe analysis of post-run glass AW-3 (494 MPa; XH2O=0.15; H2Omelt=2.46 wt%; CO2melt=0.477 wt%) <sup>5</sup>Electron microprobe analysis of post-run glass AW-50 (399 MPa; XH2O=0.50; H2Omelt=4.27 wt%; CO2melt=0.347 wt%)

<sup>6</sup>Melt inclusion analysis of a related basanite by Eschenbacher (1998)

<sup>7</sup>Melt inclusion analysis of a related basanite by Eschenbacher (1998)

<sup>8</sup>Natural alkali basalt from Etna from Lesne et al. (2010)

<sup>9</sup>Synthetic starting material from Behrens et al. (2009)

tungsten electrode. The  $H_2O$  and  $CO_2$  fluid was cryogenically separated in a series of cold traps and moved into a mercury U-tube manometer using a Toepler pump. Carbon dioxide partial pressure was measured directly, but water was reduced over a hot uranium furnace to hydrogen gas before measurement. Some non-condensable gases were present, but their abundances were very small, indicating that the experiments were performed under oxidizing conditions and that no significant amount of CO or  $CH_4$  was generated during the runs. The fluid measurements have an estimated error of  $\pm 20 \ \mu \text{mol}$  of either component, and the average total fluid was  $\sim 100 \ \mu \text{mol}$ . Results of the manometry measurements are shown in Table 3.3. Of the 15 successful experiments, only five produced satisfactory fluid manometry determinations due to vacuum line failure.

The composition of the gas phase was calculated by mass balance for the samples in which the manometry measurements failed. It is expected that some excess water will be introduced to the experimental capsule before welding due to humidity in the laboratory air, despite the storage of rock powder in a drying oven. Additional excess  $H_2O$  may also be introduced into the capsule during the run

Sample	m <sub>totalfluid</sub>	$m_{CO_2}$	$m_{H_2O}$	$\mathbf{X}_{H_2O}^{fluid}$
	(mg)	(mg)	(mg)	
AW3	1.9	1.77	0.13	0.15
AW12	1.52	1.48	0.04	0.06
AW15	2.85	2.48	0.37	0.27
AW39	7.5	4.24	3.26	0.65
AW44	4.54	2.88	1.66	0.59

Table 3.3: Low temperature fluid manometry measurements.

Notes: Masses of each fluid component  $(m_{CO_2}; m_{H_2O})$  and the total fluid  $(m_{totalfluid})$  were measured with low temperature vacuum manometry. Fluid manometry data do not exist for all samples because some analyses were unsuccessful.

via  $H_2$  diffusion from the  $H_2O$ -saturated assembly. A plot of fluid compositions measured via manometry versus those calculated by mass balance reveals a linear, but not 1:1, relationship, supporting this expectation. Assuming an offset of +0.64 mg of excess  $H_2O$  to the capsule gives the best agreement between measured and calculated values, and I use the adjusted  $H_2O^{initial}$  values for all calculations of the gas phase.

### 3.4.2 Infrared spectroscopy

Dissolved H<sub>2</sub>O and CO<sub>2</sub> contents in all resulting experimental glasses were analyzed by FTIR spectroscopy (Table 3.4). FTIR spectra of doubly polished glass chips (with thickness from ~20 to 200  $\mu$ m) were collected in the 6000–1000 cm<sup>-1</sup> wavenumber range on a Bruker IFS 66 V/S spectrometer at Arizona State University using a KBr beamsplitter and an aperture size of 2.5 mm. Additional samples were measured on a Nicolet 550 Series II Magna-IR spectrometer at the synchrotron light source at University of Wisconsin-Madison Synchrotron Research Center using a MCT-A detector and KBr beamsplitter. These samples were placed on a KBr pellet and measured using an aperture of  $14 \times 14 \mu$ m. A background measurement was made before the collection of each sample spectra to correct for the contribution of atmospheric CO<sub>2</sub> and H<sub>2</sub>O.

$Sample^1$	$A_{1420}$	$A_{1505}$	$A_{4500}$	$A_{5200}$	$A_{1630}$	$A_{3500}$	Thickness (cm)
3A-1			0.034	0.018			0.02324
3A-2			0.031	0.018			0.02324
3G-1	1						0.01148
12C-1	0.615	0.629				1.287	0.0078
15C-3	0.661	0.661				1.659	0.0071
19C-1	0.468	0.468				1.234	0.00745
27C-1	0.486	0.531				1.578	0.00885
34B-1						1.812	0.011
34B-2						1.74	0.0103
34D-1						0.815	0.0049
34D-2	0.565	0.56				0.8	0.00495
34D-3						0.699	0.0046
34D-4						0.785	0.0046
39B	0.25				0.434		0.0027
40A			0.0375	0.07			0.0205
40C	0.391				0.75		0.0037
41A			0.023	0.073			0.0169
41B	0.75	0.75					0.0083
44C-1	0.68	0.703				0.707	0.00595
44C-2	0.5828	0.523					0.0052
44C-3	0.602	0.593					0.0052
45C-1	0.598				0.654	1.767	0.00425
45C-2						1.675	0.00405
45C-3						1.611	0.00345
45C-4	0.581				0.612	1.541	0.00415
46D-1	1.153	1.224	0.015	0.014	0.418		0.00875
46D-2	1.113	1.421	0.017	0.025	0.608		0.0078
48C-1	0.537	0.518	0.017	0.025	0.588		0.00485
48C-2	0.239	0.229			0.328	1.116	0.00345
48C-3	0.516	0.516	0.015	0.013	0.544	1.969	0.0051
49B-2	0.451				0.477	1.559	0.0036
49B-3	0.616				0.654	1.748	0.0044
50A-1	0.289	0.304			0.619		0.00535
50A-3	0.211	0.23			0.461	1.27	0.0032
50D-1	0.273	0.257			0.62	1.901	0.00435
50D-3	0.259	0.259			0.585	1.811	0.0043

Table 3.4: Thickness and FTIR absorbance measurements of experimental glasses.

Notes: Samples with only one carbonate measurement (at  $A_{1420}$ ) have no splitting of the carbonate doublet (see text). Samples with total dissolved volatiles >4 wt% have merged CO<sub>3</sub> doublet in FTIR spectra sample numbers 39, 40, 41, 44, 49, 50). All other samples have total dissolved volatiles <4 wt% and show the typical split CO<sub>3</sub> doublet. Precision on the thickness measurements is  $\pm 1 \ \mu m$ 

<sup>1</sup>The number at the beginning of sample names corresponds to run number in Table 3.5. Each run capsule was peeled and its contents separated into between two and five glass pieces corresponding to the letter succeeding each run number (A-E). Each piece was then sliced and polished to obtain chips of varying thickness, corresponding to numbers after the hyphen. Thinner chips were used to measure carbonate abundance, and thicker chips were used to measure water.

Retrievals of the  $CO_2$  and  $H_2O$  amounts were based on the Beer-Lambert law (Ihinger et al., 1994):

$$c = \frac{100 \times MW \times A}{d\rho\epsilon} \tag{3.2}$$

where c is the concentration of the species in wt%, MW is the molecular weight of the species, A is the absorbance (peak height) of the band being measured, d is the thickness of the sample in cm,  $\rho$  is the density of the sample in g·L<sup>-1</sup>, and  $\epsilon$  is the absorption coefficient in L·(mol·cm)<sup>-1</sup>.

Determinations of absorbances (A) for the dissolved molecular H<sub>2</sub>O and OH (5200 and 4500 cm<sup>-1</sup>, respectively) and carbonate (1505 and 1420 cm<sup>-1</sup>) species were made using background-corrected peak heights, where backgrounds were hand drawn using a French curve. Sample thicknesses were measured using an ADE Phase-shift Microxam surface mapping microscope (white light interferometer) with a precision of  $\pm 0.5$ –2  $\mu$ m. Additional sample thicknesses were determined using a Mitutoyo digimatic indicator with an expected error of  $\pm 1 \mu$ m. Approximate hydrous glass density for all samples (~2800 g·L<sup>-1</sup>) was estimated using the partial molar volumes of the oxide components as determined by Lange & Carmichael (1987) and the partial molar volume of H<sub>2</sub>O (Ochs & Lange, 1999). Molar absorptivity coefficients ( $\epsilon$ ) determined for a basanite very similar to my composition were used:  $0.56 \pm 0.04 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  and  $0.58 \pm 0.02 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for  $\epsilon_{5200}$  and  $\epsilon_{4500}$ , respectively (Cocheo, 1993), and the calculated CO<sub>2</sub> coefficient of 359.09 L·mol<sup>-1</sup>·cm<sup>-1</sup> for both  $\epsilon_{1420}$  and  $\epsilon_{1505}$  is from Dixon & Pan (1995).

No molecular  $CO_2$  was observed at 2450 cm<sup>-1</sup> in any of the samples, so the carbonate band was used for quantification of total carbon. A pronounced doublet with peaks at 1420 and 1505 cm<sup>-1</sup> is typically found in most carbonate-bearing glasses (Ihinger et al., 1994). Almost all experiments with high concentrations of dissolved H<sub>2</sub>O and CO<sub>2</sub> (>4 wt% total dissolved volatiles) show little or none of the typical splitting of the carbonate band. Jakobsson (1997) observed a similar behavior in icelandites, where samples with low dissolved molecular H<sub>2</sub>O contents generated spectra with a split carbonate doublet, whereas samples with high

molecular  $H_2O$  contents had carbonate peaks with little or no split. In addition to volatile content, glass composition may also play a role in the degree of splitting of the carbonate peaks. Fine & Stolper (1986) report a shift in the higher-frequency peak of the carbonate band for basaltic samples relative to sodium aluminosilicate glasses. This is attributed to the distinction between mono- and divalent cations associated with carbonate groups. Because all of my experiments have the same glass composition, the splitting or non-splitting behavior of the carbonate band that I observe is likely due to some other factor. In the absence of a clear relationship between total dissolved volatile content and band splitting, however, I are unable to identify what that factor might be. Where the 1505  $\rm cm^{-1}$  peak is dominated by the 1420  $\rm cm^{-1}$  peak, only the 1420  $\rm cm^{-1}$  peak was used to determine carbon content. Because there are very few data constraining the absorption of carbonate in phonotephrite, I must assume that a non-split carbonate doublet has the same peak height as a split doublet at  $1420 \text{ cm}^{-1}$  and therefore use the same  $\epsilon_{1420}$  value for all samples. Experiments with lower dissolved H<sub>2</sub>O and CO<sub>2</sub> contents all show splitting of the band into distinct 1505 and 1420  $\rm cm^{-1}$  peaks (Figure 3.2), and in these cases, both peaks were measured and averaged.

### 3.4.3 Electron microprobe

Electron microprobe analyses of major element compositions of the starting glass and all successful run products were carried out using a JEOL 8600 Superprobe at Arizona State University. Samples were analyzed using an accelerating voltage of 15 kV, a beam current of 10 nA, and a defocused beam with a diameter of 10  $\mu$ m. Microprobe analyses confirmed no significant chemical variation between vitrified starting material and experimental charges (see Table 3.2). In general, Fe loss was minimal with only five samples showing Fe loss >25% (see Table 3.5).

#### 3.4.4 Establishment of equilibrium

Based on previous experimental studies using similar melt compositions (Behrens et al., 2009), a run time of 24 h was chosen to ensure equilibrium between the phonotephrite melt and the fluid phase in my experiments. Equilibrium was confirmed through major element analysis of all run products via electron microprobe,

			D							
$\operatorname{Sample}$	Ч	$H_2O$ melt	$CO_2$ melt	$\mathbf{X}_{H_2O}$	$f H_2 O$	$f CO_2$	Calculated	Approx.	$Fe^{total}$	$\rm FeO/Fe_2O_3$
Number	(Mpa)	(wt%)	(wt%)	(fluid)	(bar)	$(\mathrm{bar})$	$\log(fO_2)$	$\Delta NNO Buffer$	(wt%)	(wt%)
AW3	494	2.46	0.477	0.151	682.79	13121.85	-8.32	NNO-1	8.61	3.68
AW12	497	2.11	0.51	0.063	844.29	12763.41	-9.08	NNO-2	8.37	5.36
AW15	503	2.98	0.51	0.267	1296.2	11649.83	-7.83	ONN	8.1	2.85
AW19	400	1.69	0.344	$0.12^{a}$	402.08	8844.92	-8.54	NNO-1	7.95	4.11
AW27	399	2.28	0.315	$0.57^{a}$	2303.26	3903.86	I	Ι	8.88	ND
AW34	561	1.68	0.622	$0.47^{a}$	2898.63	20568	Ι	Ι	9.4	ND
AW39	506	5.76	0.493	0.653	3742.4	6114.06	-7.05	NNO+0.5	8.49	1.88
AW40	600	5.97	0.579	$0.47^{a}$	3196.9	11994.65	I	Ι	$7.91^{*}$	ND
AW41	592	6.41	0.587	$0.41^{a}$	2664.23	13215.39		Ι	8.77	ND
AW44	009	1.21	0.718	0.585	4172.89	8919.88	I	I	$7.87^{*}$	ND
AW45	675	5.83	0.81	$0.56^a$	4736.4	12836.45	I	I	6	ND
AW46	669	4.93	0.817	$0.50^{a}$	4361.71	16542.68	I	I	8.65	ND
AW48	595	4.93	0.585	$0.46^{a}$	3057.9	12114.09	I	I	$4.94^{*}$	ND
AW49	707	4.24	0.773	$0.41^{a}$	3501.88	20804.47	I	Ι	$7.10^{*}$	ND
AW50	399	4.27	0.347	$0.50^{a}$	1966.1	4669.76	I	I	$6.55^{*}$	ND
H <sub>a</sub> O meli	t and CO	melt from	FTIR: X <sub>H O</sub>	f (hind) f	from low 1	<sup>r</sup> manometa	rv. Fe <sup>total</sup> fro	m electron micro	nrohe: C	alculated
$\log(fO_2)$	from inti	tinsic $fO_2$ of	f apparatus a	ind know	n fluid co	mposition (	see text).			
$^a$ denotes	$X_{H_2}O(\hat{H})$	uid) calculat	ted by mass l	balance;	Fe <sup>total</sup> (wt	$\mathcal{M}_{0} = \mathrm{norm}$	alized total I	Fe as FeO; * den	otes sam	oles
with Fe I	$\cos > 25\%$	10								



Figure 3.2: Representative FTIR spectra of experimental samples, plotted with offset scales on the y-axes. Note how the carbonate peaks merge in samples with high total dissolved volatile concentrations (AW 44C-2). In samples with unresolved carbonate peaks, the carbonate abundance was determined by peak height at 1420 cm<sup>-1</sup>.

which yielded the same results within analytical error. Additionally, between three and five FTIR spectroscopic measurements of dissolved  $H_2O$  and  $CO_2$  content were made on the center and margins of multiple glass chips from each run product, and no heterogeneity was observed.
## 3.5 Results

#### 3.5.1 Iron oxidation state and experimental oxygen fugacity

As demonstrated in experimental studies (e.g. Behrens et al., 2009; Pawley et al., 1992), oxygen fugacity may influence the solubility of volatiles in silicate melts by controlling iron speciation, a parameter that strongly affects outputs of the Papale et al. (2006) model. For this reason, knowledge of the oxygen fugacity and iron oxidation state of my samples is necessary for the comparison of my experimental data to the literature and to the predictions of solubility models.

Iron oxidation state was not measured in my samples, so the FeO/Fe<sub>2</sub>O<sub>3</sub> ratio was calculated based on the work of Kress & Carmichael (1991). The intrinsic oxygen fugacity of the piston cylinders used in this work has been measured to be one log unit above the Ni–NiO buffer, that is, NNO+1 (R. Lange, personal communication). However, because my experimental runs contained CO<sub>2</sub>-rich fluids and therefore reduced  $fH_2O$  relative to CO<sub>2</sub>-poor fluids, the  $fO_2$  inside the experimental capsules was necessarily below NNO+1. Although oxygen fugacity was not directly measured, I can estimate the  $fO_2$  for each experimental run where  $X_{H_2O}^{fluid}$  is known. Assuming that the experimental apparatus is water saturated, I can calculate the intrinsic hydrogen fugacity,  $fH_2$ , on the outside of the capsule using the equilibrium constant of formation,  $K_F$  (Robie et al., 1978), the H<sub>2</sub>O fugacity,  $fH_2O$  (calculated with the modified Redlich-Kwong equations of Holloway (1977) and modified by Flowers (1979)), and the intrinsic oxygen fugacity,  $fO_2$ , of NNO+1:

$$K_F = \frac{fH_2O}{fH_2 \cdot fO_2^{1/2}}$$
(3.3)

Because the intrinsic  $fH_2$  of the apparatus is equal to the  $fH_2$  inside of the capsule due to the rapid diffusion of hydrogen, the oxygen fugacity inside of the capsule,  $fO_2^{inside}$ , can then be calculated as:

$$fO_2^{inside} = \left(\frac{fH_2O \cdot XH_2O^{fluid}}{fH_2 \cdot K_F}\right)^2 \tag{3.4}$$

Experimental  $fO_2$  values for my samples range from  $\sim$ NNO-2 for very CO<sub>2</sub>-rich samples to  $\sim$ NNO+0.5 for more H<sub>2</sub>O-rich samples (Table 3.5).

#### 3.5.2 H<sub>2</sub>O–CO<sub>2</sub> solubility in phonotephrite

Of the 53 experiments performed, 15 were successful in that they yielded homogeneous, crystal-free glasses within capsules that retained their fluid phase. The dissolved H<sub>2</sub>O and CO<sub>2</sub> content in successful runs ranges from 1.21 to 6.41 wt% H<sub>2</sub>O and 0.31 to 0.82 wt% CO<sub>2</sub>, over fluid compositions of ~0.1 to ~0.6 X<sub>H2O</sub> (Table 3.5). Because I was unable to quench any pure H<sub>2</sub>O-saturated experiments to a crystal-free glass, the H<sub>2</sub>O-rich end-member solubility is not constrained. It is possible that the formation of crystals during quench is facilitated in these extremely H<sub>2</sub>O-rich runs due to the low viscosity of the hydrous, alkali-rich melt (Behrens et al., 2009).

## 3.5.3 Thermodynamic modeling of mixed-volatile solubility data and comparison with other solubility models

I have employed the thermodynamic approach of Dixon et al. (1995) to formulate a model for H<sub>2</sub>O and CO<sub>2</sub> solubility in Erebus phonotephrite. This method relates the fugacity of each of two volatile species (in the fluid phase) to the concentration of that volatile dissolved in the melt and assumes ideal mixing between both volatiles in the melt. The relationships between fugacity and concentration in the melt of H<sub>2</sub>O and CO<sub>2</sub> are shown in Figure 3.3, where the fugacities were calculated for the corresponding  $X_{H_2O}^{fluid}$ , pressure, and a temperature of 1190 °C using the modified Redlich-Kwong equation of state after Holloway (1977) and modified by Flowers (1979). Power law regressions of the data give the following equations:

$$H_2O(wt\%) = 6.5 \times 10^{-2} \times fH_2O^{0.541}, R^2 = 0.94$$
(3.5)

$$CO_2(wt\%) = 1.06 \times 10^{-2} \times fCO_2^{0.416}, R^2 = 0.44$$
 (3.6)

While the regression for  $H_2O$  gives a reasonable result, note the poor fit of my

 $CO_2$  data to a power law relationship.



Figure 3.3: Plots showing the relationship between the fugacity of the volatile component in the fluid phase (in bars) versus the amount of that volatile component dissolved in the melt (in wt%). Fugacities calculated with the modified Redlich-Kwong equation of state. Lines represent power regressions of the data with an  $R^2$  of 0.94 and 0.44 for H<sub>2</sub>O and CO<sub>2</sub>, respectively.

With the above relationships, I can calculate isobars, which show the change in volatile saturation with varying fluid composition at a constant pressure, and isopleths, which show the change in volatile content with increasing pressure at constant fluid composition. Given the poor correlation between dissolved CO<sub>2</sub> and  $fCO_2$  (Eq. 3.6), additional data, specifically the nearly pure-CO<sub>2</sub> experiments of Lesne et al. (2011b), were added to the regression, and the result used to calculate the isobars are shown in Figure 3.4. Saturation pressures determined by the modeled isobars in Figure 3.4 do not match my experimental data, especially at moderate to high  $X_{H_2O}^{fluid}$ . Dixon et al. (1995) H<sub>2</sub>O and Lesne et al. (2011b,c) have both used this method with great success and have demonstrated that their mixed solubility data follow essentially Henrian behavior in the melt. Some key differences exist, however, between those and my studies. First, both Dixon et al. (1995) and Lesne et al. (2011b,c) performed (nearly) pure end-member experiments [pure H<sub>2</sub>O and nearly pure CO<sub>2</sub> (<1.5 wt% H<sub>2</sub>O) experiments in Lesne et al. (2011b,c); pure H<sub>2</sub>O plus some mixed-volatile (maximum ~300 ppm CO<sub>2</sub>) experiments in Dixon et al. (1995)). All of our experiments employ a mixed H<sub>2</sub>O– CO<sub>2</sub> fluid, which yielded a range of equilibrium  $X_{H_2O}^{fluid}$ . Secondly, and possibly more importantly, both the Dixon et al. (1995) and Lesne et al. (2011b,c) studies were performed at <100 and <380 MPa, respectively, pressures much lower than those of this study (400–700 MPa). The few mixed-volatile solubility data in the literature for mafic melts at relatively high pressure have shown a strongly nonlinear relationship between CO<sub>2</sub> dissolved in the melt and fCO<sub>2</sub> (Behrens et al., 2009; Botcharnikov et al., 2005), indicating that the addition of H<sub>2</sub>O to melt above 500 MPa enhances the dissolution of CO<sub>2</sub> (see Lesne et al., 2011b). Similarly, CO<sub>2</sub> dissolution in my experimental melts is higher than that predicted by an ideal model in runs with high H<sub>2</sub>O concentrations (Figure 3.4), suggesting non-ideal mixing in the melt.

To investigate this further with respect to my data, in Figure 3.5 I compare my experimental data to the model of Lesne et al. (2011b,c) for alkali basalt from Etna, which uses the thermodynamic approach of Dixon et al. (1995), and to the model of Papale et al. (2006), which is non-ideal. Neither VolatileCalc (Newman & Lowenstern, 2002) nor SOLEX (Witham et al., 2012) is calibrated to pressures above 500 MPa, but both use the thermodynamic approach of Dixon et al. (1995) and so predict similar behavior with respect to  $H_2O-CO_2$  mixing in the melt as in the Lesne et al. (2011b,c) model (see Figure 3.1). The misfit between my experimental data and the curve fits of Lesne et al. (2011b,c) increases significantly with pressure. Conversely, Papale et al. (2006) models my data quite well for higherpressure experiments (600–700 MPa), but overestimates saturation pressures for 500 MPa and even more so for 400 MPa experimental data. A comparison of the two models reveals the distinct difference in curve form between the ideal Lesne et al. (2011b,c) model and the non-ideal Papale et al. (2006) model. At high pressures,  $CO_2$  dissolution in my experimental melts is enhanced at moderate dissolved  $H_2O$  concentrations relative to that predicted by ideal solubility models. This has not been observed in low-pressure (<500 MPa) experiments (Dixon et al., 1995; Lesne et al., 2011b,c; Witham et al., 2012), and the departure from Henrian behavior in my data appears to increase with pressure.



Figure 3.4: Thermodynamically calculated, fully ideal model of  $H_2O$  and  $CO_2$  saturation in Erebus phonotephrite modeled using the relationship between fugacity of the volatile component and the concentration of that volatile dissolved in the melt. Because of the poor fit of our  $CO_2$  data to a power law regression, the pure- $CO_2$  experiments of Lesne et al. (2011b) were used to create these isobars. This modeling approach does not work well for our high P experiments given their enhanced  $CO_2$  dissolution at moderate to high  $X_{H2O}^{fluid}$ .



Figure 3.5:  $H_2O-CO_2$  solubility data from this study compared with the predicted solubility curves (isobars) of (Lesne et al., 2011b,c, upper) and (Papale et al., 2006, lower). Curves of Lesne et al. (2011b,c) calculated for alkali basalt from Etna at 1200 °C. Those of Papale et al. (2006) calculated for the Erebus phonotephrite used in this study with an  $fO_2$  of NNO+1, the intrinsic  $fO_2$  of our experimental apparatus. Lesne et al. (2011b,c) overestimates saturation pressures for our experiments at low  $X_{H_2O}^{fluid}$ , while Papale et al. (2006) overestimates saturation pressures significantly for 400 and 500 MPa experiments. The shape of the Papale et al. (2006) curves better matches the distribution of our data at moderate to high  $X_{H_2O}^{fluid}$ , possibly owing to the fact that this model is fully non-ideal.

#### 3.5.4 Determination of empirical solubility relationships

Given that my high-pressure data are not consistent with Henrian behavior with respect to dissolved volatiles in the melt and are therefore not amenable to the thermodynamic approach of Dixon et al. (1995), I have calculated isobars via a third-order polynomial fit to my data. With this approach, my isobars mimic the curve forms predicted by Papale et al. (2006), whose model, although not calibrated for alkalic compositions, best predicts the non-Henrian behavior I observe in my data at moderate to high  $X_{H_2O}^{fluid}$ . The solubility behavior of H<sub>2</sub>O and CO<sub>2</sub> as determined by my experiments (at 1190 °C, 400–700 MPa) is shown in Figure 3.6. Third-order polynomial regressions of my data give the following equations, where CO<sub>2</sub> and H<sub>2</sub>O are in wt%:



Figure 3.6: Empirically determined  $H_2O-CO_2$  fluid saturation isobars for Erebus phonotephrite. Isobars were fitted through our experimental data using a third-order polynomial. 400 MPa runs are shown as red diamonds, 500 MPa runs as blue diamonds, 600 MPa runs as green diamonds, and 700 MPa runs as yellow diamonds.

$$CO_2 = 0.43 - 0.073 \times H_2O + 0.017 \times H_2O^2 - 0.0015 \times H_2O^3$$
  
for 400 MPa,  $R^2 = 0.99$  (3.7)

$$CO_2 = 0.57 - 0.067 \times H_2O + 0.015 \times H_2O^2 - 0.0012 \times H_2O^3$$
  
for 500 MPa,  $R^2 = 0.99$  (3.8)

$$CO_2 = 0.73 - 0.07 \times H_2O + 0.014 \times H_2O^2 - 0.0011 \times H_2O^3$$
  
for 600 MPa,  $R^2 = 0.99$  (3.9)

$$CO_2 = 0.89 - 0.06 \times H_2O + 0.011 \times H_2O^2 - 0.0009 \times H_2O^3$$
  
for 700 MPa,  $R^2 = 0.99$  (3.10)

Thin dashed gray lines in Figure 3.6 represent isopleths, which were constructed by first calculating the  $fH_2O$  for a given  $X_{H_2O}^{fluid}$ , then determining H<sub>2</sub>O content for given values of  $fH_2O$  using Eq. 3.5. The corresponding CO<sub>2</sub> contents were then calculated using the isobars (Eqs. 3.7 – 3.10) from Figure 3.6. Isopleths were then fit using a second-order polynomial. It is noteworthy that the distribution of the isopleths seems to be weighted toward a higher dissolution of CO<sub>2</sub> in the melt. In other words, CO<sub>2</sub> solubility does not vary much for a given pressure over a large range of fluid compositions ( $X_{H_2O}^{fluid}$  between ~0.1 and 0.5). This implies that even mafic alkalic melts with very little CO<sub>2</sub> in the fluid phase ( $X_{H_2O}^{fluid}$  approaching 1) will dissolve significant amounts of CO<sub>2</sub> in the melt. This tendency toward CO<sub>2</sub>rich melt is consistent with the observation that CO<sub>2</sub>-rich melt and fluid inclusions are often associated with alkalic magmas (Lowenstern, 2001; Spera & Bergman, 1980).

## 3.6 Discussion

## 3.6.1 Saturation pressures and fluid compositions of primitive Erebus magmas

By comparing my experimental data to the pre-eruptive volatile contents recorded by the primitive melt inclusions in Erebus and DVDP lavas (Oppenheimer et al., 2011a), I can estimate the minimum saturation pressures of the magmas, thereby constraining the depths at which they degas (Figure 3.7). I examine melt inclusions from two basanites: AW-82033 and DVDP 3-295. Melt inclusions from AW-82033 are examined as a representative analogue to the phonotephrite AW-82038 used in this study because of their similarity in bulk composition (see Table 3.2; Figure 2.2). DVDP 3-295 is a more primitive composition than that used in my experiments. Because it is unknown precisely how the saturation surface will change with varying melt composition, the reliability of an extrapolation of my model is uncertain.

AW-82033 melt inclusions contain an average of 0.08 wt% CO<sub>2</sub> and 0.2 wt% H<sub>2</sub>O. A comparison with the empirical curves based on my experimental data set (Figure 3.7) reveals that this magma was saturated at pressures of <100-300 MPa, corresponding to a depth of <3-9 km. The more primitive basanite melt inclusions of DVDP 3-295 contain an average of 0.6 wt% CO<sub>2</sub> and 1.5 wt% H<sub>2</sub>O. Assuming the melt inclusions were in equilibrium and saturated at the time of entrapment, I estimate that DVDP 3-295 melt inclusions formed at pressures of  $\sim400-600$  MPa ( $\sim12-18$  km). This is much shallower than previous estimates of  $\sim25-30$  km and places DVDP basanites in the lower crust rather than upper mantle as suggested by Oppenheimer et al. (2011a).

Because I obtained a direct measure of the equilibrium fluid composition of my experimental runs, I are also able to estimate the composition of the fluid in equilibrium with the melt inclusions upon entrapment. Figure 3.7 illustrates that the primitive DVDP 3-295 melt inclusions were equilibrated with a fluid of  $X_{H_2O}^{fluid}$ = 0.075, while the more evolved AW-82033 inclusions were equilibrated with a more CO<sub>2</sub>-rich fluid of  $X_{H_2O}^{fluid} = 0.01-0.05$ .

## 3.6.2 Determining the source of volatiles released in explosive eruptions through the Erebus lava lake

Observations of gas emissions from the lava lake at Erebus volcano have revealed remarkably different gas signatures associated with passive and explosive emissions. These have been interpreted as evidence for gas extracted from different depths within the magmatic system (Burgisser et al., 2012; Oppenheimer et al., 2011a). Strombolian eruptions that eviscerate much of the lava lake have the highest observed  $CO_2/H_2O$  ratio in the plume, with an  $X_{H_2O}^{fluid}$  of 0.36 (Oppenheimer et al., 2011a), while the steady-state, passive degassing is characterized by  $X_{H_2O}^{fluid} =$ 0.59 (Oppenheimer & Kyle, 2008a). Oppenheimer & Kyle (2008a) suggested that the  $CO_2$  released at the surface is substantially sourced from deep-seated basanite magma. More recently, Oppenheimer et al. (2011a) have suggested that fluxing of "nearly pure  $CO_2$  fluids rising from great depths" is responsible for both isobaric fractional crystallization within the magma system as well as the observed  $CO_2$ rich explosive eruptions.

I now use the new constraints from my solubility data to investigate the hypothesized mechanisms for the  $CO_2$ -rich explosive eruptions through the Erebus lava lake. In the following analysis, I make three assumptions: (1) For simplicity, I assume that the two end members of the system, deep basanite and lava lake phonolite, are the only magmas contributing to explosive degassing; (2) I assume that lava lake phonolite is responsible for all of the passive degassing; and (3) I use the measurements of gas composition in the plume reported by Oppenheimer et al. (2011a) as representative of the volatile budget in lava lake phonolite rather than melt inclusions in phonolite bombs (sample EA1 melt inclusions; Eschenbacher, 1998). I do this because gas measurements directly record the gas emissions, whereas melt inclusions may be degassed, especially with respect to hydrogen (Chen et al., 2011; Portnyagin et al., 2008; Wallace, 2005).

With these assumptions, I explore two possible mechanisms for explosive de-



Figure 3.7: Volatile contents in olivine-hosted basanite and phonotephrite melt inclusions from Erebus volcano (Oppenheimer et al., 2011a) superimposed on my empirically determined, non-ideal H<sub>2</sub>O–CO<sub>2</sub> solubility curves and isopleths for Erebus phonotephrite at 400, 500, 600, and 700 MPa and at  $X_{H_2O}^{fluid} = 0.01, 0.05, 0.1$ , and 0.2. Red diamonds represent DVDP 3-295; blue triangles represent AW-82033. Primary basanite DVDP 3-295 became saturated and began degassing at about 600 MPa, and phonotephrite AW-82033 began degassing at about 300 MPa.

gassing in the Erebus lava lake: (1) coupled ascent of  $CO_2$ -rich volatiles and magma to shallow regions (similar to Oppenheimer & Kyle, 2008a), and (2) the ascent of decoupled,  $CO_2$ -rich gas derived from a magma at great depth (after Oppenheimer et al., 2011a).

As both scenarios require a CO<sub>2</sub>-rich gas separate from that in the lava lake, it begs the question: What is the source of this gas, and how does a parental basanite with  $X_{H_2O}^{fluid} = 0.075$  evolve into a phonolite with  $X_{H_2O}^{fluid} = 0.36$ ? This is where hypotheses (1) and (2) diverge. Hypothesis (1) calls for the degassing of volatile-rich magma beneath the lava lake. As the most evolved composition at Erebus, phonolite magma will have a higher H<sub>2</sub>O/CO<sub>2</sub> solubility ratio in the melt relative to the basanite. As such, the persistent degassing of small batches of CO<sub>2</sub>-rich phonolite at moderate to low pressures will fractionate out CO<sub>2</sub> such that, by the time it is integrated into the lava lake, the melt is holding mostly H<sub>2</sub>O. This scenario is similar to that proposed by Oppenheimer & Kyle (2008a) in which CO<sub>2</sub>-rich fluid is delivered into the magma lake via a deep basanite magma source, except that here I invoke phonolite magma as the gas source rather than basanite.

In support of hypothesis (2), where decoupled  $CO_2$ -rich gas ascends into the lava lake, I consider two different gas sources: (a) deep basanite magma (i.e., DVDP) and (b) a  $CO_2$ -rich source from some depth greater than that recorded by melt inclusions. The first case (a) requires the deep separation of  $CO_2$ -rich gas from basanite magma after melt inclusion entrapment, leaving behind a melt richer in H<sub>2</sub>O. Because of the lower solubility of  $CO_2$  relative to H<sub>2</sub>O,  $CO_2$  will degas at a greater depth, leaving a more H<sub>2</sub>O-rich magma upon ascent. The decoupled  $CO_2$ -rich gas could theoretically ascend quickly and contribute to the  $CO_2$ -rich explosions in the Erebus lava lake, while the now relatively H<sub>2</sub>O-rich basanite magma could evolve, via closed-system degassing, into H<sub>2</sub>O-rich phonolite.

The second case (b) is the hypothesis proposed by Oppenheimer et al. (2011a), which suggests that  $CO_2$  fluxing induces polybaric differentiation of melts and also accounts for the gas signatures in the lava lake. This hypothesis does not discount

any contribution to crystallization by cooling, but rather the authors suggest that if  $CO_2$  fluxing were occurring, crystal formation would be accelerated due to the depression of the liquidus temperature. Assuming that the melt inclusions are representative of the equilibrium composition at saturation and that a fluid phase was present upon inclusion formation, my data show that the composition of a fluid rising from a depth below that recorded by melt inclusions (i.e., >600 MPa, or about 18 km) will have a composition of  $X_{H_2O}^{fluid} = 0.075$  between approximately 12–18 km depth (Figure 3.7). This supports the hypothesis that fluxing by a "nearly pure  $CO_2$  fluid" would contribute to explosive gas emissions detected from the Erebus lava lake. This deeply sourced  $CO_2$ -rich gas alone is not sufficient to account for explosive eruptions in the Erebus lava lake, however, as surface gas measurements are significantly more H<sub>2</sub>O-rich ( $X_{H_2O}^{fluid} = 0.36$ ; Oppenheimer et al., 2011a). This suggests that, barring the addition of  $H_2O$ -rich fluid, the explosive eruptions at Erebus must be a mixture of  $CO_2$ -rich gas with  $H_2O$ -rich lava lake phonolite gas. Using a lava lake phonolite with  $X_{H_2O}^{fluid} = 0.59$  (Oppenheimer et al., 2011a), a CO<sub>2</sub>-rich gas with  $X_{H_2O}^{fluid} = 0.075$ , and explosive eruptions with  $X_{H_2O}^{fluid} =$ 0.36, I calculate that the explosively released gas could be constituted of a simple mixture of 53 mol% phonolite gas and 47 mol% CO<sub>2</sub>-rich gas, very similar to the 50:50 mixture proposed by Oppenheimer et al. (2011a).

It should be noted that I rely here on solubility data from experiments with phonotephrite melt to interpret melt inclusions hosted in Erebus basanites. It is unknown precisely how the saturation surfaces change with composition, and so this extrapolation of my data may add significant error to the numbers I calculate here. Still, my data are the closest in composition to Erebus basanites at relevant pressures and temperatures and are therefore best suited to this kind of evaluation.

## 3.7 Conclusions

There is significant disagreement between current volatile solubility models on the saturation pressures and dissolution behavior of  $H_2O$  and  $CO_2$  in mafic alkalic magmas. This has hindered the interpretation of volatile-rich melt inclusions and volcanic gas emissions from Erebus volcano. My experimental study has for the

first time facilitated the analysis of volatile concentrations in Erebus melts in a context appropriate to their bulk compositions and P/T conditions.

Further, I compared my experimental results to four thermodynamic volatile solubility models. My high-pressure (400–700 MPa) experimental data best match the curve forms of isobars predicted by the model of Papale et al. (2006). The models of VolatileCalc (Newman & Lowenstern, 2002), SOLEX (Witham et al., 2012), and (Lesne et al., 2011b,c) have been shown by previous studies to work well for lower-pressure (<400 MPa) data sets. This suggests a departure from Henrian behavior of volatiles in my data above pressures of about 400 MPa, as the model of Papale et al. (2006) is the only model that makes no *a priori* assumption of ideal mixing of dissolved H<sub>2</sub>O and CO<sub>2</sub>. Still, the Papale et al. (2006) model overestimates saturation pressures for Erebus lavas, reflecting the very small number of experimental solubility studies on basanite and phonotephite melts.

As currently available volatile solubility models do not give reliable estimates for the saturation pressures of  $H_2O-CO_2$  fluids in mafic alkaline melts, experimental results from this study have made possible a more precise quantitative analysis of primitive Erebus melt inclusion volatile contents. Results from this work provide a starting point for the interpretation of Erebus melt inclusions and highlight the need for further experimental studies to model the alkalic magma plumbing beneath Erebus and its contributions to degassing and eruptive behavior in the Erebus lava lake over a wider range of alkaline magma compositions, pressures, and temperatures.

Previous studies have used Erebus melt inclusion data to explain why periodic explosive eruptions in the Erebus lava lake are significantly more  $CO_2$ -rich than passive gas emissions. I use my results to refine their hypotheses and propose three possible mechanisms to explain bimodal eruptive behavior in the Erebus lava lake in which  $CO_2$ -rich explosive gas emissions result from:

1. the degassing of  $CO_2$ -rich phonolite beneath the lava lake, which is derived from a parental  $CO_2$ -rich basanite magma (after Oppenheimer & Kyle,

2008a).

- 2. the ascent of CO<sub>2</sub>-rich gas that had decoupled from a deep basanite magma after melt inclusion entrapment.
- 3. a 53:47 mixture (on a molar basis) of lava lake phonolite and a nearly pure-CO<sub>2</sub> fluid (99.25 mol% CO<sub>2</sub>; 0.75 mol% H<sub>2</sub>O) derived from some source deeper than that recorded by melt inclusions (after the CO<sub>2</sub> fluxing hypothesis of Oppenheimer et al., 2011a).

These hypotheses each require that nearly pure  $CO_2$  gas at some point decouples from its host melt and leaves the system (shallow degassing of  $CO_2$  from phonolite or deep degassing of  $CO_2$  from basanite or a deeper source) to explain surface gas measurements from the Erebus lava lake. Investigation into the permeability of Erebus magmas could indicate whether or not the decoupled flow of gas through the system is plausible. Isotopic measurements of the Erebus gases could help identify their source regions and indicate whether H and C species are derived from radically different depths within the system.

## Chapter 4

# Phase Equilibrium Constraints on the Deep and Intermediate Magma Plumbing Beneath Ross Island

Material in this chapter is in review for publication in Journal of Petrology, submitted September 2013 as:

Erebus volcano as an archetype for CO<sub>2</sub>-dominated rift volcanism: Experimental constraints on the magma plumbing of Ross Island, Antarctica Kayla Iacovino, Clive Oppenheimer, Bruno Scaillet, Philip Kyle

#### 4.1 Abstract

I present the results of phase equilibrium experiments carried out on a basanite (Dry Valley Drilling Project "DVDP" Lineage) and phonotephrite (Erebus Lineage) from Ross Island, Antarctica. These two compositions represent the most primitive end-members of the silica-undersaturated alkaline lava suites found in outcrop on Ross Island. Experiments were performed in internally heated pressure vessels (IHPVs) over a range of temperatures (1000-1150 °C) and pressures (200-400 MPa), with XH<sub>2</sub>O of the H<sub>2</sub>O-CO<sub>2</sub> fluid varying between 0 and 1. Fe-Ti spinel is on the liquidus for both compositions, the growth of which is likely facilitated by the oxidizing experimental conditions (NNO+0.7 to NNO+2.9). Under

these relatively oxidizing conditions, the overall mineralogy and phase compositions of natural lavas was reproduced, suggesting similarly oxidizing conditions for the deep plumbing system beneath Erebus, in stark contrast to the reducing conditions (QFM to QFM-1) in the Erebus lava lake. In basanite, crystallization of spinel is followed by olivine and clinopyroxene. In phonotephrite, the first silicate phase is kaersutite (even for  $H_2O$ -poor conditions). Only in the most  $CO_2$ -rich experiments  $(XH_2O \text{ approaching } 0)$  could the natural phase assemblages be approximated. I suggest that both Erebus Lineage (EL) and DVDP Lineage lavas are derived from a common basanitic parent located beneath Erebus. All mineralogical differences in the DVDP lavas relative to the EL result from a drop in equilibration temperature to below 1000 °C, whereas EL lavas must be above 1075 °C. I propose a single plumbing system beneath Ross Island in which DVDP lavas (and likely other peripheral volcanic products) were erupted through radial fractures associated with the upwelling of parental magma into the lower crust. The longer travel time of DVDP lavas through the crust due to lateral movement along fractures and the lack of a direct, sustained connection to the continuous heat flux that characterizes the main Erebus conduit is likely responsible for the lower temperatures and hence the change in mineralogy observed. In addition, my results indicate that the maximum  $H_2O$  content of both EL and DVDP magmas is ~1-2 wt%. This observation, combined with evidence from recent volatile solubility, melt inclusion, and in-situ gas measurement studies, substantiates the case that magmatic and volcanic activity at Erebus volcano and the surrounding volcanic centers are strongly influenced by the storage and exsolution of mantle-sourced carbon.

#### 4.2 Experimental Overview

In this study, I use experimentally determined phase equilibria to constrain the deep and intermediate regions of the Ross Island plumbing system with regard to pressure, temperature, oxygen fugacity, and principal volatiles ( $H_2O$  and  $CO_2$ ). Phase equilibria experiments are a tool commonly used to constrain the preeruptive storage conditions of magmas (Andújar et al., 2010; Di Carlo et al., 2010; Freise et al., 2003; Martí et al., 2008; Moore & Carmichael, 1998; Sack et al., 1987). While non-equilibrium processes such as magma mixing and repeated replenishment of the system are important to consider, high pressure-temperature experimentation nevertheless illuminates the fundamental processes that control magma evolution from mantle to surface. Further, experiments with  $H_2O-CO_2$ fluid compositions ranging from  $XH_2O = 0$ -1 help elucidate not only the role of  $H_2O$  in controlling phase equilibria, but also constrain the effect of  $CO_2$  on crystallization processes via melt dehydration. Given that carbon dioxide is known to play an important role in the genesis of alkaline magmas both in the mantle (Spera, 1984) and crust (Kaszuba & Wendlandt, 2000), it is important to understand its role at Erebus throughout the magmatic system (from mantle to surface). Experiments at 200, 300, and 400 MPa can constrain the role of  $CO_2$  in the intermediate and deep system at Erebus, where much crystallization likely occurs.

I have conducted a set of experiments using as starting material two mafic alkaline lavas (basanite and phonotephrite) that represent primitive members of the two most abundant lava lineages on Ross Island in order to investigate the deep and intermediate regions of the Erebus-Ross Island plumbing system. One sample was chosen from each lineage as starting material. Resulting experimental samples span the entire fractional crystallization sequence seen in natural lavas (from basanite to phonolite), therefore elucidating the compositional evolution of the Erebus and Ross Island lavas with respect to temperature, pressure, volatile content, and oxygen fugacity. Furthermore, I place tight constraints on the generation of two distinct lava lineages from a single basanitic parent source magma.

#### 4.3 Experimental Techniques

#### 4.3.1 Preparation of Experimental Capsules

Phase equilibria experiments were run at isothermal and isobaric conditions between 1000–1150 °C and 200–400 MPa at an oxygen fugacity of about one log unit above the Ni-NiO buffer (NNO+1). Basanite KI-04 and phonotephrite AW-82038 were chosen as starting materials in order to investigate magma evolution in the deep and intermediate portions of the Erebus plumbing system. Details of these starting materials and natural rock samples are given in Tables 4.1 & 4.2. 30-60mg of glassy starting material powder was added to Au<sub>80</sub>Pd<sub>20</sub> capsules with lengths of  $\sim 20$  mm, an outer diameter of 2.9 mm, and inner diameter of 2.5 mm. Liquid  $H_2O$  was added via microsyringe (~0-6 mg), and  $CO_2$  was added as silver oxalate powder (Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>,  $\sim$ 0-18 mg). The XH<sub>2</sub>O in the H<sub>2</sub>O/CO<sub>2</sub> mixture of pre-run charges was varied at steps between 0-1 (i.e.  $XH_2O = 0$ , 0.25, 0.5, 0.75, and 1), and fluid proportion in the charge was always  $\sim 10\%$  to ensure fluid saturation. Once filled, capsules were weighed, crimped at their open end, arc welded shut with a graphite electrode, and then subsequently re-weighed to check for any mass loss or gain during welding. After welding, capsules were placed in an oven at 110  $^{\circ}\mathrm{C}$  for several minutes and then re-weighed to check for any leaks in the capsule. Any capsules that showed a change in mass >0.2 mg either after welding or after heating were considered to have leaked at least part of their fluid phase and were discarded. As a tertiary method to check for leaks, some capsules were held with tongs in a beaker of oil at 300 °C for a few seconds. If bubbles were observed escaping from the capsule, it was considered to have leaks and was thus discarded.

Experiments were run in vertically working internally heated pressure vessels (IHPVs; see Holloway (1971)) equipped with double wound Kanthal furnaces at the Institut des Sciences de la Terre d'Orléans (ISTO) at isothermal and isobaric conditions. Each run contained 5-10 sample capsules separated from one another by silica wool and placed into a ceramic sample holder suspended near the top of the vessel by a thin platinum wire (quench wire). An  $Ar-H_2$  gas mixture loaded sequentially at room temperature was used as the pressure medium. The  $Ar/H_2$  ratio was chosen for each run so as to achieve an  $fO_2$  of NNO+1 although the  $fO_2$  within each experimental charge varied slightly depending on its specific  $H_2O/CO_2$  fluid mixture (see section 4.4.6). Pressure was measured with a transducer calibrated against a Heise-Bourdon tube gauge to an accuracy of  $\pm 20$  bars. Temperature was measured with two chromel-alumel (type K) thermocouples located roughly on either side of the sample capsules, which allows for precise control over the size of the hotspot ( $\sim 4$  cm) to within  $\pm 5$  °C. After the chosen experimental duration had elapsed, capsules were drop quenched into the lower, cold part of the pressure vessel ( $\sim 10$  °C) and cooled at a rate of about 1000 °C/min (Roux & Lefevre,

1992).

## 4.4 Analytical Techniques

After completion of the experimental run, capsules were weighed to check that no fluid loss occurred during the run. The conventional weight-loss method was employed as a first order measure of the composition of the equilibrium  $H_2O/CO_2$ fluid phase (see Behrens et al., 2009). It should be noted that this method is an indirect measure of the composition of the fluid phase in my runs and is prone to significant analytical error. After initial weighing, the capsule was submerged in a liquid nitrogen bath and then punctured. Typically, a hissing noise and bubbles at the puncture site were observed. After warming for up to 1 min, the capsule was weighed to determine the mass of  $CO_2$  in the fluid phase. The capsule was then placed in a drying oven at 110 °C for several minutes and weighed to determine the mass of the H<sub>2</sub>O fluid. Capsule weight was checked periodically until mass remained constant. The AuPd capsule was then peeled away, and the sample was mounted in resin and polished for analysis with scanning electron microscope (SEM) and electron microprobe (EMP). Selected samples were then doubly polished for analysis via Fourier Transform Infrared (FTIR) spectroscopy.

#### 4.4.1 SEM and Electron Microprobe

Charges were initially observed under a JEOL WINSET JSM 6400 Scanning Electron Microscope (SEM) at ISTO for preliminary phase identification, modal abundance, and textural analysis. Most phases could be easily identified by visual inspection, and several crystals from each phase were measured using the energydispersive spectrometer (EDS) with which the SEM is equipped. EDS analyses are not reported here, as they were only used for mineral identification.

Electron microprobe (EMP) analyses of major-element compositions of the glass and crystal phases in natural samples, starting glasses, and experimental run products were made primarily using a Cameca SX-100 microprobe at the

	$\begin{array}{l} \text{Whole} \\ \text{Rock}^1 \end{array}$	$St.$ $Gls^2$	Ol-6	Ol-10	Plag- 5	Plag- 12	Ap-1	Sp-1	gnd Ol-5	gnd Plag- 5
$\mathrm{SiO}_2$	48.01	48.03	38.72	38.47	54.1	53.69	0.26	nd	36.27	55.46
$TiO_2$	2.77	2.84	0.02	0.03	0.14	0.15	nd	26.18	0.06	0.16
$Al_2O_3$	18.56	18.12	0.05	0.05	28.54	29.24	nd	4.34	0.04	28.56
$FeO^*$	9.49	9.59	20.47	22.54	0.35	0.31	0.33	63.15	29.08	0.39
MnO	0.22	0.23	0.28	0.45	0	0.04	0.1	0.8	0.64	0.03
MgO	3.18	3.08	41.79	39.84	0.03	0.03	0.26	5.29	35.09	0.05
CaO	7.65	7.57	0.3	0.3	11.11	11.53	55.11	0.04	0.44	10.62
$Na_2O$	5.99	6.04	0	0.03	4.9	4.66	0.07	0.04	0.02	5.2
$K_2O$	2.88	3.07	0	0.01	0.62	0.5	nd	nd	nd	0.7
$P_2O_5$	1.24	1.41	0	0.01	0.02	0	42.02	nd	0.04	0.01
Total	98.29	99.54	101.72	101.8	99.82	100.21	98.16	100.04	101.74	101.19
Mo#	37	36	78	76					68	
Or	01	50	10	10	23	18			00	2.6
An					<u>69</u> 8	71.9				67.5
Ab					27.9	26.3				29.9
110			Number	of Cati	ons in S	 Structura	l Formu	ala		20.0
Si			0.978	1.045	2.451	2.482	0.044		0.954	2.475
Ti				0.002	0.005	0.005		0.685	0.001	0.005
Al			0.001	0.047	1.524	1.499		0.178	0.001	1.502
Fe3+			0.042					0.451	0.088	
Fe2+			0.391	0.633	0.013	0.01	0.046	1.387	0.552	0.015
Mn			0.006	0.014		0.001	0.014	0.024	0.014	0.001
Mg			1.574	1.246	0.002	0.004		0.275	1.377	0.003
Ca			0.008	0.013	0.539	0.502	9.912		0.012	0.508
Na					0.43	0.458				0.45
Κ					0.036	0.039				0.04
Р							5.972			

Table 4.1: Composition of AW-82038 starting glass, bulk rock, and representative analyses of phenocrysts and microphenocrysts in the natural rock

Notes: Glass analyses are given in wt% and normalized to 100% with original analysis totals given. Mineral analyses are not normalized, original analysis totals given. St. Gls – starting glass after vitrification; Ol – olivine; Plag – plagioclase; Ap – apatite; Sp – spinel; gnd Ol – groundmass olivine; gnd Plag – groundmass plagioclase; nd – not detected.

\*Total iron given as FeO; Mg  $\# = 100[Mg/(Mg+Fe^*)]$ 

<sup>1</sup>Whole rock composition. AW-82038 analyzed by Kyle et al. (1992) and KI-04 by this study, using X-ray Fluorescence (XRF).

<sup>2</sup>Electron microprobe (EMP) analyses of glass composition after vitrification in 1-atm furnace, but before run in pressure vessel. AW-82038 vitrified at an oxygen fugacity of NNO+1, Analysis from Iacovino et al. (2013a); KI-04 vitrified in air.

		~		01.0	• •			
	Whole	St.	Ol-1	OI-2	Aug-1	Aug-2	Plag-1	Plag-2
	rock <sup>1</sup>	$Gls^2$						
$SiO_2$	43.06	43.15	38.04	37.62	47.09	42.35	49.91	50.1
$\mathrm{TiO}_2$	4.26	4.43	0.04	0.05	2.57	4.99	0.23	0.18
$Al_2O_3$	13.8	13.94	0.04	0.04	4.92	9.16	29.95	30.91
FeO	9.73	$12.35^{*}$	17.61	19.83	7.98*	$6.99^{*}$	0.66	0.53
$Fe_2O_3$	2.87							
MnO	0.19	0.17	0.22	0.31	0.25	0.1	0	0
MgO	8.92	8.46	43.56	40.66	13.34	12.1	0.1	0.09
CaO	11.07	11.16	0.29	0.39	22.49	22.7	14.11	14.62
$Na_2O$	3.64	3.81	nd	nd	0.46	0.45	3.41	3.31
$K_2O$	1.63	1.68	nd	nd	nd	nd	0.35	0.29
$P_2O_5$	0.83	0.85	nd	nd			nd	nd
Total	98.61	97.68	100	98.99	99.1	99.06	98.72	100.04
Mg#	55	55	82	79	75	76		
Or							1.2	1
An							81.1	82.2
Ab							17.7	16.8
		Numb	ber of Cat	tions in S	tructural	Formula		
Si			0.960	0.965	1.767	1.597	2.276	2.307
Ti			0.001	0.001	0.073	0.142	0.006	0.008
Al			0.001	0.001	0.218	0.407	1.680	1.623
$\mathrm{Fe}^{3+}$			0.077	0.068	0.136	0.148		
$\mathrm{Fe}^{2+}$			0.290	0.306	0.114	0.072	0.020	0.024
Mn			0.005	0.005	0.008	0.003		
Mg			1.660	1.647	0.746	0.680	0.006	0.005
Ca			0.006	0.008	0.904	0.917	0.713	0.692
Na					0.033	0.033	0.283	0.326
Κ							0.017	0.015
Notatio	on the sar	ne as in T	Table 4.1					

 Table 4.2: Composition of KI-04 starting glass, bulk rock, and representative analyses of phenocrysts and microphenocrysts in the natural rock

University of Cambridge. Some samples were analyzed on a Cameca SX-100 at the University of Arizona or on a Cameca SX-50 at the Università degli Studi di Padova. Glass was measured using an accelerating voltage of 15 keV, a beam current of 3 nA, a defocused beam size of 10  $\mu$ m, and a counting time of 10 s, analyzing Na first to minimize measurement error due to Na migration. Crystal phases were analyzed with an accelerating voltage of 15 keV, a beam current of 10 nA, and a focused beam size of 1  $\mu$ m. In each experimental charge, typically 20–30 analyses were performed on glass and 8–12 analyses were performed on each crystal phase. All electron microprobe data are available online (Iacovino, 2014a).

#### 4.4.2 Visual analysis of samples and measure of crystallinity

Each experimental run product was observed under SEM for preliminary phase identification, modal abundance, and textural analysis. Several images depicting areas of particular interest for later analysis (large melt pools, rare phases) and areas representative of the sample as a whole were collected for each sample.

Representative images from each sample were imported into Adobe Photoshop CS5 and digitally manipulated to measure total crystallinity and the modal abundance of all phases. Images were first converted to gray scale, and a surface blur filter was applied to reduce graininess. A threshold was then applied to the image and adjusted in order to isolate one particular phase. The threshold converts the image to binary black and white (with color values of only 0 or 255), where everything below the user-defined threshold limit is set to a 0 color value, and everything above the threshold is set to a 255 color value (see Figure 4.1). Using the histogram window, one of these color values can be selected, and the total area of this color value as a percent of the total image is displayed. Any areas of the image that contained no sample (holes, cracks, etc.) were not included in the total sample area.



Figure 4.1: Normal SEM image selected for analysis (left), the same image thresholded to isolate crystals and melt (middle), and the image thresholded to isolate only oxide crystals (right).

#### 4.4.3 Mapping FTIR Spectroscopy

The H<sub>2</sub>O and CO<sub>2</sub> concentrations in the glass phase of each experimental run were measured using a Thermo Scientific Nicolet iN10 MX mapping FTIR at the USGS in Menlo Park, California. Transmission infrared spectra of doubly polished glass chips ranging in thickness from ~20-150  $\mu$ m were obtained in the 6000-1000 cm<sup>-1</sup> wavenumber range using a KBr beamsplitter with a variable aperture size between 25-500  $\mu$ m<sup>2</sup>. The sample stage was continuously purged with dry air and a background measurement was made before the collection of each spectrum to minimize and correct for the contribution of atmospheric H<sub>2</sub>O and CO<sub>2</sub>.

Using the OMNIC Picta software, I was able to create maps of the peak height of any selected band across a user-defined region of the sample. Figure 4.2 is an example of one such map, where the peak height of the total water 3500 cm-1 peak is color-coded. The most extreme variations in the 3500 cm<sup>-1</sup> peak height in this map (e.g. on sample edges and near a large hole in the sample) are due to changes in sample thickness and therefore changes in path length of the IR beam through the sample. As some of my samples are highly crystalline, the sample maps were useful for determining the most crystal-free regions of the sample through which to measure a spectrum. In addition, the maps illustrate the homogeneity of my samples with respect to dissolved volatile contents. Crystal- and vesicle-free re-



Figure 4.2: Graduated color map of the peak height of the 3500 cm<sup>-1</sup> (total H<sub>2</sub>O) infrared band in sample KI-10 based on 36 separate FTIR analyses overlain on an optical image of the sample. Variations in peak height are a result of variations in sample thickness (e.g. at the edge of the glass chip) and the presence of holes or crystalline phases within the IR beam. Use of FTIR maps illustrates the homogeneity of dissolved volatiles in crystalline samples and elucidates the locations best suited for analysis.

gions where the best FTIR measurements could be obtained were determined using coarse maps (e.g., Figure 4.2) made over large portions of the sample with a very large beam diameter of typically 100-500  $\mu$ m. Detailed maps were then created for select small regions using a focused-beam diameter of typically 25  $\mu$ m, where crystalline areas could be easily identified. Spectra from crystal-free regions of detailed maps were then used to determine volatile concentrations. The concentrations of OH, H<sub>2</sub>O, CO<sub>2</sub>, and CO<sub>3</sub> species were calculated using the Beer-Lambert Law (Ihinger et al., 1994) as outlined in Chapter 3.

Sample thicknesses were measured to an accuracy of  $\pm 2 \ \mu m$  using a digital tabletop micrometer equipped with a fine tip that allowed for measurement at multiple spots on the sample surface. Additional sample thicknesses for some samples were also measured using an ADE Phaseshift Microxam surface-mapping microscope (with white light interferometer) to an accuracy of  $\pm 0.5$ -2  $\mu m$ . In very thin samples, the presence of interference fringes in reflectance IR spectra allowed for the measurement of the sample thickness in the precise spot as was analyzed with transmitted light. Following the method of (Nichols & Wysoczanski, 2007), I use the following to measure sample thickness using interference fringes:

$$t = \frac{m}{2n(v_1 - v_2)} \tag{4.1}$$

where t is the sample thickness at the measurement spot (cm), m is the number of waves that occur in the selected wavenumber interval (between  $v_1$  and  $v_2$ ), and n is the refractive index of the glass. For these calculations, I assume a refractive index of 1.51 for phonotephrite experiments (Church & Johnson, 1980) and 1.569 for basanite experiments (value for tholeiite glass at low P; Kuryaeva & Kirkinskii, 1997). Only these two values were used, as the refractive index is not expected to change much as melt compositions evolve.

Glass densities were calculated for each sample using the model of Lange & Carmichael (1987), assuming an H<sub>2</sub>O molar volume of 22.9 cm<sup>3</sup>mol<sup>-1</sup> (Ochs & Lange, 1999). Molar absorption coefficients strongly depend on glass composition (Pandya et al., 1992). Because of variation in the crystallinity of my samples,

and therefore significant variation in glass chemistry, an attempt was made to use absorption coefficients appropriate for each individual sample. All absorption coefficients used in this study are listed in Table 4.3. Where possible, the model of Dixon & Pan (1995) was used to calculate  $\epsilon$ 1525 and  $\epsilon$ 1430 (carbonate absorption) for individual samples. This calculation can only be applied to glasses with a Na/(Na+Ca) ratio between 0.25-0.5 (in my case, most glasses classified as phonotephrite and tephriphonolite fall in this range). For glasses with Na/(Na+Ca) less than 0.25 or greater than 0.5,  $\epsilon$ 1525 and  $\epsilon$ 1430 values were selected from the literature (see Table 4.3).

Composition	Wavenumb $(cm^{-1})$	eßpecies	Coefficient	Citation
Phonolite	2345 3500	$\begin{array}{c} \mathrm{CO}_2 \\ \mathrm{H}_2\mathrm{Otot} \end{array}$	$\begin{array}{c} 890\\ 64\pm8\end{array}$	Morizet et al. (2002) Cioni (2000)
Tephriphonolite	$1410 \\ 1530 \\ 3500 \\ 4500 \\ 5200$	$\begin{array}{c} \mathrm{CO}_{3} \\ \mathrm{CO}_{3} \\ \mathrm{H}_{2}\mathrm{Otot} \\ \mathrm{OH} \\ \mathrm{H}_{2}\mathrm{O}_{m} \end{array}$	Calculated Calculated $64 \pm 8$ $0.62 \pm 0.02$ $1.02 \pm 0.06$	Dixon & Pan (1995) Dixon & Pan (1995) Cioni (2000) Behrens et al. (2009) Behrens et al. (2009)
Phonotephrite	$     \begin{array}{r}       1410 \\       1530 \\       3500 \\       4500 \\       5200 \\     \end{array} $	$\begin{array}{c} \mathrm{CO}_{3} \\ \mathrm{CO}_{3} \\ \mathrm{H}_{2}\mathrm{Otot} \\ \mathrm{OH} \\ \mathrm{H}_{2}\mathrm{O}_{m} \end{array}$	Calculated Calculated $63.9 \pm 5.4$ $0.62 \pm 0.02$ $1.02 \pm 0.06$	Dixon & Pan (1995) Dixon & Pan (1995) Behrens et al. (2009) Behrens et al. (2009) Behrens et al. (2009)
Basanite	$     \begin{array}{r}       1410 \\       1530 \\       3500 \\       4500 \\       5200 \\     \end{array} $	$\begin{array}{c} \mathrm{CO}_{3} \\ \mathrm{CO}_{3} \\ \mathrm{H}_{2}\mathrm{Otot} \\ \mathrm{OH} \\ \mathrm{H}_{2}\mathrm{Om} \end{array}$	$\begin{array}{c} 375 \pm 20 \\ 375 \pm 20 \\ 63.9 \pm 5.4 \\ 0.58 \pm 0.02 \\ 0.56 \pm 0.04 \end{array}$	Fine & Stolper (1986) Fine & Stolper (1986) Behrens et al. (2009) Cocheo (1993) Cocheo (1993)

Table 4.3: Absorption Coefficients used to determine concentrations of dissolved volatiles in experimental charges via FTIR.

Spectral backgrounds were measured by fitting computer-generated polynomial curves to selected sections of the FTIR spectra. Typically, 5200 and 4500 cm<sup>-1</sup> OH peaks were measured relative to a second order polynomial background, the 3500

cm<sup>-1</sup> total water peak was assumed to have a straight-line background, and the 1640 water peak and the 1525 and 1430 cm<sup>-1</sup> carbonate doublet were measured relative to a 4th or 5th order polynomial background. The near IR and total water peaks consistently had very good fits with the generated background curves, with the 1640, 1525, and 1430 cm<sup>-1</sup> peaks requiring more trial and error before a good background curve fit could be found (i.e. the points included or excluded from the curve fit and the function order were adjusted until the background curve was deemed good). A background curve fit in this region was deemed best when the heights of the 1525 and 1430 cm<sup>-1</sup> peaks were closest in value, as these two peaks form the carbonate doublet and should be roughly equivalent. Some backgrounds were additionally hand drawn using a French curve, which gave similar results to the computer-generated background fits. The code used to generate curve fits (Iacovino, 2014b) was a very early version of an FTIR retrieval program (Iacovino et al., 2013b) written as a plug-in to the extensible plotting tool AvoPlot (Peters, 2014) and can be downloaded at http://dx.doi.org/10.6084/m9.figshare.928142.

## 4.4.4 Calculation of Dissolved Volatiles in Highly Crystalline Samples

Some highly crystalline samples contained glass pools too small to be analyzed by FTIR but could be analyzed via electron microprobe, and so their dissolved  $H_2O$  contents were calculated in two ways: using the "by difference" method of Devine et al. (1995) and by mass balance. In the "by difference" method, the total amount of dissolved volatiles in a sample is taken as 100% minus the major element analytical total from microprobe analysis. Mass balance calculations were performed as follows:

$$H_2 O^{melt}(wt\%) = \frac{mH_2 O^{initial} - mH_2 O^{fluid}}{mH_2 O^{initial} - mH_2 O^{fluid} + mGlass}$$
(4.2)

where  $mH_2O^{initial}$  is the mass of water added to the experimental capsule,  $mH_2O^{fluid}$  is an estimate of the mass of H<sub>2</sub>O in the fluid post-run (see Section 4.4), and mGlass is the mass of starting material powder, corrected for the crystal content of the sample. Notably, some H<sub>2</sub>O was present in all runs, even those where no liquid water was added to the experimental capsule. Despite the storage of rock powders in a drying oven, H<sub>2</sub>O can be introduced to the experimental capsule via remnant water within the starting powder and through H<sub>2</sub>O generation during the run via reduction of Fe<sub>2</sub>O<sub>3</sub>. To account for this excess water, I have added a correction factor of +0.4 mg to the value of  $mH_2O^{initial}$  for KI-04 runs, which are expected to be the most strongly affected by the addition of water through iron reduction as this starting material was vitrified in air. AW-82038 starting material was vitrified at an  $fO_2$  near that of the experiments, and so no correction was applied.

In order that these calculations can be calibrated, they both require the use of standards, which have a known  $H_2O$  concentration as determined by FTIR. Calculated and measured values can then be compared, and a straight line fit through the data provides a calibration that can be applied to calculated  $H_2O$  contents of samples for which no FTIR data are available. Comparisons of dissolved  $H_2O$ content as calculated via "by difference" and mass balance with those measured by FTIR are shown in Figure 4.3. For my samples, the "by difference" method proved a very poor estimate of dissolved  $H_2O$ , with linear fit  $R^2$  values of 0.25 and 0.02 for phonotephrite and basanite experiments, respectively. The significant scatter of my data can be attributed to several factors. First, my experiments are characterized by varying ratios of H<sub>2</sub>O and CO<sub>2</sub>. A comparison of total volatiles calculated by difference and total volatiles calculated by FTIR spectroscopy resulted in a similarly scattered relationship, however the varying  $H_2O$  contents of my glasses may contribute non-linearly to varying degrees of Na-migration during microprobe analysis, a common problem for hydrous alkaline glasses. Secondly, microprobe analyses on my samples were performed at three separate laboratories over many analysis sessions. Variations in standardization and beam settings between sessions may also contribute to scatter in these data. I suggest that the "by difference" method may work better for samples with similar XH<sub>2</sub>O that are measured during the same microprobe session and when Na-migration is not significant (or can be corrected).



Figure 4.3: Calculated dissolved volatile contents of experimental charges via: a) the "by difference" method; and b) mass balance, both compared with measured values via FTIR. The solid blue line is a linear best fit to AW-82038 phonotephrite samples (blue squares), the dashed red line is a linear best fit to KI-04 basanite samples (red diamonds), and the gray line is a 1:1.

Conversely, there is a much more well-defined linear relationship between H<sub>2</sub>O concentrations as calculated by mass balance and those measured by FTIR spectroscopy. For this reason, I have used these mass balance calibration lines to calculate H<sub>2</sub>O contents in all samples for which FTIR spectra could not be obtained (see Table 4.4). The same method was applied to CO<sub>2</sub> contents, which can be calculated by mass balance but not by difference. A good linear fit for measured and calculated CO<sub>2</sub> concentrations was found for KI-04 samples (R<sup>2</sup>=0.68), and so I report these calculated CO<sub>2</sub> values in Tables 4.5 & 4.6. Due to the high amount of scatter and resulting poor fit for CO<sub>2</sub> in AW-82038 samples (R<sup>2</sup>=0.23), I do not use calculated values for these experiments.

#### 4.4.5 Establishment of Equilibrium

The very low viscosities of my mafic alkalic glasses facilitated the attainment of equilibrium even given relatively short run times of 17-24 h. In similar studies on

Experiment	$\mathrm{H}_{2}\mathrm{O}^{i,a}$	$Ag_2C_2O_4^{i,b}$	$mCO_2^{fluid}$	$\mathrm{mH}_{2}\mathrm{O}^{fluid}$	$XH_2O^{fluid}$	$\mathrm{mSM}^c$
AW 82038 n	honotenh	rite ernerim	ents			
AW-13	2	2 2	0.8	07	0.68	29.8
AW-14	15	2.2 4 9	2	0.1	0.00	30.5
AW-06	0	2.7	2 0.6	0.2	0	30.5
AW-10	3	0	0.0	14	1	33.8
AW-17	15	57	1.6	0.5	0.43	36.7
AW-18	2.1	3.2	1.0	11	0.71	30.7
AW-19B	0	0.2 21.5	6.1	0.4	0.14	60 1
AW-20B	14	17.0	4	0.1	0.35	60.1
AW-21	1.4	6.3	17	0.9	0.56	30.2
AW-22	1. <del>1</del> 9.9	3.1	0.7	0.5	0.50 0.74	30.2 30.7
AW-22	2.2 3.1	0	0	14	1	20.8
AW-25	0.6	86	0 2 2	0.3	0.25	30.9
AW-26	1.4	5.6	1.6	0.5	0.20	30.2
AW-27	1. <del>1</del> 9.1	3	1.0	0.9	0.40 0.67	30.1
AW-28	3	0	0.4	0.5	1	30.3
AW-29	0	21.5	0.4	3.5	1	62.5
AW-33	° 26	10	02	0.2	0.71	60.6
AW-34	2.0 5.9	0	0.8	0. <u>2</u> 1.6	0.83	0
AW-24B	0.5	17.2	4.6	0.3	0.13	52.8
AW-37	0	17.9	0	1.9	0.10	50.3
AW-38	51	0	0.9	2.3	1	51.1
AW-39	3.5	5 5	1.8	2.0 1.3	0.86	50.7
AW-40	2.0	9.0 9.1	2.7	1.9	0.64	50.1 50.6
AW-41	1	13.7	2.1 4 3	0.5	0.52	50.0 50.4
AW-42	0	17.3	4.6	0.0	0.02	50.4 51.4
AW_43	0	17.7	1.0 2.8	1.9	0.18	50.0
AW_44	1	13.7	2.0 1.5	1.2	0.51	50.9 50 1
AW-45	2.2	10.1	1.2	1.4	0.71	50.8

Table 4.4: Measurements of pre- and post-run volatile contents

Experiment	$\mathrm{H}_2\mathrm{O}^{i,a}$	$Ag_2C_2O_4^{i,b}$	$mCO_2^{fluid}$	$\mathrm{mH}_{2}\mathrm{O}^{fluid}$	$XH_2O^{fluid}$	$\mathrm{mSM}^c$
AW-46	3.6	5.5	0.1	1.2	0.74	51.5
AW-47	5.1	0	0	0.2	1	50.7
KI-04 basani	ite experi	ments				
KI-01	0	2.3	0	0.2	0	nd
KI-05	3	0	nd	nd	nd	nd
KI-06	2	2.6	6.9	5.8	0.67	31.5
KI-07	1.3	4.8	nd	nd	nd	31.1
KI-08	0.6	7.1	nd	nd	nd	30.3
KI-09	0	19.9	4.9	0.4	0.17	62.8
KI-10	1.1	4.7	1.2	0.6	0.55	60
KI-11	2.6	11.2	3.1	1.9	0.6	62
KI-12	4.2	6.5	1.8	2.6	0.78	60.5
KI-14	0	22.2	5.8	0.6	0.2	60.2
KI-15	1	13.4	3.2	1	0.43	49.9
KI-16	2.2	10.2	2.7	1.3	0.54	50.1
KI-17	3.5	5.1	1.5	2.1	0.77	50.1
KI-18	5	0	0	3.5	1	52.7
KI-19	5	0	0.2	2.2	0.96	51.3
KI-20	3.6	5.4	1.7	1.1	0.61	51.4
KI-21	2.2	10	2.6	1	0.48	51.5
KI-22	1	13.5	3.5	0.5	0.26	50.7
KI-23	0	17.2	4.6	0.3	0.14	50.3
KI-25	3.6	5.6	1.2	2.4	0.83	51.5
KI-24	4.9	0	0	2.3	1	50.7
KI-26	2.3	10.2	2.9	0.9	0.43	50.9
KI-27	1	13.7	3.6	0.7	0.32	51.8
KI-28	0	17.7	4.7	0.5	0.21	50.1
KI-29	0	17.9	4.9	0.3	0.13	50.2
KI-30	1	14.1	3.8	0.7	0.31	52.2

Table 4.4: Measurements of pre- and post-run volatile contents

Experiment	$H_2O^{i,a}$	$Ag_2C_2O_4^{i,b}$	$mCO_2^{fluid}$	$\mathrm{mH}_{2}\mathrm{O}^{fluid}$	$XH_2O^{fluid}$	$\mathrm{mSM}^c$
KI-31	2.3	9.6	2.5	1.5	0.59	49.7
KI-32	3.5	5.8	1.5	2.4	0.8	50.8
K1-33	5.1	0	0.1	3.2	0.99	52.3
KI-36	1.1	14.2	2.4	1.1	0.53	52.1
KI-37	2.4	9.7	1.5	2.4	0.8	51.2
KI-38	3.7	6.1	0	3.7	1	50.3

Table 4.4: Measurements of pre- and post-run volatile contents

Notes: All masses shown in mg.  $mCO_2^{fluid}$  calculated as the difference in total post-run capsule mass and capsule mass after subsequent liquid nitrogen bath and puncture.  $mH_2O^{fluid}$  calculated as the difference in capsule mass after liquid nitrogen bath and puncture and capsule mass after drying oven. nd: not determined <sup>a</sup>Mass of liquid water added to experimental capsule.

<sup>b</sup>Mass of silver oxalate powder added to experimental capsule.

<sup>c</sup>Mass of starting material added to experimental capsule.

mafic melts, the attainment of equilibrium was observed in runs of similar duration (Di Carlo et al., 2006; Feig et al., 2010). Crystals were homogeneously distributed throughout the charges and were typically euhedral in shape. In addition, samples were homogeneous with respect to glass composition and the concentrations of dissolved volatiles in the glass throughout each charge. All of these observations indicate that chemical equilibrium was obtained in the experiments.

#### 4.4.6 Oxygen Fugacity

The  $fO_2$  of all IHPV runs was controlled by loading the pressure vessel with enough H<sub>2</sub> so as to achieve an apparatus  $fO_2$  of ~NNO+1 (see Section 4.3). The  $fO_2$  inside each experimental capsule will vary depending on the H<sub>2</sub>O/CO<sub>2</sub> ratio of the fluid phase contained therein. Assuming that the  $fH_2$  of the pressure vessel will be the same as the  $fH_2$  inside an experimental capsule owing to the very fast diffusion rates of hydrogen, I can calculate the  $fO_2$  inside each capsule following the method described in Section 3.5.1. First, since the partial pressure of H<sub>2</sub> is

0D	Table 4.5:	Experi	mental	condition	ns and run prod	lucts of AW-820	38 phc	motephrite experiments
или	Experiment	$^{\rm F}_{\rm (MPa)}$	(°C)	АП2О <sup>т</sup> и Г	12O <sup>3</sup> ****** (WL 70)*	UUž (ppm)'	$f O_2^{O_2}$	$0^{c}$
PV-2	AW-13	200	1100	0.75	4.27 (0.2)	$833 \ (76)$	2.2	Gl 99, Ox 1
PV-2	AW-14	200	1100	0.5	1.86	245	1.1	Gl 99, Ox 1
PV-3	AW-06	200	1050	0	1.40(0.09)	1266(88)	$\operatorname{pd}$	Gl 92, Plag 7, $Ox < 1$
PV-3	AW-10	200	1050	1	$5.56\ (0.11)$	0	2.5	Gl 99, Ox 1, $Ap < 1$
PV-3	AW-17	200	1050	0.5	$3.14\ (0.11)$	444(30)	1.8	Gl 99, Ox 1
PV-3	AW-18	200	1050	0.75	$3.96^{*}$	nd	2.2	Gl 99, Ox 1
PV-4B	AW-19B	200	1000	0	1.1	88	0.7	Gl 5, Kaers 10, Plag 83, Ap 1, $Ox 3$
PV-4B	AW-20B	200	1000	0.25	1.71	1079	1.5	Gl 81, Kaers 16, Ox 3
PV-4B	AW-21	200	1000	0.5	$3.59\ (0.64)$	974	2	Gl 87, Kaers 9, Ox 4
PV-4B	AW-22	200	1000	0.75	2.38(0.17)	661	2.2	Gl 87, Kaers 8, Ox 5
PV-4B	AW-23	200	1000	1	$5.54\ (0.1)$	0	2.4	Gl 96, Ox 4
PV-5	AW-25	300	1100	0.25	$2.25\ (0.09)$	$1238\ (101)$	1.6	Gl 99, $Ox < 1$
PV-5	AW-26	300	1100	0.5	$3.59\ (0.03)$	993 (67)	2	Gl 99, $Ox < 1$
PV-5	AW-27	300	1100	0.75	$3.03\ (0.56)$	$1625\ (313)$	2.4	Gl 99, $Ox < 1$
PV-5	AW-28	300	1100	1	$6.64\ (0.85)$	0	2.6	Gl 99, $Ox < 1$
PV-6	AW-29	300	1050	0	1.00(0.03)	1140(143)	2.7	Gl 93, Plag 7
PV-6	AW-33	300	1050	0.5	$2.94\ (0.06)$	$1704 \ (359)$	2.4	Gl 99, Ox 1
PV-6	AW-34	300	1050	1	4.53(0.42)	0	2.6	Gl 97, Ox 3
PV-8	AW-24B	250	1100	0	$1.13\ (0.01)$	2040 (182)	0.9	Gl 100
PV-10	AW-37	300	1100	0	$0.82^{*}$	nd	2.8	Gl 99, Ox 1
PV-11	AW-38	300	1000	1	$7.82\ (0.32)$	0	2.5	Gl 95, Ox 5
PV-11	AW-39	300	1000	0.75	$3.65\ (0.29)$	$1598 \ (753)$	2.3	Gl 91, Ox 9, $Ap < 1$
PV-11	AW-40	300	1000	0.5	2.08(0.07)	$1977\ (331)$	2.1	Gl 94, Kaers 2, Ox 5
PV-11	AW-41	300	1000	0.25	0.8	668	1.4	Gl 80, Kaers 15, Ox 5
PV-11	AW-42	300	1000	0	$0.68\ (0.04)$	573 (44)	1.2	Gl 80, Kaers 13, Ox 7
PV-15	AW-43	400	1000	0	0.66*	nd	2.2	Gl 36, Kaers 22, Plag 35, Ox 7
PV-15	AW-44	400	1000	0.25	$0.98^{*}$	nd	2.5	Gl 77, Kaers 19, Ox 6
PV-15	AW-45	400	1000	0.5	4.03(0.1)	$3381 \ (827)$	2.6	Gl 80, Kaers 13, Ox 7
PV-15	AW-46	400	1000	0.75	$9.01\ (0.65)$	4921 (518)	2.8	Gl 87, Kaers 9, Ox 4
PV-15	AW-47	400	1000	1	$9.04\ (0.31)$	0	2.8	Gl 74, Ox 26
<sup><math>a</math></sup> Mole fr	action of $H_2O$	in H <sub>2</sub> O-0	$CO_2$ mix	cture addec	l to capsule during	g capsule prep		
$^b$ Weight	percent $H_2Oc$	or ppm C	O <sub>2</sub> diss	olved in the	e glass, measured	via FTIR. Standar	d devia	tion shown in parentheses.
<sup>c</sup> Calcula	ted oxygen fug	acity of	the expe	eriment in 1	terms of $\Delta NNO$ (c	change in log units	from th	ne Ni-NiO buffer). See text for details.
<sup><i>a</i></sup> Phase I	roportions cale	culated a	s volume	e percent; (	il: glass, Ol: olivir	ie, Cpx: clinopyrox	tene, Ka	er: kaersutite, Fsp: feldspar, Ap: apatite,
• Ux: Tit: *Walatile	nomagnetite,	Q: Quen ralculat	ch Cryst ad by m	als ass balance	T ni seules value e	shla 4.4 Connecto	d walnes	a neine tha relationshins in Fierma 4-3 and
	bene				T THE CONTRA STITICN O	MANINA ILL MAN		am and and trimming in Parts in a
reporteu 1175164:16	nere.	المتراحية المح		ים המתוכייה לבו	Lannation La		 	10 when we were helened data week
- Volatlik	concentration	calculat	ted by c	lifference a	nd correctea using	g the relationships	ngi t ng	ire 4.3 when no mass balance data were

available.

nd: not determined

	Tabl	le 4.6: Ex	xperiment	al conditio	ons and run produ	acts of KI-04 ba	sanite exp	oeriments
$\operatorname{Run}$	Experiment	P (MDa)	$(O_{\circ})$ T	${ m XH_2O^a_{in}}$	$\mathrm{H}_{2}\mathrm{O}^{glass}$ (wt %) <sup>b</sup>	$\mathrm{CO}_2^{glass}~(\mathrm{ppm})^b$	$fO_2$	vol% phases <sup><math>d</math></sup>
		(p 1111)						
PV-2	KI-01	200	1100	0	$0^1$	nd	2.5	Gl 77, Ol 5, Cpx 17, Tit 1
PV-2	KI-05	200	1100	1	$\operatorname{nd}$	nd	$\operatorname{nd}$	All Quench
PV-2	KI-06	200	1100	0.75	$2.48^{1}$	nd	2.2	Quench + rare Ol
PV-2	KI-07	200	1100	0.5	2.9(0.08)	$1133\ (102)$	$\operatorname{nd}$	Gl 93, Ol 4, Tit 3
PV-2	KI-08	200	1100	0.25	$2.04^{1}$	nd	nd	Gl 86, Ol 11, Tit 2
PV-7	KI-09	200	1050	0	$0.73\ (0.17)$	$531 \ (244)$	0.9	Gl 70, Cpx 23, Tit 7
PV-7	KI-10	200	1050	0.25	1.51(0.11)	678 (213)	2	Gl 53, Cpx 44, Tit 3
PV-7	KI-11	200	1050	0.5	2.57*	2067*	2	Gl 60, Cpx 37, Tit 4
PV-7	KI-12	200	1050	0.75	$3.54^{*}$	$1371^{*}$	2.3	Gl 65, Ol 6, Cpx 25, Tit 5
PV-8	KI-14	250	1100	0	$1.15^{*}$	$4068^{*}$	1.3	Gl 52, Ol 26, Cpx 23
PV-8	KI-15	250	1100	0.25	1.91(0.02)	$3078 \ (628)$	1.9	Gl 91, Ol 9, Tit $<1$
PV-8	KI-16	250	1100	0.5	3.32	4344	2.1	Gl 69, Ol 27, Cpx 1, Tit 1
PV-8	KI-17	250	1100	0.75	$3.64^{*}$	$1220^{*}$	2.4	Gl 58, Ol 21, Ol 21
PV-8	KI-18	250	1100	1	$3.67^{*}$	*0	2.7	All Quench
PV-10	KI-19	300	1100	1	$5.28^{*}$	*0	2.7	All Quench
PV-10	KI-20	300	1100	0.75	$1.65\ (0.37)$	1270(442)	2.3	GI, Q
PV-10	KI-21	300	1100	0.5	2.79(0.58)	2802 (585)	2.1	Gl 91, Ol 9, Tit $<1$
PV-10	KI-22	300	1100	0.25	2.47*	$3105^{*}$	1.6	Gl 92, Ol 8, Tit $<1$
PV-10	KI-23	300	1100	0	1.11(0.04)	$2632 \ (258)$	1	Gl $80$ , Ol $15$ , $Cpx 5$
PV-12	KI-25	300	1150	0.75	$3.34^{*}$	$1761^{*}$	2.7	All Quench
PV-12	KI-24	300	1150	1	$5.02^{*}$	*0	2.8	All Quench
PV-12	KI-26	300	1150	0.5	$3.61^{*}$	$2170^{*}$	2.1	All Quench
PV-12	KI-27	300	1150	0.25	$2.21 \ *$	$3038^{*}$	1.8	Gl 99, Ol 1, Tit $<1$
PV-12	KI-28	300	1150	0	$1.15^{*}$	$3844^{*}$	1.4	Gl 98, Ol 2, Tit $<1$
PV-13	KI-29	400	1000	0	1.42 *	$3726^{*}$	1	Subsolidus
PV-13	KI-30	400	1000	0.25	2.20 *	$2998^{*}$	1.8	Subsolidus
PV-13	KI-31	400	1000	0.5	$2.88^{*}$	$2355^{*}$	2.4	Gl 38, Kaers 60, Tit 2
PV-13	KI-32	400	1000	0.75	$3.04\ (0.05)$	$1603 \ (138)$	2.6	Gl 57, Kaers 41, Tit 2
PV-13	K1-33	400	1000	1	$4.16^{*}$	*0	2.8	Gl 38, Kaers 59, Tit 3
PV-14	KI-36	400	1100	0.5	3.45*	$4423^{*}$	2.4	Gl 95, Ol 5, Tit $<1$
PV-14	KI-37	400	1100	0.75	$3.48^{*}$	3377*	2.7	Gl 29, Ol 20, Q 51
PV-14	KI-38	400	1100	1	$3.63^{*}$	$3307^{*}$	2.9	All Quench
Notatio	n the same as	in Table $4$	5					

fixed for each experiment, I can calculate the  $fH_2$  of the pressure vessel for each run using the equation:

$$fH_2 = \gamma H_2 \cdot P_{H_2} \tag{4.3}$$

where  $\gamma H_2$  is the fugacity coefficient of hydrogen (Shaw & Wones, 1964), and  $P_{H_2}$  is the partial pressure of hydrogen gas added to the IHPV at the start of the run. If the XH<sub>2</sub>O<sup>fluid</sup> is known, I can also then calculate the  $fH_2O$  inside the capsule as:

$$fH_2O^{inside} = fH_2O^{pure} \cdot XH_2O^{fluid} \tag{4.4}$$

where  $fH_2O^{pure}$  is the fugacity of pure H<sub>2</sub>O vapor at the experimental P and T conditions, assuming ideal mixing between H<sub>2</sub>O and CO<sub>2</sub> in the fluid (calculated with the modified Redlich-Kwong Equation of State of Holloway, 1977 and modified by Flowers, 1979). Now, it is possible to calculate the oxygen fugacity for each experiment as follows:

$$fO_2^{inside} = \left(\frac{fH_2O^{inside}}{fH_2 \cdot K_F}\right)^2 \tag{4.5}$$

where  $K_F$  is the equilibrium constant of formation for H<sub>2</sub>O (Robie et al., 1978). Oxygen fugacities in my experiments are reported in Table 4.6 and range from a  $\Delta$ NNO of +0.7 to +2.9.

## 4.5 Results

#### 4.5.1 Textural and Mineralogical Observations

Optical and electron microscope images revealed homogeneously distributed euhedral crystals in most experimental charges, with crystals ranging in size from  $<5 \ \mu\text{m}$  to  $\sim 80 \ \mu\text{m}$  in length. In the most highly crystalline charges, melt tends to collect in pools and small subhedral crystals ("quench" texture) are ubiquitous. Quench texture is especially common in KI-04 basanite samples with high H<sub>2</sub>O contents, probably due to the extremely low viscosity melt allowing for rapid
crystallization upon quench. In samples where crystals were too small to be analyzed by electron microprobe ( $<25 \ \mu m^2$ ), phases were analyzed for identification purposes only. Those analyses are not included here.

#### 4.5.2 Experimental Phase Compositions

Compositions of the experimental mineral phases and residual glasses are shown in Figures 4.5-4.10 and Table 4.7. In general, the experimental compositions mimic those of the natural starting lavas, with the exception of a few clinopyroxenes, which have lower than typical Ca contents and are enriched in Mg.

#### 4.5.2.1 Oxides

Fe-Ti oxides (titanomagnetite based on EDS analysis) are ubiquitous in both phonotephrite and basanite experiments, probably owing to the oxidizing conditions (~NNO+1). The frequency of oxides in experimental charges mimics that in natural samples in which opaque oxides occur as microphenocrysts or in the groundmass. Similarly, oxide minerals in experimental charges are always very small (usually <25  $\mu$ m<sup>2</sup>), and so it was not possible to obtain good microprobe analyses for this phase.

#### 4.5.2.2 Olivine

Experimental mineral compositions mimic those of the natural starting lava and natural EL basanites and range from  $Fo_{77}$ - $Fo_{90}$  (Table 4.7, Figure 4.5). More evolved EL lavas have subsequently more Fe-rich olivines, ranging from  $Fo_{68}$  in natural phonotephrites to  $Fo_{51}$  in natural phonolites (Kyle et al., 1992). Experimental olivine Fo contents shows a distinct upward trend with increasing  $H_2O^{melt}$ (Figure 4.6), likely owing to an increase in the melt fraction of the charge and a change in oxygen fugacity caused by an increase in the water activity in the melt (Feig et al., 2010). Crystal-melt Fe-Mg partition coefficients ( $K_D$ ) for experimental olivines range from 0.17 to 0.63 with an average value of 0.35, suggesting that experimental olivines were in equilibrium with their host melts. These values mimic



Figure 4.4: Histogram showing the distributions of Fe-Mg crystal-melt distribution coefficients ( $K_D$  for experimental (black) and natural (gray; data from Kyle, 1981) olivines.

natural Ross Island olivine  $K_D$  values, which range from 0.12 to 0.65 and average 0.33 (Kyle, 1981). A histogram of natural and experimental olivine  $K_D$  values is shown in Figure 4.4 and shows a similar distribution of Fe-Mg  $K_D$  values for both experimental and natural olivines.

Table 4.7: Compositions of experimental phases

	$\mathbf{Phase}$	$SiO_2$	$TiO_2$	$Al_2O_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$Na_2O$	$K_2O$	$P_2O_5$	Total	Mol%
AW 820.	38 experime	nts											
AW-6	PT(9)	48.03(0.74)	2.84(0.24)	18.12(0.62)	9.60(0.89)	0.23(0.05)	3.08(0.28)	7.57(0.38)	6.04(0.12)	3.08(0.11)	1.41(0.22)	99.20(0.59)	Mg no. 36.4
	plag(4)	50.38(0.9)	1.75(0.30)	22.74(1.26)	5.29(0.85)	0.13(0.04)	1.62(0.34)	8.83(0.31)	5.00(0.20)	1.89(0.28)	pu	97.64(0.54)	An61Al31Or8
AW-10	PT(7)	49.45(0.3)	2.64(0.07)	18.74 (0.26)	8.26(0.36)	0.25(0.04)	2.73(0.07)	7.62(0.07)	5.98(0.09)	3.08(0.11)	1.26(0.03)	95.00(0.69)	Mg no. 37.1
AW-13	PT(9)	48.84(0.44)	2.74(0.07)	$18.64 \ (0.24)$	8.89(0.27)	0.23(0.04)	2.84(0.10)	7.64(0.11)	5.89(0.11)	3.00(0.06)	1.30(0.05)	96.08 (0.80)	Mg no. 36.3
AW-14	PT(7)	48.75(0.49)	2.72(0.08)	$18.59\ (0.15)$	8.94(0.34)	0.18(0.04)	2.89(0.08)	7.63(0.13)	5.99(0.12)	2.99(0.07)	1.31(0.06)	97.08 (0.72)	Mg no. 36.6
AW-17	PT(7)	49.29 (0.26)	2.63(0.08)	18.75 (0.17)	8.43(0.36)	0.21 (0.02)	2.85(0.07)	7.59(0.19)	5.94(0.17)	3.03 (0.07)	1.29(0.06)	97.52(0.43)	Mg no. 37.7
AW-18	PT(7)	49.60(0.41)	2.56(0.14)	18.76(0.28)	8.21(0.16)	0.21(0.04)	2.89(0.11)	7.60(0.08)	5.96(0.15)	2.97(0.09)	1.24(0.05)	96.41 (0.51)	Mg no. 38.5
AW-19B	P(4)	53.74 (0.87)	1.53(0.04)	19.46(0.10)	4.05(0.29)	0.15(0.07)	1.03(0.11)	4.21(0.23)	8.29 (0.23)	5.87(0.09)	1.68(0.21)	96.63(0.70)	Mg no. 31.1
	cpx (4)	45.09(1.3)	3.45(0.51)	7.75(0.45)	8.01(0.47)	0.34(0.02)	11.19(0.30)	21.17(0.71)	1.16(0.13)	0.26(0.17)	nd	98.43 (0.65)	En36Wo39Fe15
	plag $(1)$	55.16	1.06	22.61	3.8	0.1	1.64	9.72	5.07	1.26	nd	100.43	An65Al30Or5
AW-20B	T(10)	55.30(0.64)	1.72(0.04)	19.86(0.49)	4.25(0.25)	0.20(0.07)	1.30(0.09)	4.15(0.33)	8.05 (0.13)	4.74(0.23)	$0.44 \ (0.19)$	94.76(1.30)	Mg no. 35.3
	kaers (7)	37.38 (0.91)	6.33(0.35)	12.68(0.41)	$10.32\ (0.55)$	0.23 $(0.04)$	12.12(0.36)	11.33(0.64)	2.76(0.05)	1.18(0.08)	0.12 (0.10)	94.48(2.32)	Mg no. 67.7
AW-21	T(10)	53.93(0.44)	2.01(0.07)	20.07(0.36)	4.79(0.28)	0.20(0.08)	1.56(0.09)	5.80(0.19)	7.36(0.15)	3.80(0.08)	$0.48 \ (0.19)$	94.24(0.84)	Mg no. 36.7
	kaers (6)	36.75 (0.56)	5.96(0.28)	13.58(0.44)	$10.92\ (0.33)$	0.23 $(0.06)$	11.97 (0.23)	11.92(0.09)	2.64(0.08)	(0.08) $(0.08)$	0.25 $(0.33)$	95.35(0.77)	Mg no. 66.1
AW-22	T (12)	$52.51 \ (0.58)$	2.37(0.07)	19.69(0.17)	5.23(0.21)	0.22(0.05)	2.24(0.10)	7.12(0.14)	6.57 (0.13)	3.47(0.11)	$0.59\ (0.17)$	$92.11 \ (0.71)$	Mg no. 43.3
	kaers $(10)$	37.56(0.69)	5.27(0.23)	13.00(0.37)	$10.15\ (0.17)$	0.16(0.05)	$13.22 \ (0.22)$	$12.16\ (0.30)$	2.57(0.08)	1.09(0.06)	$0.22 \ (0.30)$	95.42(0.71)	Mg no. 69.9
AW-23	T (11)	51.91(0.53)	2.57(0.04)	$19.62\ (0.25)$	5.41(0.29)	0.20(0.07)	2.52 (0.16)	7.46(0.23)	6.37 (0.15)	3.32(0.11)	$0.62\ (0.10)$	90.83(0.60)	Mg no. 45.4
AW-24B	PT (11)	49.77 (0.63)	2.85(0.05)	18.97(0.23)	7.36(0.25)	0.19 (0.06)	3.00(0.15)	7.47(0.14)	6.25(0.12)	2.95(0.07)	1.18(0.10)	93.35(0.89)	Mg no. 42.1
AW-25	PT(5)	48.80(0.38)	2.85(0.04)	18.80(0.44)	9.23(0.06)	0.23(0.04)	2.95(0.03)	7.59(0.08)	5.87(0.17)	2.80(0.12)	0.88(0.04)	95.45(0.45)	Mg no. 36.3
AW-26	PT (6)	$48.54 \ (0.38)$	2.80(0.06)	18.49(0.17)	9.34(0.21)	0.23(0.06)	2.81(0.07)	7.58(0.10)	5.87(0.09)	3.03(0.05)	1.31(0.03)	96.49 (0.52)	Mg no 34.9
AW-27	PT (27)	48.54 (0.36)	2.87(0.03)	18.95(0.44)	9.52(0.24)	0.25(0.03)	2.91(0.04)	7.62(0.05)	5.72(0.35)	2.83(0.12)	$0.79 \ (0.04)$	93.53(0.66)	Mg no. 35.2
AW-29	PT (12)	48.44 (0.49)	3.10(0.10)	$18.03\ (0.56)$	8.26(0.53)	0.25(0.09)	3.10(0.17)	7.72(0.31)	6.49(0.14)	3.35(0.18)	1.25(0.12)	94.84(0.76)	Mg no. 40.1
	plag $(3)$	51.84(1.4)	1.37(0.76)	24.80(2.60)	4.14(2.30)	0.10(0.08)	1.07 (0.67)	9.72(1.01)	4.83(0.21)	1.40(0.58)	pu	99.27 (0.61)	An65Al29Or6
AW-33	PT(6)	49.07 (0.4)	2.61(0.05)	$18.41 \ (0.18)$	8.63(0.33)	0.24(0.08)	2.74(0.03)	7.70(0.29)	6.18(0.11)	3.19(0.11)	1.20(0.27)	94.66(0.85)	Mg no. 36.2
AW-34	PT(6)	48.78 (0.79)	2.85(0.05)	18.78(0.15)	8.37(0.29)	$0.23 \ (0.05)$	2.56(0.08)	7.88(0.09)	6.07(0.12)	3.06(0.05)	1.42(0.08)	90.41(1.05)	Mg no. 35.3
AW-37	PT (10)	48.39 (0.77)	3.02(0.07)	$18.64\ (0.31)$	8.76(0.26)	$0.25 \ (0.06)$	2.95(0.08)	7.69(0.13)	5.94(0.11)	3.05(0.05)	1.30(0.06)	96.86(1.47)	Mg no. 37.5
AW-38	PT(6)	49.97 (0.51)	2.68(0.07)	$19.64\ (0.21)$	7.92(0.13)	$0.19 \ (0.07)$	2.82(0.03)	7.58(0.12)	5.11(0.26)	2.96(0.06)	1.14(0.06)	92.42(0.98)	Mg no. 38.8
AW-39	PT(11)	51.30(0.55)	2.40(0.07)	19.95(0.30)	6.49(0.20)	0.19 (0.06)	2.70(0.16)	7.47(0.20)	5.65(0.19)	3.12(0.11)	$0.71 \ (0.04)$	94.25(0.92)	Mg no. 42.6
AW-40	PT (11)	$50.51 \ (0.62)$	2.46(0.07)	$19.55\ (0.28)$	7.20(0.11)	0.23(0.05)	2.76(0.10)	7.42(0.17)	5.89(0.11)	3.15(0.06)	0.83(0.06)	95.74(1.23)	Mg no. 40.6
AW-41	T (12)	53.73 (0.82)	1.72(0.05)	20.18(0.38)	5.97(0.14)	0.22 (0.06)	1.57(0.07)	5.25(0.14)	6.86(0.14)	4.03(0.08)	$0.46\ (0.03)$	95.79(1.40)	Mg no. 32.0
	kaers $(5)$	38.19(0.3)	6.08(0.21)	$13.61 \ (0.17)$	11.44(0.31)	0.24(0.02)	11.45(0.26)	11.79 (0.33)	2.73(0.05)	1.14(0.04)	(00.0) pu	96.66(0.25)	Mg no. 64.1
AW-42	T (9)	52.77 (0.46)	1.63(0.05)	20.30(0.30)	6.16(0.24)	0.23(0.07)	1.94(0.03)	4.25(0.11)	7.37(0.21)	4.68(0.07)	0.67 (0.06)	97.88(0.95)	Mg no. 35.9
	kaers $(2)$	$38.78 \ (0.8)$	7.03 (0.36)	13.15(0.12)	11.38(0.35)	$0.28 \ (0.05)$	11.27 (0.09)	11.86(0.40)	2.57(0.08)	1.32(0.04)	pu	97.63(0.45)	Mg no. 63.8
	plag $(4)$	55.57(2)	0.69(0.34)	25.75(1.28)	1.42(0.61)	0.05(0.03)	0.28(0.13)	9.15(1.42)	5.96(0.25)	1.14(0.27)	pu	$100.03 \ (1.58)$	An60Al36Or4
AW-43	PT(1)	52.00	2	21.12	5.96	0.22	1.21	4.95	7.62	4.05	(0.86)	98.55	Mg no. 27.0
	cpx (4)	45.37 (0.66)	2.46(0.50)	6.68(1.09)	8.72(0.40)	$0.38 \ (0.02)$	11.44(0.46)	21.63(0.71)	$1.01 \ (0.12)$	0.08(0.01)	pu	97.77 (0.68)	En36Wo49Fe15
	plag $(3)$	56.35(1)	0.91(0.58)	24.12(1.13)	2.58(1.43)	$0.08 \ (0.05)$	$0.84 \ (0.68)$	7.97(0.50)	5.36(0.32)	1.87(0.13)	nd	$100.09\ (0.65)$	An57Al35Or8
AW-44	T(11)	54.57(0.8)	1.63(0.05)	20.59(0.32)	5.29(0.13)	$0.17 \ (0.06)$	1.28(0.06)	4.71(0.12)	7.07(0.16)	4.30(0.08)	$0.38 \ (0.04)$	96.74 (1.46)	Mg no. 30.2
	kaers $(6)$	38.20(0.41)	5.92(0.19)	$13.58\ (0.16)$	12.34(0.19)	0.28(0.03)	11.92(0.16)	11.44(0.20)	2.75(0.07)	1.27(0.04)	$0.21 \ (0.19)$	97.93(0.65)	Mg no. 63.3
AW-45	T (4)	53.03(0.89)	1.91(0.05)	20.69(0.26)	5.55(0.23)	$0.21 \ (0.01)$	1.68(0.02)	6.34(0.06)	6.95(0.15)	3.37(0.05)	0.26(0.04)	92.94(1.32)	Mg no. 35.1
	kaers $(5)$	37.03 (0.83)	5.06(0.26)	$14.44\ (0.20)$	12.11 (0.71)	0.24(0.01)	11.42(0.43)	11.91(0.55)	2.73(0.15)	1.21(0.11)	pu	96.18 (0.67)	Mg no. 62.7
AW-46	B-TA (9)	52.98(0.87)	2.18(0.09)	20.49(0.67)	5.54(0.39)	0.20(0.08)	2.00(0.21)	7.10(0.40)	5.68(0.29)	3.16(0.19)	0.66(0.21)	93.74(1.86)	Mg no. 39.2
	kaers (4)	38.54 (0.58)	4.58(0.10)	14.07(0.36)	10.64(0.27)	$0.21 \ (0.05)$	13.28(0.16)	$12.23 \ (0.18)$	2.66(0.03)	1.15(0.06)	(00.0) pu	97.41(0.38)	Mg no. 69.0
AW-47	B-TA (10)	51.80(0.2)	2.53(0.04)	20.16(0.26)	6.56(0.12)	0.22(0.07)	2.79(0.07)	7.31(0.07)	4.66(0.23)	3.17(0.07)	0.79 $(0.05)$	92.26(0.43)	Mg no. 43.2

Table 4.7: Compositions of experimental phases

	Phase	$SiO_2$	$TiO_2$	$Al_2O_3$	$FeO^T$	MnO	MgO	CaO	Na <sub>2</sub> O	$K_2O$	$P_2O_5$	Total	Mol%	
KI-04 b.	asanite expe	riments												
KI-01	B (43)	43.27 (0.80)	4.42(0.21)	14.05(0.68)	12.31 (1.11)	$0.17 \ (0.04)$	8.44 (1.48)	10.90 (0.73)	3.85(0.26)	1.72(0.13)	0.88 (0.07)	99.99 $(1.05)$	Mg no. 55.0	0
	ol (1)	40.30	1.02	4.3	17.3	33.21	0.25	2.96	nd Č	, pu	, pu	100.92	Fo77	
KI-06	B (3)	$45.92 \ (0.21)$	4.37(0.02)	$14.42\ (0.11)$	$10.22\ (0.05)$	0.25(0.04)	7.81(0.18)	13.03(0.31)	3.35(0.32)	$0.64\ (0.01)$	pu	90.87 (0.03)	Mg no. 57.7	7
	ol (5)	40.67 (0.08)	0.09(0.01)	0.03(0.01)	9.41(0.25)	0.25(0.02)	49.09(0.23)	0.35(0.01)	$0.01 \ (0.01)$	0.01 (0.00)	pu	99.93(0.13)	$F_{o90}$	
KI-07	B(15)	$44.61 \ (0.38)$	4.37(0.09)	$14.41 \ (0.20)$	$10.61 \ (0.40)$	$0.17 \ (0.04)$	7.69(0.19)	11.55(0.25)	3.93(0.11)	1.74(0.13)	0.92(0.04)	96.88 (0.63)	Mg no. 56.4	4
	ol (3)	38.33 $(1.35)$	0.65(0.45)	0.50(0.38)	14.11(2.45)	0.22(0.01)	45.11 $(2.17)$	0.49(0.10)	0.10(0.02)	0.03(0.01)	pu	99.75(1.09)	Fo85	
KI-08	B (16)	44.04(0.49)	4.54(0.13)	14.46(0.44)	11.51(0.61)	0.16(0.05)	7.11 (1.31)	11.59(0.46)	3.90(0.14)	1.79(0.08)	0.91 (0.05)	98.24(0.79)	Mg no. 52.4	4
	ol (5)	39.56 (0.52)	0.21(0.13)	0.12(0.11)	12.93(0.55)	0.27 (0.02)	46.09(0.59)	0.40(0.03)	0.02(0.01)	0.01 (0.00)	pu	99.63(0.22)	Fo86	
	cpx (4)	44.34 (0.82)	3.44(0.37)	8.29(1.03)	7.82(0.57)	0.12(0.04)	12.35 (0.76)	20.82(0.73)	0.65(0.08)	0.18(0.12)	pu	98.06 (0.18)	En39Wo47F	Fe14
KI-09	PT (9)	49.66 (0.37)	2.87(0.06)	18.78 (0.37)	7.01(0.38)	0.14(0.05)	3.13(0.09)	6.42(0.14)	7.01(0.14)	3.76(0.08)	1.22(0.11)	94.67(0.72)	Mg no. 44.5	3
KI-10	B (8)	47.27 (0.79)	3.65(0.26)	$16.32\ (1.20)$	7.96(0.38)	0.20(0.08)	5.89(1.61)	9.28(1.34)	5.44(0.57)	2.60(0.32)	1.39(0.23)	92.05(1.04)	Mg no. 56.9	6
	ol (3)	38.82 (0.18)	0.19(0.07)	0.17(0.14)	17.98(0.40)	0.33(0.01)	41.25(0.49)	0.71 (0.28)	0.02(0.00)	0.02(0.00)	pu	99.51(0.22)	$F_{O80}$	
	cpx (5)	43.08(0.46)	4.38(0.22)	9.98(0.31)	8.46(0.43)	0.12(0.03)	11.14(0.21)	20.96(0.33)	0.82(0.09)	0.18(0.05)	$\mathbf{p}\mathbf{n}$	99.23(0.45)	En36Wo49F	Fe15
KI-11	B (5)	47.87 (0.26)	3.78(0.06)	$16.71 \ (0.24)$	8.25(0.22)	0.20(0.07)	4.86(0.20)	9.18(0.09)	5.35(0.22)	2.34(0.13)	1.47 (0.09)	92.99(0.25)	Mg no. 51.2	2
	kaers $(5)$	37.68(1.47)	5.75(0.38)	12.08(0.15)	11.79(2.45)	$0.11 \ (0.03)$	$15.25 \ (0.31)$	11.66(0.70)	2.51(0.07)	1.07(0.06)	pu	97.97(1.22)	Mg no. 70.0	0
KI-12	B (11)	45.59(0.48)	4.54(0.08)	$16.01 \ (0.15)$	8.54(0.30)	0.16(0.11)	5.89(0.34)	11.32(0.38)	4.88(0.13)	1.90(0.20)	$1.17 \ (0.11)$	91.56(0.98)	Mg no. 55.2	2
	ol (7)	38.65(0.32)	0.14(0.04)	$(90.0) \ 60.0$	11.64(0.16)	0.25(0.03)	47.16 (0.50)	0.43(0.23)	0.05(0.02)	0.01 (0.01)	pu	98.48(0.36)	Fo88	
	cpx (4)	44.23 (0.98)	3.05(0.28)	5.92(0.47)	6.95(0.49)	0.12(0.01)	14.45(0.48)	22.75(0.14)	0.65(0.12)	0.07 (0.01)	$\mathbf{pn}$	98.26(0.52)	En42Wo47F	Fe11
KI-14	B (7)	44.62(0.39)	5.11(0.06)	15.75(0.28)	10.25(0.44)	$0.21 \ (0.13)$	5.58(0.17)	10.56(0.14)	4.68(0.13)	2.20(0.12)	1.03(0.09)	96.57 (1.00)	Mg no. 49.3	33
	ol (4)	$38.05 \ (0.16)$	0.16(0.02)	$(90.0) \ 60.0$	20.19(0.31)	$0.32 \ (0.05)$	$40.21 \ (0.47)$	0.53(0.13)	0.05(0.04)	0.03(0.01)	$\mathbf{pn}$	99.71 (0.26)	Fo78	
KI-15	B (15)	43.55(0.37)	4.94(0.08)	$14.37\ (0.24)$	11.28(0.32)	$0.19 \ (0.06)$	6.73(0.22)	12.11 (0.28)	4.06(0.12)	1.81(0.14)	(0.0) 70.09	93.70(0.69)	Mg no. 51.5	5
	ol (8)	$38.72 \ (0.13)$	0.11(0.02)	$0.04 \ (0.02)$	$16.69\ (0.14)$	0.26(0.06)	$42.84 \ (0.27)$	$0.41 \ (0.02)$	$0.01 \ (0.01)$	$0.01 \ (0.01)$	$\mathbf{p}\mathbf{n}$	99.17(0.29)	Fo82	
KI-16	B(15)	$43.81 \ (0.30)$	4.83(0.09)	$14.35\ (0.23)$	$11.52\ (0.23)$	$0.19 \ (0.12)$	6.73(0.30)	12.20(0.48)	4.03(0.12)	1.40(0.20)	0.95(0.08)	94.20(0.59)	Mg no. 51.0	0
	ol (8)	39.25 (0.27)	0.13(0.03)	0.07 (0.03)	$15.27\ (0.08)$	0.26(0.03)	43.90(0.23)	0.40(0.03)	0.07 (0.02)	$0.02 \ (0.01)$	nd	99.42(0.21)	Fo84	
KI-17	B (1)	44.80	4.43	14.88	11.17	0.2	6.68	11.66	3.84	1.73	0.57	95.16	Mg no. 51.6	6
	ol (4)	39.42(0.52)	0.11(0.02)	0.05(0.02)	$13.51 \ (0.29)$	0.24(0.03)	$45.76 \ (0.27)$	0.33(0.01)	0.02(0.02)	0.00(0.01)	pu	99.58(0.92)	Fo86	
KI-20	B (5)	45.05(0.41)	4.44(0.10)	14.40(0.11)	11.23(0.17)	$0.21 \ (0.02)$	7.74(0.60)	$12.31 \ (0.88)$	3.11(0.34)	0.91 (0.27)	0.60(0.04)	92.55(0.61)	Mg no. 55.1	1
KI-21	B (8)	43.60(0.36)	4.69(0.07)	14.17(0.09)	11.77(0.23)	0.15(0.04)	8.03 (0.09)	11.38(0.19)	3.62(0.05)	1.66(0.11)	0.93 $(0.07)$	95.28(0.69)	Mg no. 54.9	6
	ol (4)	39.00(0.44)	0.12(0.03)	0.05(0.03)	14.38(0.33)	0.23(0.02)	46.75 $(0.97)$	0.34(0.03)	0.02(0.02)	0.00(0.01)	pu	$101.01 \ (0.68)$	Fo85	
KI-22	B (10)	43.42(0.43)	4.74(0.10)	14.46(0.21)	$11.71 \ (0.34)$	0.20(0.05)	7.32(0.25)	11.60(0.13)	3.81(0.09)	1.82(0.06)	0.92 (0.06)	96.02(1.19)	Mg no. 52.7	7
	ol (8)	$39.07 \ (0.45)$	0.12(0.09)	0.13(0.23)	15.90(0.83)	0.26(0.04)	$45.24 \ (0.97)$	0.52(0.46)	0.03(0.03)	0.01 (0.01)	$\mathbf{p}\mathbf{u}$	$101.36\ (0.72)$	Fo83	
KI-23	B(10)	43.63(0.61)	4.95(0.08)	15.04(0.30)	11.26(0.31)	0.19(0.05)	6.49(0.12)	11.49(0.12)	4.11(0.07)	1.88(0.04)	0.96(0.03)	97.21(1.30)	Mg no. 50.7	7
	ol $(5)$	38.71 (0.37)	0.13(0.01)	0.05(0.01)	18.74(0.19)	0.26(0.04)	43.25(0.23)	0.51(0.01)	0.01 (0.01)	$0.01 \ (0.01)$	$\mathbf{p}\mathbf{n}$	101.74 (0.69)	Fo80	
	cpx (6)	43.57 (1.60)	4.44(0.54)	11.33(1.99)	8.29(1.21)	$0.17 \ (0.01)$	9.82(1.89)	17.67(2.74)	1.60(0.78)	0.79(0.48)	$\mathbf{nd}$	97.96(1.25)	En36Wo47F	Fe17
KI-26	B (6)	43.76(0.58)	4.48(0.11)	13.75(0.19)	11.45(0.49)	0.16(0.07)	9.33(1.38)	11.04(1.59)	3.49(0.17)	1.64(0.68)	0.90(0.04)	96.65(0.35)	Mg no. 59.2	2
KI-27	B (6)	43.48(0.63)	4.48(0.04)	$14.63\ (0.21)$	$10.79\ (0.17)$	0.15(0.05)	9.06(0.15)	11.74(0.11)	4.09(0.09)	1.57(0.15)	$\mathbf{p}\mathbf{n}$	92.24(0.82)	Mg no. 59.9	6
KI-28	B (6)	$44.61 \ (0.41)$	4.55(0.05)	$14.25\ (0.16)$	9.89(0.11)	$0.21 \ (0.04)$	8.98 (0.07)	11.40(0.08)	3.76(0.12)	1.69(0.11)	0.66(0.02)	95.99(0.33)	Mg no. 61.8	8
KI-31	PT(3)	51.87 (0.66)	2.68(0.16)	18.59(0.33)	8.22(0.31)	0.23(0.05)	2.98(0.08)	7.70(0.05)	5.19(0.13)	2.55(0.01)	pu	92.06(0.66)	Mg no. 39.2	2
	kaers (8)	39.82 (0.73)	4.88(0.17)	11.94(0.49)	11.05(0.45)	0.15(0.05)	$14.04 \ (0.40)$	11.58(0.14)	2.64(0.06)	1.21(0.05)	0.09 (0.10)	97.49(0.44)	Mg no. 69.4	4
KI-32	PT(7)	49.92(0.75)	3.22(0.30)	17.06(0.57)	8.94(0.53)	0.23(0.01)	4.43(1.30)	9.14(0.41)	4.19(0.36)	2.18(0.20)	0.69(0.09)	91.46(1.71)	Mg no. 46.9	6
	kaers (6)	39.67 (0.78)	4.04(0.19)	11.91(0.42)	10.45(1.33)	0.18(0.02)	$14.94 \ (1.24)$	$11.84 \ (0.12)$	2.58(0.07)	1.24(0.13)	$0.15 \ (0.17)$	97.09(0.50)	Mg no. 71.7	7
KI-33	TB (7)	47.39 (0.70)	3.69(0.06)	$16.09\ (0.20)$	9.81(0.32)	0.18(0.05)	5.57(0.27)	9.99(0.15)	3.83(0.14)	2.18(0.09)	1.26(0.06)	$89.81 \ (1.41)$	Mg no. 50.3	33
	kaers $(4)$	39.82(0.82)	4.38(0.07)	11.80(0.56)	10.59(0.35)	0.14(0.04)	$14.79 \ (0.31)$	11.77 (0.27)	2.60(0.05)	1.25(0.05)	0.12(0.19)	97.37(0.20)	Mg no. 71.3	3
KI-36	B (10)	43.75(0.61)	4.70(0.08)	14.24(0.28)	11.33(0.27)	$0.18 \ (0.08)$	8.21(0.31)	11.46(0.35)	3.56(0.10)	1.66(0.11)	0.91 (0.07)	94.04(1.40)	Mg no. 56.4	4

	$\mathbf{Phase}$	$SiO_2$	$TiO_2$	$Al_2O_3$	$FeO^T$	MnO	MgO	CaO	$Na_2O$	$K_2O$	$P_2O_5$	Total	Mol%
	ol (13)	39.22(0.21)	0.09(0.02)	0.04(0.01)	15.30(0.35)	0.24(0.03)	45.80(0.28)	0.33(0.02)	0.02(0.01)	0.01 (0.01)	nd	$101.17\ (0.57)$	Fo84
KI-37	ol $(10)$	39.72 (0.35)	0.09 (0.02)	0.04(0.01)	14.17(0.43)	0.22(0.04)	46.99 (0.41)	0.28(0.02)	0.01 (0.01)	0.01 (0.01)	pu	$101.70 \ (0.66)$	Fo86
Note: A	nalyses give	n in wt% and	normalized to	o 100% with o	riginal analysi	s totals given	. Number in <sub>1</sub>	parentheses ne	ext to analyse	s			
are stan	dard deviati	ions; those nex	t to phase na	vmes are numb	er of analyses.	nd = not de	termined. Rel	ported values	for glasses ar	e			
average	composition	is for each chai	rge. $FeO^T$ is	total iron give	in as FeO. Gla	ss name class	sifications are	as follows: B:	: basanite; PT	<i>.</i>			
phonote	phrite; T: te	<pre>&gt;phriphonolite;</pre>	P: phonolite	;; B-TA: basalt	ic trachyande	site; TB: trac	hybasalt.						

Table 4.7: Compositions of experimental phases

#### 4.5.2.3 Clinopyroxene

Experimental clinopyroxenes are classified as augite calculated on the basis of six oxygens (Morimoto, 1988). Although clinopyroxene often represents a large volume proportion of the experimental samples when present, the crystals were often too small to be reliably analyzed by electron microprobe, and so analyses from only five charges are shown here. Orthopyroxene is absent from both natural and experimental samples, reflecting the low silica activity in Erebus melts. Compositions of some experimental pyroxenes match those of the Ca-rich natural samples, but many have lower Wo contents than observed in nature (Figure 4.5). Pyroxenes that fall outside of the compositional range of natural samples are slightly enriched in Fe and Al and are significantly enriched in Mg. In natural melts, clinopyroxene must compete with olivine for available Mg, whereas a lower olivine proportion in the experimental samples means more Mg is available to be taken up by pyroxene crystallization. Therefore, high Mg/Ca ratios in clinopyroxenes may reflect oxidizing run conditions and/or insufficient olivine fractionation compared with the natural melts. This is consistent with the MgO vs.  $SiO_2$  trends observed in the residual glass compositions (see section 4.5.2.6). In most samples, the  $\mathcal{K}_D^{Fe-Mg}$ values of experimental clinopyroxenes, which range from 0.31 to 0.46 and average 0.36, are similar to the  $K_D^{Fe-Mg}$  values observed in natural KI-04 basanite clinopyroxenes, which average 0.40, suggesting equilibrium crystal growth. Two experimental charges (KI-04-08 and KI-04-10) have very high  $K_D^{Fe-Mg}$  values (1.23) and 1.05, respectively) reflecting the high MgO contents in the coexisting melts.

#### 4.5.2.4 Kaersutite Amphibole

Amphiboles that crystallized in experiments are sodic-kaersutite (Hawthorne et al., 2012) on the basis of 23 oxygens. Compositions of all experimental kaersutites that crystallized in phonotephrite and basanite experiments are shown in Figure 4.7. The compositions of amphiboles in experimental charges (filled orange diamonds in Figure 4.7) match those of the natural rocks (open diamonds) quite well, indicating that my experiments reproduced the natural system in terms of  $fO_2$ -T-H<sub>2</sub>O conditions.



Figure 4.5: Ternary diagram showing compositions of experimental (symbols) and natural (fields) olivine (green) and clinopyroxene (yellow). Clinopyroxenes are plotted in terms of recalculated end-member compositions enstatite, ferrosillite, wollastonite. Olivine is plotted along the baseline of the ternary in terms of recalculated end-members forsterite (Mg) and fayalite (Fe).



Figure 4.6: Chemical compositions of experimental olivines in terms of Fo content versus the calculated equilibrium  $XH_2O^{fluid}$ . Isobars are shown for 250, 300, and 400 MPa. The Fo content of natural KI-04 olivines is indicated by the horizontal red line.



Figure 4.7: Chemical compositions of experimental (filled diamonds) and natural (open diamonds) kaersutite amphibole, plotted in terms of magnesium number versus Na+K (a) and versus  $Al_2O_3$  (b). Natural kaersutites are from intermediate and evolved DVDP lavas from Kyle (1981).

Kaersutite is common in AW-82038 phonotephrite crystallization experiments, even for charges with very low water contents including those that contained no added  $H_2O$  (XH<sub>2</sub>O<sup>in</sup> = 0). In KI-04 basanite experiments, kaersutite is present in only a few low-temperature, high-pressure charges (1000 °C, 400 MPa), and, as with phonotephrite experiments, its presence is independent of the  $H_2O$  content of the charge. It should be noted that some  $H_2O$  was always present in my "dry" experiments, even without the purposeful addition of water to the experimental capsule. Despite the storage of rock powders in a drying oven,  $H_2O$  can be introduced to the experimental capsule via remnant water within the starting powder and through  $H_2O$  generation during the run via reduction of  $Fe^{3+}$ , but this excess water is minimal (typically <1-2 wt%). Even my driest runs, with <1 wt% H<sub>2</sub>O dissolved in the glass, show ubiquitous kaersutite crystallization. Rather than water, temperature seems to exert the strongest control over kaersutite stability with the phase only crystallizing in experiments at 1000 °C, the lowest experimental temperature investigated. Kaersutite is stable at all pressures investigated (200-400 MPa) for low-temperature phonotephrite experiments. In basanite experiments, kaersutite is only present in high-pressure charges (400 MPa).

#### 4.5.2.5 Plagioclase Feldspar

Plagioclase was observed only in the driest experiments on phonotephrite AW-82038. It was not found in any of the experiments on basanite KI-04. An contents in experimental phonotephrite feldspars range from  $An_{57}$ - $An_{65}$  and mimic the compositions of natural phonotephrite feldspars (Figure 4.8). Or contents of experimental plagioclases are on average slightly higher than those of the natural rocks, however this is probably due to error in the microprobe analyses due to the contamination of each analysis by the glass surrounding the very small experimental plagioclase crystals.

#### 4.5.2.6 Glass Compositions

The compositions of residual experimental glasses elucidate the evolution of the melts from primitive starting material to intermediate and evolved terms. Chemi-



Figure 4.8: Ternary diagram showing the compositions of experimental plagioclase crystals (purple squares) and natural plagioclase from EL lavas (open fields, data from Kyle et al., 1992).

cal compositions of both experimental series (squares and diamonds) and natural EL melt inclusions (green fields) are shown in Harker diagrams in terms of their major oxides versus silica in Figure 4.9. Due to the rarity of melt pools large enough to be measured in DVDP lavas, no residual melt compositions exist in the literature. FeO, CaO, and TiO<sub>2</sub> all show continuous decreasing trends with melt evolution owing to the crystallization of pyroxene, kaersutite, and titanomagnetite. MgO, Al<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O show continuous increasing trends. Many of the experimental glass compositions match the natural trends quite well, but some are clearly offset indicating a difference in natural versus experimental P-T-H<sub>2</sub>O- $fO_2$  conditions.

Mismatch between natural and experimental glass compositions is severe in particular for CaO, MgO and to a lesser extent Al<sub>2</sub>O<sub>3</sub>. Higher than observed CaO values may indicate an insufficient fractionation of plagioclase in the experiments compared to natural lavas, and hence that the liquid line of descent I establish experimentally is wetter than that of the natural system, especially in KI-04 experiments where plagioclase did not crystallize. This very tightly constrains the natural Erebus basanites to a maximum H<sub>2</sub>O content of <1-2 wt% and natural phonotephrites to a maximum of ~1 wt%. Coupled with the lower than observed Al<sub>2</sub>O<sub>3</sub> values, high CaO values in the melt may also reflect the low Ca contents of some experimental clinopyroxenes, although the trends in melt MgO content do not seem to reflect the Mg enrichment in low-Ca pyroxenes. The higher than observed MgO contents in KI-04 experiments may reflect either a higher experimental  $fO_2$  and/or, more likely, the lack of a cardinal phase consuming this element, such as olivine.

Trends in  $K_2O$  and  $P_2O_5$  contents of natural EL glasses are distinct from those in EL and DVDP whole rocks (see Figure 1.7). Experimental  $K_2O$  contents mimic those of the whole rock samples in that they are depleted relative to EL melt inclusions, probably reflecting the dominant role of kaersutite in my experiments and in natural DVDP rocks. The crystallization of kaersutite as a function of  $XH_2O^{fluid}$ in my experiments is well illustrated by the trends in the  $K_2O$  contents of residual glasses (Figure 4.10). An increase in the mole fraction of water added to the exper-



Figure 4.9: Harker variation diagrams (SiO<sub>2</sub> vs major oxides) showing compositions of experimental residual glasses (KI-04 as red squares; AW-82038 as blue diamonds) atop compositions from olivine-hosted melt inclusions in EL lavas (green fields; data from Eschenbacher, 1998 and Oppenheimer et al., 2011a). The parent basanite composition is shown as a black dot, and compositions of starting materials used in this study are shown as pale red (basanite KI-04) and pale blue (phonotephrite AW-82038) dots.

imental capsule  $(XH_2O^{in})$  correlates with a marked decrease in the K<sub>2</sub>O content of the residual glass, and thus an increase in the fractionation of kaersutite, in that charge. This correlation is also well illustrated in Figures 4.10b and 4.10c, which demonstrates the relationship between kaersutite abundance, the equilibrium fluid composition, and K<sub>2</sub>O concentration in the residual melt. Kaersutite abundance in natural DVDP rocks is about 16 vol% (15 wt%; Kyle et al., 1992) as shown by the vertical line in Figure 4.10c. According to the trend observed in my experiments, this should equate to a residual melt  $K_2O$  content between 3-5 wt% when  $SiO_2$  is >48 wt%, precisely what is observed in the natural melts (Figure 4.9). The strong role of water in controlling kaersutite fractionation is not apparent in phase diagrams, as the stability of kaersutite in my experiments correlates mostly with temperature and does not correlate with H<sub>2</sub>O content. A comparison of the isopleths in Figure 4.10a with the K<sub>2</sub>O contents in natural whole rock samples as shown in Figure 1.7 suggests the appearance of kaersutite at a  $XH_2O^{fluid}$  of ~0.25. This suggests that, while DVDP lavas are still quite dry (tightly constrained by plagioclase stability), the presence of kaersutite suggests that they are slightly more water-rich than EL lavas, which do not contain kaersutite. This does not necessarily require two distinct basanite parents with differing  $H_2O$  contents, however, as the drier EL lava suite could be explained by dehydration via  $CO_2$  fluxing, as proposed by Oppenheimer et al. (2011a).

The trends in natural  $P_2O_5$  content illustrate well the onset of apatite saturation in experimental charges and natural EL melt inclusions. In EL lavas, apatite saturation occurs when the melts have fractionated such that the silica content is  $\geq 48-49$  wt%, after which  $P_2O_5$  decreases with increasing SiO<sub>2</sub> (see Figure 4.9). As stated above, according to Harrison & Watson (1984), apatite is more soluble (and, thus, less likely to appear as a crystalline phase) in high-temperature, lowsilica melts. This suggests a hotter temperature of approximately >1100 °C for primitive and intermediate EL lavas, and a lower temperature (indicated by the onset of apatite saturation) for evolved lavas.



Figure 4.10: The effect of  $H_2O$  content on the fractionation of kaersutite amphibole in AW-82038 phonotephrite experimental charges. Figure a) is a Harker variation diagram showing the composition of the residual melt for each charge. Isopleths represent the XH<sub>2</sub>O added to the experimental capsule. No isopleth is drawn for pure-H<sub>2</sub>O experiments (XH<sub>2</sub>O = 1), as there was not enough data to establish a fractionation path. Figures b) and c) illustrate the relationship between the K<sub>2</sub>O content of residual melts versus the calculated fluid composition of each run and versus the amount of kaersutite fractionation, shown as kaersutite abundance in volume percent. The kaersutite abundance in natural DVDP lavas is shown in (c) as a red vertical line (data from Kyle, 1981).



Figure 4.11: Conventional phase diagrams for experiments with AW-82038 phonotephrite at fixed pressures of 200 MPa (a) and 300 MPa (b) in terms of the equilibrium fluid composition (calculated by gravimetery) and temperature. Numbers next to symbols represent the volume percentage of melt in the charge. Apatite was only observed in the most water-rich charges, but the steadily decreasing  $P_2O_5$  content in residual glasses suggests that it did crystallize in drier charges but that crystals were too small for microprobe analysis.



Figure 4.12: Experimental phase relations in terms of wt%  $H_2O$  dissolved in the residual melt versus pressure for: a) AW-82038 phonotephrite experiments (blue circles); and b) high-temperature (1050-1150 °C) KI-04 basanite experiments (red diamonds). Shaded regions indicate where the natural phase assemblages were best reproduced. Figure c) shows the phase relations for KI-04 basanite experiments conducted at 1100 °C in terms of the equilibrium fluid composition versus pressure. Numbers next to symbols represent the volume percentage of melt (or melt+quench) in the charge.



Figure 4.13: Composite phase diagrams showing the stability of various phases in terms of wt%  $H_2O$  dissolved in the residual melt versus temperature. Note that experiments conducted at all investigated pressures (200, 300, and 400 MPa) are plotted in order to illustrate the phase relations in general. Blue circles (top) are for AW-82038 phonotephrite experiments; red diamonds (bottom) are for KI-04 basanite experiments.

#### 4.5.3 Experimental Phase Relations

The equilibrium phase relations for both phonotephrite and basanite experiments are shown in Tables 4.5 and 4.6 and Figures 4.11, 4.12, & 4.13. In phonotephrite experiments, I establish a large kaersutite stability field largely independent of melt water content. Plagioclase is observed only at very low melt water contents (<2 wt%). Apatite is constrained to experiments below 1100 °C. In basanite experiments, olivine is the liquidus phase followed by clinopyroxene and kaersutite. A peritectic-like relationship exists at median melt water contents and  $1050 \,^{\circ}\mathrm{C}$ (see Figure 4.13b) where olivine is replaced by kaersutite at low temperatures. Although neither experimental series completely reproduced the natural phase assemblages of the Erebus starting lavas, my results shed light on critical aspects of the Erebus system and elucidate key differences in the formation conditions of the two natural lava suites on Ross Island. The shaded regions in Figures 4.11 & 4.12 indicate where the natural phase assemblages were best reproduced by my experiments in P-T-H<sub>2</sub>O space. For both compositions, certain key phases (plagioclase in phonotephrite and augite in basanite) only occur at very low  $H_2O$ -high  $CO_2$  conditions. This indicates upper limits for  $H_2O$  concentrations at Erebus of 1 wt% in phonotephrite and 1-2 wt% in basanite at the explored P-T conditions. This trend in low  $H_2O$  content is consistent with the recent study of Moussallam et al. (2013), who found a maximum  $H_2O$  content of 0.5 wt% in Erebus phonolite based on phase equilibrium experiments. In order to show the general phase relations in  $T-H_2O$  space, I have constructed a composite phase diagram for each composition (Figure 4.13) in which experiments from all experimentally investigated pressures are potted. This composite diagram allows for the phase relations to be better defined due to the larger data set that can be plotted, however it should be noted that the pressure range  $(300 \pm 100 \text{ MPa})$  adds intrinsic error to the relationships shown.

Olivine only occurs in KI-04 basanite experiments despite its presence in both natural lavas. It is interesting to note, however, that in the natural DVDP lavas, olivine phenocrysts occur only in basanite whereas in all other DVDP lavas only xenocrysts occur (Kyle, 1981). Xenocrysts were identified by their rounded and resorbed shape and the fact that they always had a reaction rim of oxidized kaersutite. Given the influence of temperature upon olivine stability in KI-04 experiments (Figure 4.13b), this suggests that the basanites are the hottest lavas in the DVDP suite (>1075 °C).

Because of the high abundance of plagioclase phenocrysts in natural AW-82038 samples, I consider this mineral a key petrologic indicator. The presence or lack of plagioclase in experimental samples, therefore, is highly indicative of the degree to which I approximated the natural pre-eruptive conditions of Erebus phonotephrites. The confinement of the phase to only very dry experiments suggests a maximum H<sub>2</sub>O content in phonotephrites of ~1 wt%, decreasing with pressure (see Figure 4.12a).

Interestingly, apatite, a minor phase in both natural and experimental samples, was most easily detected in experiments with very high  $H_2O$  contents. Even the largest experimental apatite grains were too small to be reliably analyzed by electron microprobe and so their analyses are not shown here. Typically, temperature plays the strongest role in controlling the growth of crystalline apatite in any given magma composition since apatite solubility is positively dependent upon temperature and negatively dependent upon  $SiO_2$  content of the melt (Harrison & Watson, 1984). Melt  $H_2O$  content strongly affects phosphorous diffusivity, however this is merely a rate-limiting factor of apatite dissolution. Instead, melt  $H_2O$  content controls apatite crystallization primarily by decreasing the  $SiO_2$  activity in the melt, thus increasing the solubility of the phase at a given T. Given that apatite was only observed in my most  $H_2O$ -rich runs, this suggests that the phase was stable in all runs, but that the kinetics necessary for apatite growth were too slow in all but the wettest experiments to grow crystals large enough to be detected by electron microprobe. The temperature dependence of apatite crystallization in my experiments is clearly illustrated by the apatite-in curve in Figures 4.11 and 4.13, which show that apatite is stable up to temperatures of  $1075 \pm 25$  °C. It is likely that apatite did crystallize in more charges than just those in which it was observed but that, due to slow crystallization kinetics, the crystals were too small and rare to be easily detected. This hypothesis is supported by the steady decrease in the  $P_2O_5$  content of residual liquids in phonotephrite experiments as illustrated in Figure 4.9.

# 4.6 Discussion

# 4.6.1 Phase Equilibrium Constraints on the Natural Erebus System

A main goal of this study was to investigate variations in formation conditions of the EL and DVDP lava suites, which make up the vast majority of Mount Erebus and the Hut Point Peninsula region. To this end, I employed the use of one starting lava from each natural suite: AW-82038 from EL and KI-04 from DVDP. The key mineralogical distinction between the natural rocks is the lack or presence of kaersuite amphibole in EL and DVDP lavas, respectively. Given that both experimental series produced kaersuite, I propose that the EL and DVDP lavas are in fact derived from the same parental magma source and that temperature is the principal control on kaersuite crystallization, in addition to a slight increase in H<sub>2</sub>O activity in DVDP magmas.

The presence of kaersutite in the experimental samples is largely independent of  $H_2O$  content. The growth of the amphibole in even the driest experiments indicates that some other component is taking the place of  $OH^-$  in the crystal structure. Unusually low H contents have been measured in other natural kaersutites (notably those from Martian meteorites) suggesting that the amphibole does not require a hydrous environment to grow (Popp et al., 1995). In addition to  $CI^-$  and  $F^-$  occupying O3 site occupancies, oxy substitutions in kaersutites are favored by high Ti and Fe<sup>3+</sup> contents (Popp & Taras Bryndzia, 1992) via the reactions:

$$Fe^{2+} + OH^{-} = Fe^{3+} + O^{2-} \tag{4.6}$$

$${}^{[6]}Al^{3+} + OH^{-} = Ti^{4+} + O^{2-} \tag{4.7}$$

This may explain the growth of kaersutite in our dry experiments, especially given the oxidizing experimental conditions, which will favor oxy substitutions via the reaction in equation 4.6. The presence of kaersutite in relatively dry natural samples thus may indicate the prevalence of oxidizing conditions for DVDP lavas with more reducing conditions for EL lavas. A flux of  $CO_2$ -rich gas through the EL conduit and not the DVDP off-shoot conduit could explain the difference in redox conditions for the two lava suites.

The inferred oxidizing conditions (~NNO) for deep and intermediate lavas from both lineages is in direct contrast to the reducing conditions (~QFM) inferred for Erebus's phonolitic lava lake (based on the phase equilibria experiments of Moussallam et al., 2013). This suggests that the plumbing system of Erebus follows a reducing upwards redox trend. While this seems counterintuitive given the quite oxidizing environment on Earth's surface, the trend is consistent with  $fO_2$  values for Erebus lavas calculated based on magnetite-ilmenite pairs in natural rocks. Using the oxide pairs method, intermediate tephriphonolites (sample 97009) have an estimated oxygen fugacity of  $10^{-9.99}$  (Kyle et al., 1992), or  $fO_2 = NNO-1.04$  at  $1081 \,^{\circ}C$  and 300 MPa, and lava lake phonolite (sample Phon-8) has an estimated oxygen fugacity of  $10^{-12.2}$  (Kyle, 1977), or  $fO_2 = QFM-1.22$  at  $1000 \,^{\circ}C$  and near atmospheric pressure (<10 bars). In addition, coupled chemical-physical modeling of conduit flow by Burgisser & Scaillet (2007) has shown that reducing upwards behavior is expected for some sulfur-bearing volcanic systems.

For both compositions, kaersutite is only stable at the low temperatures ( $<\sim$ 1025 °C). The lack of kaersutite amphibole and the presence of olivine in all of the EL lavas suggests a minimum temperature of  $\sim$ 1075 °C for the entire lineage at pressures as low as 200 MPa. Conversely, DVDP lavas containing kaersutite cannot greatly exceed a temperature of 1000 °C. Only a small change in temperature is necessary to switch from the EL to DVDP mineralogical regime, and so the appearance of kaersutite in DVDP lavas, for which outcrops are laterally separated from the source region by nearly 40 km, could be facilitated by a drop in temperature caused partly by a longer travel time through the shallow crust relative to EL lavas. In other words, a single parent magma undergoing two distinct temperature-time paths could give rise to the two lava lineages we see at the surface. The relationship between XH<sub>2</sub>O<sup>fluid</sup>, kaersutite fractionation, and the K<sub>2</sub>O content of the

residual melt found in my experiments indicates an  $XH_2O^{fluid}$  of ~0.25 in natural kaersutite-bearing DVDP rocks. EL lavas co-exist with an even drier fluid phase, probably around  $XH_2O^{fluid} = 0.1-0.05$  (See Chapter 3). I propose that the lower temperature and slight increase in fluid water content in the DVDP lineage relative to the EL is due to the lack of a sustained connection of the DVDP conduit to the mantle source region. This is supported by the fact that the eruption of DVDP lavas has ceased, while the EL lavas continue to erupt from the Erebus summit, which can be explained by the lack of a sustained flux of heat and CO<sub>2</sub>-rich fluid that characterizes the main Erebus conduit and serves to dehydrate EL magmas (see Oppenheimer et al., 2011a).

#### 4.6.2 Comparison with Other Volcanic Systems

To date, ours is the first study of the phase equilibria in a melt composition analogous to the deep Erebus system and therefore can only be compared broadly with similar studies on basaltic systems. In general, my phase relations can be compared with those of MORB (Berndt, 2002), calc-alkaline basaltic and esite (Moore & Carmichael, 1998), and medium-to-high-K basalt (Di Carlo et al., 2006; Sisson et al., 2005), with some marked distinctions. For example, the lack of plagioclase crystallization in my experiments with melt  $H_2O$  contents greater than ~1.5 wt% places very tight constraints on the melt water contents at Erebus. In other systems, however, it seems that the suppression of plagioclase occurs at much higher water contents: up to  $\sim 2.3 \text{ wt\%}$  in medium-to-high K basalts at 1025 °C (Sisson et al., 2005); up to  $\sim 3 \text{ wt}\%$  in high-K basalt at 1050 °C (Di Carlo et al., 2006); and up to  $\sim 4 \text{ wt}\%$  above 1050 °C in basaltic and esite (Moore & Carmichael, 1998). Given that the experimental parameters of these studies were similar, it is likely that starting melt composition is the controlling factor in determining the maximum  $H_2O$  contents for which plagioclase is stable. In fact, it has been demonstrated that the H<sub>2</sub>O-controlled suppression of the plagioclase liquidus plays a strong role in defining calc-alkaline versus tholeiitic magma differentiation trends (Sisson & Grove, 1993; Zimmer et al., 2010).

It is interesting to note that strongly silica-undersaturated, highly alkaline volcanic rocks like those at Erebus are commonly found in continental rift zones (Gee & Sack, 1988). Prominent examples include Oldoinyo Lengai volcano in Tanzania and Nyiragongo volcano in DR Congo, which, like Erebus, hosts an active lava lake in its summit crater. The very thin lithosphere and high geothermal gradient beneath rift volcanoes allows for the surficial emplacement of very deeply sourced magma with little to no differentiation or crustal contamination occurring upon ascent (Gee & Sack, 1988), thus explaining the presence of deeply derived basanites on the surface at Ross Island. This direct connection of the volcanic edifice to its deep mantle source region may facilitate the stability of a surficial lava lake via a constant flux of heat, magma, and volatiles to the surface. It is also of note that extremely  $CO_2$ -rich, H<sub>2</sub>O-poor conditions prevail at these three alkaline rift volcanoes (Koepenick et al., 1996; Oppenheimer et al., 2002), probably also facilitated by a direct mantle connection from which these fluids originate.

The highly alkaline and  $CO_2$ -rich nature of melts in rift zones is often explained by the metasomatization of an enriched mantle source by carbon-rich fluid, forming low-degree partial melts. This is consistent with redox melting, where reduced fluids from the lower mantle interact with a more oxidized upper mantle. Oxidation of reduced C-O-H fluids will produce H<sub>2</sub>O, which in turn initiates melting by lowering the mantle solidus temperature (Foley, 1988). If the system remains carbon-rich, only small degrees of partial melting will occur, thus producing  $CO_2$ -rich, alkaline magma. Isotopic studies of gases from the Erebus lava lake and targeted isotopic and trace element studies of Erebus lava could in the future elucidate the processes underpinning the formation of parental Ross Island basanites.

# 4.6.3 One Source, Two Lavas: Pre-eruptive Histories of EL and DVDP Rocks

Based on my experimental results and the observations presented here, I propose two differentiation pathways from a single basanitic parent source for Ross Island lavas: a high-temperature pathway, followed by EL lavas, and a low-temperature pathway, followed by DVDP lavas. Figure 4.14 depicts a theoretical cross-section beneath Ross Island, showing the P-T pre-eruptive histories of EL and DVDP lavas. The parental magma beneath Erebus is a high-temperature (>1075 °C)basanite accumulated at high pressure, perhaps in the upper mantle (Oppenheimer et al., 2011a) or lower crust (Chapter 3). Both EL and DVDP basanites must have ascended rapidly (with little to no fractionation during ascent; Kyle, 1981) sourced directly from this high temperature region near the crust/mantle boundary since they both contain olivine phenocrysts. Rapid ascent is supported by the observation of mantle xenoliths within some basanites. The EL and DVDP lavas follow very similar fractionation trends, with some key differences occurring due to a variation in temperature. The fact that all EL lavas contain olivine and none contain kaersutite suggests a sustained high temperature regime (>1075  $^{\circ}$ C), possibly facilitated by the direct connection of the EL conduit to the hot source region beneath Erebus. The sustained open-vent nature of Erebus volcano suggests a continual resupply of heat and gas from a deep source region (see Chapter 3; Moussallam et al., 2013; Oppenheimer & Kyle, 2008a; Oppenheimer et al., 2009, 2011a). The difference in high- and low-temperature regimes coupled with the fact that EL lavas have erupted continuously while DVDP lavas have stopped erupting suggests that the DVDP plumbing system was a shorter-lived offshoot of the main Erebus conduit with little resupply of heat from the source region. The DVDP conduit was likely formed as magma followed a radial fracture created by the updoming of material into the crust directly beneath Erebus (Kyle & Cole, 1974; Kyle et al., 1992) and by overpressure associated with the accumulation of deep fluids (Oppenheimer et al., 2011a).

DVDP magmas travel along an offshoot of the main Erebus conduit, culminating at the surface on Hut Point Peninsula. During their rapid ascent, some olivine is removed from the DVDP basanites and emplaced in subsequently produced intermediate magmas as xenocrysts. Temperature decreases markedly to  $\sim 1000$  °C or below during fractionation of the intermediate and evolved magmas, evidenced by the lack of olivine phenocrysts and presence of kaersutite in all subsequent lava types. This drop in temperature may be facilitated by the lack of continuous heat input from the source region coupled with long travel times through the shallow crust compared to the EL lavas.



Figure 4.14: Cross section schematic of the magmatic plumbing system beneath Ross Island showing both the main EL (Erebus Lineage) conduit and the off-shoot DVDP (Dry Valley Drilling Project lineage) conduit. Figure is drawn to scale but vertically exaggerated to show detail.

#### 4.6.4 The Case for CO<sub>2</sub>-dominated volcanism at Erebus

The results from this work add to the compelling evidence that Erebus volcano has been and continues to be a remarkably  $CO_2$ -rich system with a high C/H ratio. As discussed above, the natural phase assemblages of the starting lavas could only be approximated under extremely  $H_2O$ -poor,  $CO_2$ -rich conditions. Even for the DVDP lineage lavas, which are slightly wetter than the EL lavas, my experiments suggest that high CO<sub>2</sub>, low H<sub>2</sub>O conditions dominate (XH<sub>2</sub>O<sup>fluid</sup> ~0.25) and that the key difference between the two lineages that make up the majority of Ross Island is a very minor change in temperature and water content, DVDP rocks being formed at slightly colder and slightly wetter conditions. Even though my driest experimental melts contain only 1-2 wt% H<sub>2</sub>O, insufficient plagioclase crystallization and higher than observed CaO and Al<sub>2</sub>O<sub>3</sub> contents in my experimental glasses indicate that my experimentally established liquid line of descent is wetter than the natural system. This suggests a maximum  $H_2O$  content of 1-2 wt% in Erebus basanites and a maximum of  $\sim 1 \text{ wt}\%$  in Erebus phonotephrites. Moussallam et al. (2013) demonstrated that Erebus phonolite melts must have extremely low water contents, with a maximum of  $\sim 0.5 \text{ wt}\%$  (but probably even below 0.2 wt%). The very tight constraints that these two studies place on the maximum water contents of Erebus melts very closely match the trends in  $H_2O$  contents of natural Erebus melt inclusions (Oppenheimer et al., 2011a), which range from 1-2 wt%in basanite to <0.5 wt% in all other magmas, phonolites having <0.2 wt%. The decoupled ascent of  $CO_2$ -rich vapor through the magmatic system of Erebus may explain the extreme dehydration of the Erebus Lineage melts, as  $CO_2$  will degas early and deep and leach  $H_2O$  from the melt and into the vapor phase upon ascent (Métrich & Wallace, 2008). The slightly lower temperatures and higher fluid water contents in DVDP melts indicates a lack of a CO<sub>2</sub>-rich fluid flux through the offshoot DVDP conduit. In addition to sustaining the high-temperature and largely dehydrated nature of the main Erebus conduit, the ascending CO<sub>2</sub>-rich bubbles, which carry heat from the deep to the shallow system, may ultimately contribute to explosive degassing in the lava lake (Oppenheimer & Kyle, 2008a; Oppenheimer et al., 2011a).

The fluxing of a CO<sub>2</sub>-rich fluid through the Erebus plumbing system hypothesized by Oppenheimer et al. (2011a) is thought to be responsible for fractional crystallization throughout the Erebus system via dehydration of the melts and thus an increase in the solidus temperature. Using the results of my phase equilibria experiments and the solubility laws established in Chapter 3, a quantitative relationship between melt dehydration via CO<sub>2</sub> fluxing and crystallization can be established. First, we can relate the loss of  $H_2O^{melt}$  to a change in the equilibrium fluid composition. Simply, the loss of  $H_2O$  due to CO<sub>2</sub>-induced dehydration can be expressed as:

$$H_2Oloss, wt\% = H_2O_i^{melt} - H_2O_f^{melt}$$
 (4.8)

where *i* and *f* represent initial and final  $H_2O^{melt}$  contents, respectively. Using the relationship between the  $H_2O^{melt}$  and the fugacity of  $H_2O$  in the fluid phase from Equation 3.5, this equation then becomes:

$$H_2Oloss, wt\% = 6.5 \times 10^{-2} \cdot fH_2O_i^{0.541} - 6.5 \times 10^{-2} \cdot fH_2O_f^{0.541}$$
(4.9)

In order to express this in terms of  $XH_2O^{fluid}$ , which is generally more readily known than  $fH_2O$ , we can use the relation for ideally mixed fluids where the fugacity of some volatile component is equal to the product of the mole fraction of that component in the fluid phase and the pure component fugacity at a specified pressure and temperature, or:

$$fi = fi_{pure} \cdot Xi^{fluid} \tag{4.10}$$

Thus, Equation 4.9 then becomes:

$$H_2Oloss, wt\% = 6.5 \times 10^{-2} \cdot fH_2O^{pure}(P,T)^{0.541} \cdot (XH_2O_i^{0.541} - XH_2O_f^{0.541}) \quad (4.11)$$

where  $f H_2 O^{pure}$  can be calculated for a given P and T using a Modified Redlich Kwong equation of state. With this relationship established, the effect of  $H_2 O$  loss on the crystal content of the magma, C, can be derived using results from this chapter. The crystal contents in my experiments correlate inversely with the H<sub>2</sub>O content of the melt (Figures 4.15 & 4.16). My data is not sufficient to establish precise relationships, so for this analysis I use a linear fit to the data. Excluding outliers (samples KI-09, KI-15, and AW-19B), linear fits take the general form:

$$C(P,T) = m(H_2O^{melt}) + C_{dry}(P,T)$$
(4.12)

where C(P,T) is the pressure and temperature dependent crystal content and m is the slope of the line. The slopes given by the linear fits to the KI-04 data average ~-5. Because the KI-04 data conform much more strongly to linear relationships than the AW-82038 data (based on R<sup>2</sup> values, see Figures 4.15 & 4.16), a value of -5 is used for the value m in our general equation. The y-intercept represents the dry crystal content of the melt  $(C_{dry})$  and varies depending on P and T. Because only the change in crystal content, and not absolute crystal content, is required, P-T dependencies on the dry crystal content can be ignored for the purposes of this analysis. The change in crystal content,  $\Delta C$ , is thus related to the H<sub>2</sub>O loss by:

$$\Delta C = 5 \times (H_2 Oloss, wt\%) \tag{4.13}$$

and so our final model equation relating a change in  $H_2O^{melt}$  due to dehydration by  $CO_2$  fluxing to a change in crystal content of the magma becomes:

$$\Delta C = 5[6.5 \times 10^{-2} \cdot (fH_2O^{pure}(P,T))^{0.541} \cdot (XH_2O_i^{0.541} - XH_2O_f^{0.541})] \quad (4.14)$$

Given this general equation, we can now calculate how much crystallization would be induced given a change in the H<sub>2</sub>O content of the system. As an example, I examine here dehydration-crystallization at 400 MPa and 1000 °C. No change in XH<sub>2</sub>O will result in no change in crystal content, whereas a maximum change in XH<sub>2</sub>O, from pure H<sub>2</sub>O to dry, results in a maximum dehydration-induced change in crystal content of 29.7 vol% at the given P and T. In reality, it is reasonable to assume a starting XH<sub>2</sub>O value between 0.1–0.5. Based on our general equation



Figure 4.15: The relationship between the  $H_2O$  content of the glass and the crystal content in AW-82038 experimental charges. An increase in  $H_2O$  lowers the liquidus temperature of the melt, thus resulting in a lower volume % of crystals. Sample AW-19B was considered an outlier and is not plotted on this graph. With the one outlier excluded, straight lines were fit to the data. Because the AW-82038 starting material charges (this figure) have poor straigh line fits to the data compared with those for KI-04 starting material, the average slope from KI-04 charges were used. Still, AW-82038 charges generally exhibit the expected inverse relationship between  $H_2O$  content of the charge and crystal content.



Figure 4.16: The relationship between the  $H_2O$  content of the glass and the crystal content in KI-04 experimental charges. An increase in  $H_2O$  lowers the liquidus temperature of the melt, thus resulting in a lower volume % of crystals. Samples KI-09 and KI-15 are outliers of these linear trends and were omitted from this graph. With outliers excluded, straight lines were fit to the data. These relationships were then used to model dehydration-induced crystallization at Erebus.

and that range of starting conditions, dehydration of the melt due to flushing of a  $CO_2$ -rich fluid could be responsible for a change in crystal content of 8.5–20.5 vol% for the given P and T. Because the system is expected to be experiencing depressurization and cooling congruently with  $CO_2$  flushing, the actual change in crystal content will be somewhat higher. Still, these first order calculations illustrate that dehydration alone can lead to a significant change in crystal content of the magma, thus implying that  $CO_2$  flushing could play a strong role in magma evolution at Erebus.

Erebus is known to be a remarkably chemically stable system, supported by the fact that the chemistry of erupted products has remained unchanged for at least 17 ka and possibly for as long as 0.7 Ma (Kelly et al., 2008; Kyle, 1977). This implies that differentiation has occurred repeatedly under identical conditions throughout the recent life of the volcano. Open-path FTIR spectroscopic measurements of emissions from the Erebus lava lake show them to be rich in  $CO_2$  (~30 mol%) and comparatively low in  $H_2O$  (65 mol%; Burgisser et al., 2012; Oppenheimer et al., 2011a), mimicking the volatile compositions implied by melt inclusions and phase equilibria for the deeper system. The longevity of the lava lake itself is hypothesized to reflect, in part, the constant fluxing of heat and  $CO_2$ -rich fluid (Oppenheimer et al., 2011a) that originates from depths greater than those recorded by the most primitive melt inclusions (Chapter 3). All of this points to a volcanic system that is, and always has been, controlled by the flux of mantle-derived carbon. Indeed, many separate studies have concluded that various aspects of the Erebus system are controlled by the influx of heat and carbon, including polybaric fractional crystallization throughout the magmatic system (Oppenheimer et al., 2011a), bimodal eruptive behavior in the lava lake (Oppenheimer & Kyle, 2008a), shallow magma chamber processes (Moussallam et al., 2013), fumarolic degassing and the formation of ice caves and ice towers (Curtis & Kyle, 2011), and now crystallization in earlier erupted, primitive lavas (this study).  $CO_2$  flushing has been invoked to explain characteristics of degassing and melt inclusions at other volcanoes including Stromboli (Allard, 2010), Vesuvius (Marianelli et al., 2005), Etna (Shinohara et al., 2008; Spilliaert et al., 2006; Tagliani et al., 2012) and those in southeastern Guatemala (Walker et al., 2003) that sit atop large sedimentary

carbonate reservoirs, the devolatilization of which could provide the necessary excess carbon (Iacono-Marziano et al., 2009). As Erebus has no such shallow carbon reservoir and likely derives all of its volatiles from the same mantle source responsible for magma production, I propose Erebus as an archetype for mantle-sourced carbon-controlled volcanism on Earth.

## 4.7 Conclusions

In this study I have performed phase equilibria experimentation on natural basanite and phonotephrite lavas aimed at understanding the deep and intermediate portions of the plumbing system beneath Erebus volcano located on Ross Island, Antarctica. Results indicate that the two most prolific rock suites on Ross Island, the Erebus Lineage (EL) lavas found on the Erebus cone and Dry Valley Drilling Project (DVDP) lavas found on nearby Hut Point Peninsula, are likely sourced from the same region where parental basanitic melt is produced from the partial melting of mantle material. Although EL and DVDP rocks are quite similar, key mineralogical differences (notably, the lack or presence of kaersutite amphibole in EL and DVDP lavas, respectively) can be attributed to the following distinct differentiation conditions:

- 1. The EL lavas are extremely dry, with the equilibrium  $XH_2O^{fluid}$  approaching 0. This, plus a sustained high-temperature regime >1075 °C, points to the extreme dehydration of EL lavas via the continuous influx of CO<sub>2</sub>-rich gas sourced from quite deep (perhaps in the mantle), which flushes the system of H<sub>2</sub>O and promotes crystallization throughout the plumbing system.
- 2. DVDP lavas, while still quite dry, are slightly more water-rich, with an equilibrium XH<sub>2</sub>O<sup>fluid</sup> ~0.25. This increase in water activity is likely caused by the lack of CO<sub>2</sub> fluxing through the DVDP fracture network, which characterizes the main EL conduit, and not by a distinct parental magma. In addition, while DVDP basanites were formed at temperatures similar to the EL, the intermediate and evolved DVDP lavas must have been formed in colder conditions (maximum ~1000 °C). These observations coupled with

the fact that DVDP lavas, in contrast to the EL, are not still erupting suggests that the conduit feeding the lava flows that formed Hut Point Peninsula was a short-lived offshoot of the main Erebus conduit, which is not subject to the influx of hot  $CO_2$ -rich gas that likely sustains the Erebus lava lake.

My results have important implications for the influence of  $CO_2$  degassing deep within evolving magmatic systems. In addition, I provide more evidence that sustained high-temperature alkalic volcanism at the surface (i.e. the Erebus lava lake) is enabled by the direct connection to mantle reservoirs at depth that provide a constant input of heat and gas, and that these such systems form in continental rift systems.

# Chapter 5

# Sulfur Degassing at Erebus: Contributions from Basanite and Phonolite Melts

# 5.1 Abstract

Here I present the results of experiments performed to investigate the solubility behavior of sulfur in C-O-H-S-bearing melts. Fluid saturated experiments using phonolite and basanite melts from Erebus volcano were equilibrated with C-O-H-S fluids. S-rich, but fluid undersaturated runs containing no CO<sub>2</sub> and minimal ( $<\sim$ 1.5 wt %) H<sub>2</sub>O were also performed. The starting material compositions represent the compositional end-members of the Erebus lava suite. Experimental results thus allow me to place broad constraints on sulfur degassing throughout the Erebus plumbing system. Experiments show an increase in sulfur dissolution with increasing sulfur fugacity, in agreement with previous studies. The partitioning of sulfur between fluid and melt is strongly influenced by the composition of the fluid phase and of the melt (particularly with respect to FeO and SiO<sub>2</sub> in the melt). Further, a thermodynamic approach has been developed to quantify the experimental data. This approach allows for the calculation of the composition of an equilibrium fluid phase given a minimal set of parameters, such as pressure, temperature, and  $fO_2$ .

# 5.2 Experimental Overview

The sulfur carrying capacity of basanite and phonolite melts has been experimentally investigated both at and below sulfide saturation. Four imposed redox states have been investigated for each composition, with final oxygen fugacities ranging from  $\Delta NNO = -7.03$  to +1.68 in phonolites and  $\Delta NNO = -2.50$  to +2.57 in basanites ( $\Delta NNO$  being the deviation in log units from the nickel-nickel oxide buffer). For each redox state, sample capsules have been prepared both with and without  $CO_2$ . Samples with  $CO_2$  typically have extremely high  $XCO_2^{fluid}$  (>0.75) in order to represent the extremely dry and  $CO_2$ -rich conditions characteristic of the Erebus volcanic system.

#### 5.2.1 Why Does Sulfur Degas?

Because so many factors influence sulfur solubility, fluid/melt partitioning, and the storage of large proportions of sulfur in a crystalline phase, modeling sulfur degassing in a natural system is extremely complex. This complexity is compounded by the fact that sulfur can exist in one of nine oxidation states from  $S^{2-}$  to  $S^{6+}$ . Unlike H<sub>2</sub>O and CO<sub>2</sub> whose solubilities are largely pressure dependent, factors such as melt composition, temperature,  $fO_2$  and  $fS_2$  place the strongest controls on whether or not sulfur will degas from a melt.

An understanding of how all of these parameters work in concert to control sulfur solubility and exsolution is crucial to modeling sulfur degassing from a volcano such as Erebus, as contributions to the surface gas output from several regions within the magma plumbing system must be considered. Sulfur dioxide fluxes have, over the past 40 years, been widely measured at volcanoes the world over, and SO<sub>2</sub> emission rates are often used as a proxy for volcanic activity. For ancient eruptions, a direct measurement of the sulfur output is not possible, and so we must rely on measurements of sulfate concentrations in polar ice cores and/or the sulfur concentration of melt inclusions to constrain sulfur outputs (and, thus, environmental impacts) of these eruptions. Unfortunately, melt inclusions do not
record the amount or composition of any coexisting pre-eruptive fluid phase. Excess sulfur included in this fluid phase has been invoked to explain discrepancies in remote sensing and melt inclusion data at many volcanoes (famously for the 1991 eruption of Mt. Pinatubo; Wallace & Gerlach, 1994, also see the review of Shinohara, 2008). Experimental studies are thus necessary if we wish to begin to model S exsolution in melts with the ultimate goal of constraining total volatile budgets of eruptions.

## 5.3 Experimental Methods

### 5.3.1 Starting Material

In order to investigate the sulfur transport capacity of both primitive basanite and evolved phonolite melt, two starting materials were used, reflecting these two extremes (KI-04 basanite and ERE-97018 phonolite; Table 2.1). The chosen starting compositions represent the two end-members of the Erebus lava suites (see Chapter 2), which are related by fractional crystallization (Kyle et al., 1992). Elemental S was mixed with the starting material before loading into the experimental capsules to create batches of starting material each containing a specific concentration of S. For ERE phonolite runs, batches of Low S (containing no added elemental S), 125 ppm S, 500 ppm S, and 1 wt% S were used. For KI basanite runs, batches of Low S, 500 ppm S, 2500 ppm S, and 1 wt% S were used.

### 5.3.2 Preparation of Experimental Capsules

Because the starting materials were fused in air (extremely oxidizing conditions), it was expected that reduction of iron during experiments under more reducing conditions would contribute extra H<sub>2</sub>O to the system via the reaction:

$$Fe_2O_3 + H_2 \Leftrightarrow 2FeO + H_2O$$
 (5.1)

The amount of  $H_2O$  added through this reaction varies depending on the starting glass composition and the oxygen fugacity of the run (i.e., more reducing conditions will produce more  $H_2O$ ). At the most reducing experimental conditions  $(\log fO_2 = -12)$ , the amount of  $H_2O$  introduced to the experimental capsule via iron reduction is 0.49 wt% in ERE-97018 and 1.45 wt% in KI-04. In order that all run product glasses contained approximately 1 or 1.5 wt%  $H_2O$  (for experiments with ERE and KI starting material, respectively), the  $H_2O$  addition via iron reduction was calculated for each experimental  $fO_2$  condition, and the necessary amount of liquid  $H_2O$  was subsequently added to the experimental capsule via micro-syringe. In order to simulate the very C-rich, dry conditions of Erebus lavas (see Chapter 4; Moussallam et al., 2013), enough silver oxalate ( $Ag_2C_2O_4$ ) to produce ~10 wt% CO<sub>2</sub> upon volatilization was added to some runs. Details of all experimental capsules are listed in Table 5.1.

Noble metal capsules – Au for ERE-97018 and  $Au_{90}Pd_{10}$  for KI-04 – were used as sample containers. Capsules were ~2 cm long with an inner diameter of 2.5 mm and an outer diameter of 2.9 mm. Capsules were crimped and welded on one end, and appropriate amounts of liquid water and silver oxalate were added to the capsule followed by ~50-60 mg of starting material powder. Capsules were weighed, then welded shut while wrapped in a wet paper towel to limit capsule heating and subsequent volatile loss. Capsules were then weighed again to check for volatile loss or gain during welding, placed in a drying oven at ~110 °C, and weighed a third time to check that no leaks were present. Capsules that showed a weight loss >0.2 mg after either welding or oven were considered to have leaked at least part of their fluid phase and were discarded.

Experiments were run in vertically working IHPVs at the Université d'Orléans, France. The pressure vessels and furnaces used for these experiments are the same as in Chapter 4. The amount of hydrogen added to the pressure vessel was varied to obtain a range of oxygen fugacities, and hydrogen partial pressure was monitored using a Shaw membrane (Scaillet et al., 1992). The equilibrium oxygen fugacity of the experiment was calculated using the reading from the Shaw membrane just before quench and the composition of any coexisting C-O-H-S fluid phase (see Section 5.4.4). Run temperatures were chosen so as to be close to the liquidus (1030-1050 °C for phonolite, 1200 °C for basanite), and all experiments were run

Experiment	Batch Used	Duratio	n P	T (00)	$\log fO_2 \star$	pH <sub>2</sub>	mGlass	$\mathrm{mAg}_{2}\mathrm{C}_{2}\mathrm{O}_{4}$	$\rm mH_2O$
		(h)	(bar)	(°C)					
ERE-97018 I	Phonolite Exper	riments							
PV_PHON-1	1								
$E_{S01}$	1  wt% S	70	1016	1050	-6	0	0.05	0.02	0.0006
$E_{S02}$	500  ppm S	70	1016	1050	-6	0	0.0512	0.0215	0.0007
$E_{S03}$	125  ppm S	70	1016	1050	-6	0	0.0504	0	0.0005
DU DUON									
PV_PHON-3	3	10	1010	1090	10	17 19	0.0500	0.0107	0.0004
E_507	1 wt% S	40	1012	1030	-10	17.13	0.0503	0.0197	0.0004
E_508	500 ppm S	46	1012	1030	-10	17.13	0.0495	0.0198	0.0002
E_S09	125 ppm S	40	1012	1030	-10	17.13	0.0509	0	0.0003
E_S010	500 ppm S	40	1012	1030	-10	17.13	0.0504	0	0.0005
PV PHON-	1								
E S011	1 wt% S	70.5	1026	1030	-8	29	0 0595	0.0187	0.0003
$E_{S012}$	500 ppm S	70.5	1026	1030	-8	2.9	0.0000 0.0397	0.0107	0.0003
$E_{S012}$	125 ppm S	70.5	1026	1030	-8	2.9	0.0692	0	0.0005
	FF							•	
PV PHON-5	5								
$E \overline{S}015$	500  ppm S	72	963	1030	-12	18.29	0.0611	0.0196	0.0003
ES016	500  ppm S	72	963	1030	-12	18.29	0.0776	0	0.0003
ES017	Low S	72	963	1030	-12	18.29	0.0806	0	0.0004
KI-04 Basan	ite Experiment	s							
PV_BAS-1B	2 <b>7</b> 00 0	_	1001	1000					
K_S02B	2500  ppm S	5	1001	1200	-6	0.5	0.0509	0.0197	0.0006
K_S04	Low S	5	1001	1200	-6	0.5	0.0502	0	0.0004
K_S05	500 ppm S	5	1001	1200	-6	0.5	0.0699	0	0.0005
K_S06	1  wt% S	5	1001	1200	-6	0.5	0.0707	0.0198	0.0006
DV DAGO									
FV DAS-2 K S03	Low S	55	1000	1200	-10	12.04	0.063	0	0
K_505 K_507	2500 ppm S	5.5	1000	1200	-10	12.94 12.94	0.005	0 0202	0
K_S08	500  ppm S	5.5	1000	1200	-10	12.94	0.0611	0.0198	0
11_500	ooo ppin o	0.0	1000	1200	10	12.01	0.0010	0.0100	0
PV BAS-3									
$K \overline{S}09$	1  wt% S	5	1000	1200	-8	2.27	0.0613	0.0216	0.0003
KS010	2500  ppm S	5	1000	1200	-8	2.27	0.0611	0.0223	0.0003
$\overline{K}$ S011	500  ppm S	5	1000	1200	-8	2.27	0.0806	0	0.0003
K S012	Low S	5	1000	1200	-8	2.27	0.0814	0	0.0003
PV_BAS-4									
K_S013	1  wt% S	5	1039	1200	-12	28.16	0.0612	0.021	0
K_S014	2500  ppm S	5	1039	1200	-12	28.16	0.0603	0.0205	0
$K_{S015}$	500  ppm S	5	1039	1200	-12	28.16	0.0862	0	0
$K_{S016}$	Low S	5	1039	1200	-12	28.16	0.095	0	0

Table 5.1: Details of experimental capsules

All masses (m) reported in grams, times in hours, pressure (P) in bars, and temperature (T) in °C. Name above each group of experiments is the run name. Sulfur concentrations under "Batch Used" refer to the amount of elemental S mixed with the starting material powder before being loaded into capsule. mX is the mass of each component X (Glass = starting material powder;  $Ag_2C_2O_4$  = silver oxalate powder (CO<sub>2</sub> source);  $H_2O$  = liquid water) added to the capsule.  $\log fO_2 \star$  is the oxygen fugacity used to calculate the amount of liquid water to add to each experimental capsule (see Section 5.3.2) and was determined based on the  $fO_2$  achieved for previous runs perfumed in the same pressure vessel with the same target pH<sub>2</sub>. at a total pressure of 1000 bars. Experimental duration ( $\sim 5$  h for basanite or  $\sim 3$  days for phonolite) was chosen based on the minimum time deemed necessary to attain chemical equilibrium while minimizing the amount of time the noble metal capsules were in contact with the corrosive, sulfur-bearing fluids within the capsules.

## 5.4 Analysis

After the experimental run, the capsules were examined and weighed to check that no fluid loss occurred during the run. Capsules were then punctured, weighed, placed in a drying oven at 110 °C for several minutes, and then weighed again. The difference in weight was attributed to the fluid phase. Typically, a hissing noise and variably strong sulfur smell was noted upon capsule puncture. The metal capsule was then peeled away, and the sample was mounted in epoxy resin and polished for analysis on electron microprobe (EMP). Selected samples were then doubly polished for analysis via Fourier Transform Infrared (FTIR) spectroscopy.

#### 5.4.1 Major Element Chemistry of Run Products

Electron microprobe (EMP) analyses of the major-element compositions of the glass and crystal phases in starting glasses and experimental run products were performed on a Cameca SX-50 at the Università degli Studi di Padova or on a Cameca SX-100 at the University of Cambridge. Glass was measured using an accelerating voltage of 15 keV, a beam current of 3 nA, a defocused beam size of 10  $\mu$ m, and a counting time of 10 s, analyzing Na first to minimize measurement error due to Na migration. Crystals were measured using an accelerating voltage of 15 keV, a beam current of 10 nA, and a focused beam of 1  $\mu$ m diameter. The immiscible sulfide liquid phases were measured with an accelerating voltage of 20 keV and a beam current of 20 nA.

### 5.4.2 S Speciation via Wavelength Shifts of SK $\alpha$ X-rays

Because experiments were performed over a range of oxygen fugacities, it is expected that sulfur in the experimental glasses will be present as some variable mixture of sulfide and sulfate ions. Using the method of Carroll & Rutherford (1988, also used by Jugo et al., 2005; Lesne et al., 2011a; Métrich & Clocchiatti, 1996; Wallace & Carmichael, 1994), I have measured the wavelengths of SK $\alpha$  radiation [ $\lambda$ (SK $\alpha$ )] in experimental glasses in order to determine the valence state of the dissolved sulfur species therein. This was achieved on electron microprobe by measuring the shifts in the peak wavelengths of emitted SK $\alpha$  X-rays in experimental glasses from those in FeS based on crystalline standards of FeS<sub>2</sub> (pyrite, S as sulfide) and SrSO<sub>4</sub> (celestine, S as sulfate).

Measurement of  $\lambda(SK\alpha)$  was made using the focusing geometry of three spectrometers on a Cameca SX-100 microprobe at the University of Cambridge. Two PET crystals and one LPET crystal was used in order to obtain three independent measurements of the X-ray wavelength shift, thereby decreasing error. Unknowns and standards were measured using an accelerating voltage of 20 keV, a beam current of 40 nA, and a beam size of 25  $\mu$ m. A step scan was made over a range of 0.004 sin  $\theta$  units, centered at the theoretical peak of sulfide. For each point in the scan, the spectrometers were moved 0.00004 sin  $\theta$  units (i.e. 100 steps). For unknowns, each step had a dwell time of 2000 to 2600 ms, and for standards a dwell time of 100 ms/step was used (equivalent to a total beam exposure time of 200–260 s for unknowns and 10 s for standards). High counting times are necessary to obtain reasonable counting statistics (i.e. to maximize the signal to noise ratio). Pyrite and celestine standards were measured once for every two measurements of unknowns, with the shift in the  $\lambda(SK\alpha)$  peak in the unknowns calculated based on the nearest standard measurement. All peak shifts reported here are in terms of shift from the FeS peak. The S oxidation state in samples with very low S (approaching 100 ppm) could not be measured, as the uncertainty in the peak position at such low concentrations is greater than the peak shift itself (Matthews et al., 1999).

The shift of the K $\alpha$  peak from celestine (S<sup>6+</sup>) to FeS (S<sup>2-</sup>) was calculated by measuring the shift from celestine to pyrite  $(S^{-})$  standards and then adding the remaining difference in wavelength from pyrite to FeS. Wallace & Carmichael (1994) obtained a value of the  $\Delta SK\alpha$  of pyrite relative to FeS that was approximately 1/8 (12.66%) of the total shift between FeS (S<sup>2-</sup>) and anhydrite (S<sup>6+</sup>) standards. The authors note that this value is consistent with a linear increase of SK $\alpha$  energy with increasing valance of S. However, many authors utilizing this technique have noted a difference in the SK $\alpha$  peaks of various sulfates, all of which are stoichiometrically  $S^{6+}$ . The shift from pyrite (S<sup>-</sup>) to S<sup>2-</sup> has been measured as 14.8% relative to barite to FeS (Matthews et al., 1999), 17.86% relative to celestine to FeS (Matthews et al., 1994), and as much as 20.19% relative to celestine to ZnS (Winther et al., 1998). I have therefore used the value of Matthews et al. (1994) and have multiplied measured values of  $\Delta SK\alpha$  in celestine standards relative to pyrite by 1.217 to obtain values for the  $\Delta SK\alpha$  relative to FeS. 17.86% of this value was then added to measured values of  $\Delta SK\alpha$  in unknown glasses to obtain values relative to FeS for each sample.

Each sample spectrum was fitted to a Gaussian function and the mean of that Gaussian used as the SK $\alpha$  peak center. The wavelength can then be related to the  $\sin\theta$  values using Bragg's law ( $n\lambda = 2dsin\theta$ ). Values from the three spectrometers were averaged (except in cases where data from the smaller PET crystals were too poor to apply a Gaussian fit, in which case values from only the larger LPET crystal were used).

#### 5.4.3 Dissolved Volatile Contents via FTIR Spectroscopy

Glass chips from each sample capsule (except samples ERE\_S15, ERE\_S16, and ERE\_S17, the chips of which were too small to be mounted and polished) were prepared for Fourier transform infrared (FTIR) spectroscopy by doubly polishing each chip until its thickness was approximately 50-250  $\mu$ m. After polishing one side, sample chips were mounted onto a glass slide with crystal bond, and the second side was carefully polished by hand such that the faces of the chip were roughly parallel. Chips were then removed from the glass slide by soaking in ace-

tone and stored in plastic gel caps. Chip thickness was measured with a Mitutoyo digital micrometer with an estimated precision of  $\sim 2 \ \mu m$ .

The concentrations of dissolved  $H_2O$  and  $CO_2$  were measured by FTIR spectroscopy at the Open University using a Thermo Nicolet Nexus FTIR spectrometer and attached Nicolet Continu $\mu$ m infrared microscope. A KBr beamsplitter and MCT detector were used. Spectra were measured in the range 1000-6000 cm<sup>-1</sup> through a 25  $\mu$ m aperture and consisted of 256 scans each at 4 cm<sup>-1</sup> resolution. The background was measured before each sample in order to eliminate any significant contribution of atmospheric water and CO<sub>2</sub> to the sample spectrum. Sample chips were placed across a small hole (~2 mm diameter), which was drilled into an aluminum plate. Measurements were also made with chips placed on a silica glass slide, which reduced noise in the near IR but did not allow for quantification of any carbon species. The concentrations of OH, H<sub>2</sub>O, CO<sub>2</sub>, and CO<sub>3</sub> species were calculated using the Beer-Lambert Law (Ihinger et al., 1994) as outlined in Chapter 3.

Determinations of the concentrations of  $H_2O$ , OH,  $CO_2$ , and  $CO_3$  species were made using background-corrected spectra. Backgrounds were drawn using the same software as in Chapter 4, which allows the user to define regions of a spectrum over which to fit a polynomial of user-determined order to a set of points on either side of the peak of interest. Backgrounds for the near IR peaks (4500 and 5200 cm<sup>-1</sup>) and the molecular  $CO_2$  peak (2345 cm<sup>-1</sup>) were fit to second order polynomials, the total water peak (3500 cm<sup>-1</sup>) to a straight line, and the carbonate and molecular water peaks (1430, 1510, and 1640 cm<sup>-1</sup>) were fit to a third or fifth order polynomial where the fit order was chosen such that the two peaks of the carbonate doublet were roughly equivalent in height.

Sample density was calculated for each sample using the partial molar volumes of the oxide components as determined by Lange & Carmichael (1987) and the partial molar volume of  $H_2O$  from Ochs & Lange (1999). Because the concentration of  $H_2O$  dissolved in the melt affects its density and, in turn, the calculated amount of dissolved  $H_2O$  via FTIR, calculations of the  $H_2O$  contents and densities were done iteratively. The  $H_2O$  concentration was first calculated based on the density of the dry melt. The density was then recalculated based on the "dry"  $H_2O$  content, and a new  $H_2O$  content was calculated. This process was iterated until the change in  $H_2O$  concentration was less than 0.01 wt%.

Absorption coefficients were chosen from the literature based on determinations made for similar glass compositions to those used in this study. For phonolite ERE-97018, the following coefficients in units of L·(mol·cm)<sup>-1</sup> were used: 1.25 and 1.1 for  $\epsilon_{4500}$  and  $\epsilon_{5200}$ , respectively (Carroll & Blank, 1997); 890 for  $\epsilon_{2345}$  (Morizet et al., 2002); 64 for  $\epsilon_{3500}$  (Cioni, 2000); and 249 for  $\epsilon_{1430}$  and  $\epsilon_{1510}$  calculated using the method of Dixon & Pan (1995). For basanite KI-04, the following coefficients were used: 0.58 and 0.56 for  $\epsilon_{4500}$  and  $\epsilon_{5200}$ , respectively (Cocheo, 1993); 63.9 for  $\epsilon_{3500}$  Behrens et al. (2009); and 405.4 for  $\epsilon_{1430}$  and  $\epsilon_{1510}$  calculated from Dixon & Pan (1995). No molecular CO<sub>2</sub> at 2345 cm<sup>-1</sup> was found in basanite samples, while both CO<sub>2</sub> and carbonate were found in phonolite samples. Because the measurement of the total water peak at 3500 cm<sup>-1</sup> is prone to error resulting from a saturated signal in thicker samples, the near IR peaks were used to quantify H<sub>2</sub>O concentrations in the glasses. A comparison of H<sub>2</sub>O concentration values measured via the 3500 cm<sup>-1</sup> or near IR peaks revealed a linear offset of the form:

$$H_2 O^{tot,3500} = a H_2 O^{tot,nearIR} + b (5.2)$$

where a = 1.1701 and b = 0.1769 (R<sup>2</sup>=0.83). For consistency, a correction using this relationship was applied to the 3500 cm<sup>-1</sup> values for samples for which no near IR measurement was made. These corrected near IR values were then used in subsequent analysis.

# 5.4.4 Modeling of the Experimental Fluid Phase Compositions

Because the fluid phase was not measured directly, I have estimated the fugacities of all major species in the fluid using a set of thermodynamic and mass balance relationships. My thermodynamic approach assumes that all species in the fluid mix ideally. See Section 6.1.1 for a discussion of why an ideal mixing approach was chosen.

First, it is necessary to estimate the composition of the fluid phase in terms of mole fractions of each volatile component in the fluid. Because the total amount of each volatile species ( $H_2O$ ,  $CO_2$ , and  $S_{tot}$ ) added to the experimental capsule is known and the concentrations of those species in the glass is known, it is straightforward to calculate the composition of the fluid phase (for samples with no solid S phases) as the difference of these two values. In these mass balance calculations, I have not corrected for crystal content, as it is generally low (<5 vol%) and should have a negligible effect. For experiments in which sulfur-bearing phases crystallized, the amount of sulfur in the fluid phase could be calculated if the total mass of the fluid (measured by weight loss; see Section 5.4) was known. Alternatively, the phase proportions were calculated by image analysis (see Section 4.4.2) and the mass of S in the solid phases calculated using EMP analyses. Even for runs with no sulfur added to the experimental capsule (Low S batch of starting material), some S was measured in the glass, indicating that the starting material powder was not S-free after vitrification. The highest amount of S measured in the glass for a run with Low S starting material is from run KI S04, which has 514 ppm S in the glass (equivalent to  $2.61 \times 10^{-05}$  g S). A correction of this amount, in grams, was added to the value for the amount of S added to the experimental capsule for all samples.

The only direct measure of the fluid phase during the experiment was the measure of  $P_{H_2}$  made via Shaw membrane. The partial pressure of hydrogen is related to its fugacity by:

$$fH_2 = \gamma H_2 \cdot P_{H_2} \tag{5.3}$$

where  $\gamma H_2$  is the fugacity coefficient of hydrogen gas. Because the composition of the fluid phase has been calculated, I can also calculate the fugacities of H<sub>2</sub>O and CO<sub>2</sub> in the fluid by:

$$fH_2O = fH_2O^{pure} \cdot X^{fluid}_{H_2O} \tag{5.4}$$

$$fCO_2 = fCO_2^{pure} \cdot X_{CO_2}^{fluid} \tag{5.5}$$

where  $fH_2O^{pure}$  and  $fCO_2^{pure}$  are the fugacities of the pure species at experimental P and T, and  $X_i^{fluid}$  is the mole fraction of that species in the fluid phase. Knowing the fugacities of  $H_2O$  and  $H_2$  I can then calculate the  $fO_2$  of the experiment using the reaction of formation of  $H_2O$  from the elements, which yields:

$$fO_2 = \left(\frac{fH_2O}{K_F^{H_2O} \cdot fH_2}\right)^2 \tag{5.6}$$

where  $K_F^{H_2O}$  is the equilibrium constant of formation. With these values I can now calculate the partial pressure of each species: H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, and S<sub>tot</sub>, which is the sum of all S species:

$$P_{S_{tot}} = P_{S_2} + P_{SO_2} + P_{H_2S} \tag{5.7}$$

The partial pressure is calculated by dividing the fugacity of a species with its fugacity coefficient, as in Equation 5.3. Because all partial pressures must add up to the total pressure ( $P_{tot}$ , the experimental pressure), I can calculate  $P_{S_{tot}}$  as:

$$P_{S_{tot}} = P_{tot} - \Sigma P_j \tag{5.8}$$

where  $\Sigma P_j$  is the sum of the partial pressures of all non-sulfur species. I then rewrite Equation 5.7 in terms of fugacity as:

$$P_{S_{tot}} = \frac{fS_2}{\gamma S_2} + \frac{fSO_2}{\gamma SO_2} + \frac{fH_2S}{\gamma H_2S}$$
(5.9)

As with  $fH_2O$  in Equation 5.6, the fugacities of SO<sub>2</sub> and H<sub>2</sub>S can be written in terms of the reactions of formation from the elements:

$$fSO_2 = K_F^{SO_2} \cdot fS_2^{\frac{1}{2}} \cdot fO_2 \tag{5.10}$$

$$fH_2S = K_F^{H_2S} \cdot fH_2 \cdot fS_2^{\frac{1}{2}}$$
(5.11)

Substituting these relationships into Equation 5.9 then allows me to isolate  $fS_2$ 

as a single variable and solve via the equation:

$$P_{S_{tot}} = \frac{fS_2}{\gamma S_2} + \frac{K_F^{SO_2} \cdot fS_2^{\frac{1}{2}} \cdot fO_2}{\gamma SO_2} + \frac{K_F^{H_2S} \cdot fH_2 \cdot fS_2^{\frac{1}{2}}}{\gamma H_2S}$$
(5.12)

The remaining two unknowns,  $f SO_2$  and  $f H_2 S$ , can then be solved for by using Equations 5.10 & 5.11. Values for the equilibrium constants of formation from the elements,  $K_F^i$ , are from Robie et al. (1978). Fugacity coefficients for all species have been calculated using a Modified Redlich-Kwong equation of state (MRK EoS; see Flowers, 1979; Holloway, 1977), given critical temperature  $T_c$ , critical pressure  $P_c$ and the acentric factor  $\omega$  (see Prausnitz et al., 1998). Values used in the above calculations can be found in Table 5.2.

Table 5.2: Critical data, acentric factors, and fugacity coefficients used in thermodynamic modeling

Species	$T_c$ (K)	$\mathbf{P}_c$ (bar)	ω	$\gamma~1000^{\circ}{\rm C}$	$\gamma$ 1200°C
$H_2$	33.0	12.9	-0.216	1.183	1.158
$O_2$	154.6	50.4	0.025	1.187	1.166
$H_2O$	647.3	221.2	0.344	0.9108	0.9669
$\rm CO_2$	304.1	73.8	0.239	1.176	1.171
$SO_2$	430.8	78.8	0.256	1.139	1.157
$H_2S$	373.2	89.4	0.081	1.129	1.136
$S_2$	1313	118	0.209	0.2356	0.3556

Notes: Critical data and acentric factors are from Prausnitz et al. (1998) except for data for  $S_2$ , which is from Gates & Thodos (1960). Fugacity coefficients calculated with a Redlich-Kwong equation of state (see text).

## 5.5 Results

#### 5.5.1 Crystalline Phase Assemblages

The crystalline phase assemblages of all experiments are listed in Table 5.3 and are shown in Figure 5.1. In ERE-97018 phonolite experiments, the only silicate phase present is feldspar (Table 5.4). All feldspars are similar in composition and are classified as anorthoclase feldspars (on average, approx.  $An_{25}-Ab_{63}-Or_{12}$ ).

Feldspars only crystallized in runs containing CO<sub>2</sub>, likely due to the dilution of H<sub>2</sub>O in the fluid and melt (lower fH<sub>2</sub>O and H<sub>2</sub>O<sup>melt</sup>). This is in agreement with the very dry feldspar liquidus established by experiments in Chapter 4. In KI-04 basanite experiments, the only silicate phase is olivine (Table 5.5). All olivines are similar in composition with an average forserite content of ~Fo<sub>80</sub>. For KI-04 samples, the stability of FeTi oxides is limited to runs with fO<sub>2</sub> > NNO, while in ERE-97018 samples, FeTi is stable down to at least NNO-2.60 (excluding sample ERE S12, see discussion below).

The only five experiments to contain sulfur-bearing solids are ERE\_S01, ERE\_S07, & ERE\_S12, which contain pyrrhotite, and ERE\_S08 & ERE\_S11, which contain immiscible sulfide liquid (ISL). Compositions of these phases (except ERE\_12 pyrrhotites, which were too small for good analysis) are reported in Table 5.6. No KI-04 basanite experiments crystallized S-bearing phases. The presence or lack of these phases is important as they mark the saturation of a melt with respect to sulfide. Because such large proportions of the sulfur in a magmatic system can be stored in these phases (typically in pyrrhotite in natural systems; Scaillet et al., 1998) sulfur "solubility" (i.e. the amount of sulfur that can be dissolved in a melt) is often referred to more correctly as the sulfur content at sulfide saturation (SCSS) or, in more oxidized systems, the sulfur content at anhydrite saturation (SCAS).

Pyrrhotites in both experiments where good analysis was possible are of similar composition, while two distinct compositions of ISL exist in sample ERE\_S11: ISL, dark & ISL, bright, so named for their coloration in both reflected light and electron backscatter images (Figure 5.2). One of the ISL compositions (ISL, dark) is similar to that of the pyrrhotites, while the other (ISL, bright) contains almost 80 wt% silver, derived from the silver oxalate (Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) added to the experimental capsule as a source of CO<sub>2</sub>. In a study on sulfur solubility in rhyolites, Clémente et al. (2004) found ISL only under oxidizing conditions. Both of my experiments that contain ISL are rather reduced ( $\Delta$ NNO = -4.51 & -5.01), however both contained silver oxalate, so I surmise that the addition of sufficient Ag may stabilize ISL to more reducing conditions. This does not explain the lack of ISL in ERE\_S01, which was saturated in sulfide (pyrrhotite), contained sil-



Figure 5.1: Phase assemblages of ERE-97018 phonolite (upper) and KI-04 basanite (lower) experiments plotted in terms of oxygen fugacity relative to the NNO buffer versus the amount of sulfur in the system (as the wt% of sulfur added to the experimental capsule). Gray vertical line represents the iron-wüstite buffer.

Run	Т	Р	$H_2O^{melt}$	$\mathrm{CO}_2^{melt}$	$\mathbf{S}^{melt}$	Run Products
	$(^{\circ}C)$	(bar)	$(\mathrm{wt}\%)$	(ppm)	(ppm)	
ERE-97018	Phono	lite Experi	ments			
$ERE\_S01$	1050	1016	1.18	681	97 (35)	Ро
$ERE\_S02$	1050	1016	0.97	1360	112(32)	FeTi, Fspar
$ERE_{S03}$	1050	1016	0.89	0	59(35)	FeTi
$ERE\_S07$	1030	1012	0.95	170	209(40)	Fspar, Po
$ERE_{S08}$	1030	1012	$0.65^{\dagger}$	$52^{\dagger}$	456(72)	FeTi, Fspar, Liquid S
$ERE_{S09}$	1030	1012	0.92	0	93(27)	FeTi
$ERE_{S10}$	1030	1012	1.40	0	270 (99)	
$ERE_{S11}$	1030	1026	0.86	765	388~(67)	Liquid S
$ERE_{S12}$	1030	1026	0.20	362	139(33)	Fspar, Po
$ERE\_S13$	1030	1026	0.70	0	139(43)	All glass
$\text{ERE}_{S15}$	1030	963	$0.80^{\dagger}$	$254^{\dagger}$	95 (36)	Fe metal, Fspar
$ERE\_S16$	1030	963	$0.88^{\dagger}$	0	103(31)	All glass
$ERE\_S17$	1030	963	$0.99^{\dagger}$	0	44(22)	All glass
VIOLD		. ,				
KI-04 Basa	nite $Ex_j$	periments	0.65	000	1005 (100)	р т:
KI_S02B	1200	1001	0.65	929	1005(183)	Fell
KI_S03	1200	1000	1.20	258	215(156)	All glass
KI_S04	1200	1001	0.83	0	514(127)	FeTi
KI_S05	1200	1001	0.72	0	493 (92)	FeTi
KI_S06	1200	1001	0.61	1574	1258 (128)	Fe'I'i, Olivine
KI_S07	1200	1000	1.12	709	199(103)	All glass
KI_S08	1200	1000	1.04	180'	48 (33)	All glass
KI_S09	1200	1000	0.21	803	216 (90)	Olivine
$KI_{S10}$	1200	1000	0.67	925	177 (65)	All glass
$KI_{S11}$	1200	1000	1.00	357	104 (80)	FeTi, Olivine
$KI_{S12}$	1200	1000	0.84	0	74	FeTi
$KI_S13$	1200	1039	0.42	0	425~(153)	
$KI_S14$	1200	1039	0.53	189	87(40)	Olivine
$KI_S15$	1200	1039	1.13	308	158 (52)	
KI_S16	1200	1039	1.24	214	150(30)	

Table 5.3: Dissolved volatile concentrations and crystal phases in experimental products.

Notes: FeTi = FeTi oxides; Fspar = feldspar; Po = pyrrhotite; Liquid S = Fe-Ag-S immiscible liquid. Numbers in parentheses are standard deviations. <sup>†</sup>Indicates  $H_2O^{melt}$  and  $CO_2^{melt}$  calculated with the model of Papale et al. (2006)

Exp.	2	sd	8	sd	12	sd	16	sd
n	6		9		10		6	
$SiO_2$	58.18	0.79	61.20	1.14	61.04	1.21	60.06	0.30
$\mathrm{TiO}_2$	0.08	0.04	0.08	0.02	0.19	0.17	0.12	0.15
$Al_2O_3$	25.88	0.47	22.98	0.97	23.41	0.68	24.87	0.56
$FeO^*$	1.09	0.06	0.78	0.07	0.66	0.76	0.48	0.49
MnO	0.02	0.02	0.03	0.02	nd	0.13	0.01	0.01
MgO	0.03	0.02	0.03	0.01	0.12	0.35	0.09	0.12
CaO	6.63	0.33	6.12	0.48	4.84	0.19	5.59	0.40
Na <sub>2</sub> O	6.87	0.23	7.29	0.23	7.47	0.49	7.03	0.13
$K_2O$	1.21	0.09	1.50	0.21	2.25	0.03	1.75	0.40
Total	96.76	1.34	94.34	1.97	99.47	0.98	98.66	0.67
An	23.89		29.37		23.01		24.49	
Ab	64.33		62.15		64.26		60.72	
Or	11.78		8.48		12.74		14.79	
*Total	iron repor	ted as FeC	)					
Concen	trations gi	ven in wt	%. n: nu	mber of ar	nalyses; sd	: standard	deviation	1

Table 5.4: Composition of experimental feldspars in phonolite ERE-97018

Exp.	6	$\operatorname{sd}$	9	sd	14	sd
n	4		10		7	
$SiO_2$	40.34	0.02	39.94	0.14	40.95	0.24
$\mathrm{TiO}_2$	0.12	0.03	0.11	0.02	0.14	0.02
$Al_2O_3$	0.18	0.18	0.07	0.01	0.08	0.02
FeO*	12.42	0.03	13.97	0.36	8.46	0.68
MnO	0.25	0.02	0.22	0.02	0.24	0.04
MgO	45.90	0.38	44.66	0.24	49.07	0.50
CaO	0.45	0.05	0.48	0.02	0.43	0.02
$P_2O_5$	0.04	0.01	0.10	0.03	0.36	0.20
$\mathrm{Cr}_2\mathrm{O}_3$	0.02	0.02	0.05	0.02	0.06	0.03
NiO	0.08	0.02	0.02	0.02	0.01	0.01
Total	99.79	0.17	99.62	0.30	99.79	0.44
Fo	78.70		76.17		85.29	

Table 5.5: Composition of experimental olivines in basanite KI-04

\*Total iron reported as FeO

Concentrations given in w<br/>t $\%.\,$ n: number of analyses; sd: standard deviation; Fo<br/>: forsterite content

Exp.	E-01 Po	sd	E-07 Po	sd	E-11 ISL, brigi	sd ht	E-11 ISL, dar	sd k	E-08 ISL	sd
n	2		3		2		2		2	
Ag	_	_	_	_	79.44	0.86	0.23	0.04	21.52	17.39
Fe	61.27	0.81	59.23	0.49	4.54	1.68	59.06	0.63	43.01	10.91
$\mathbf{S}$	36.59	2.23	35.70	2.86	15.72	0.12	38.77	0.23	29.71	7.15
Tot	97.85	1.42	94.93	3.29	99.70	0.62	98.06	0.87	94.23	2.32
			•	Ъ	D 1	TOT T		10.1 11		

Table 5.6: Compositions of experimental pyrrhotites and immiscible sulfide liquids.

Concentrations given in wt %. Po = Pyrrhotite; ISL = Immiscible sulfide liquid; sd = standard deviation; n = number of analyses.

ver oxalate, and was much more oxidized ( $\Delta NNO = -1.62$ ) than ERE\_S08 and ERE\_S11. Dark ISL phases in ERE\_S11 have a herringbone morphology and are present within amorphous blebs of bright ISL, suggesting that they may have crystallized out of solution upon quench. The markedly high Ag content in bright ISL blebs highlights the role of sulfur in the creation of ore deposits in volcanic settings.

One sample (ERE S15) contained Fe metal. The oxygen fugacity of this sample is quite low ( $\Delta NNO = -4.88$ ) and is below the iron-wüstite oxygen buffer, meaning that the replacement of iron-oxide by iron metal is in fact expected at these reducing conditions. The majority of samples that crystallized an Fe-rich phase produced the expected mineral (Fe metal or Fe-oxide) with the exception of ERE\_S12, the calculated oxygen fugacity of which is even lower than that of ERE S15 yet contains FeTi oxides. A visible tear in the capsule was observed upon removal of the run from the pressure vessel, indicating that the capsule burst at some point during the run (likely during quench or decompression). A capsule leak during the run might explain why the calculated  $fO_2$  is quite low compared to what is expected based on the phase assemblage, as the fluid phase compositions are calculated based on the assumption that no fluid is lost from the system. The equilibrium fluid in sample  $ERE\_S15$  would have been extremely  $CO_2$ -rich  $(\text{XCO}_2^{fluid} = 0.956)$  and as such would impose a low  $fH_2O$  and, therefore, a similarly low  $fO_2$ . The loss of such a fluid would therefore subject the contents of the capsule to more oxidizing conditions representative of the pressure vessel. The fact that nearly all of the 500 ppm sulfur added to the capsule was dissolved within the



Figure 5.2: Immiscible sulfide liquid (ISL) phases in sample ERE\_S11 as seen in reflected light (top) and electron backscatter (bottom). Bright ISL phases contain  $\sim 80$  wt% silver. Dark ISL phases have a composition similar to pyrrhotites in other samples.

melt after the run (S<sup>melt</sup> = 456 ppm) indicates that any leak must have occurred after enough time had elapsed to allow for S dissolution to occur but close enough to the end of the run that the dissolved S remained in solution. It is not uncommon for capsules with a volumetrically large fluid phase to burst upon quench. If this was in fact the case, this then implies that the crystallization kinetics of FeTi oxides are extremely fast in phonolite melts, as pressure vessels utilizing a fast quench device like that used in this study have a quench rate of ~1000 °C/min (Roux & Lefevre, 1992).

#### 5.5.2 Glass Compositions

Electron microprobe analyses of all experimental glasses are reported in Table 5.7. The chemical evolution of melts from both experimental series is illustrated in the Harker diagrams in Figures 5.3 & 5.4. Both ERE-97018 & KI-04 samples show a distinct decrease in FeO content with melt evolution, owing to the crystallization of iron oxides and iron sulfides. In ERE-97018 samples, none of the other major oxides show much variation with evolution except for the samples that crystallized sufficient amounts of anorthoclase, which show lowered CaO contents in the glass. KI-04 samples show much more pronounced melt evolution with respect to the enrichment or depletion of major oxides in the melt. All oxides show a general enrichment with melt evolution, except for MgO, which decreases sharply for samples containing olivine.

#### 5.5.3 Fluid Phase Compositions

My experiments span a wide range of fluid compositions, with the H<sub>2</sub>O-CO<sub>2</sub>-S fluid ranging from XH<sub>2</sub>O = 0.005–1.000; XCO<sub>2</sub> = 0–0.948; and XS (sum of the mole fractions of all S species) = 0.000–0.995. Oxygen fugacities range from  $\Delta$ NNO = -7.03 to +2.57, and sulfur fugacities range from log  $fS_2$  = -9.363 to +1.314. The fluid compositions and fugacities for all experiments are reported in Table 5.8. For fluid saturated runs (i.e. those with CO<sub>2</sub>), the fluid phase composition was calculated using the thermodynamic approach outlined in section 5.4.4. This approach may not be valid for runs containing no CO<sub>2</sub>, as they are likely fluid

Total	100.12 99.96 96.67	97.79 100.13 97.33 96.71	97.51 97.92 97.88	98.34 100.01 99.96	<ul> <li>33) 97.08</li> <li>7.16</li> <li>97.17</li> <li>96.99</li> </ul>	() 96.67 () 96.73 97.16	98.13 96.73 97.12 96.41	<ol> <li>97.49</li> <li>98.67</li> <li>96.2</li> <li>96.11</li> <li>11 wt% and</li> </ol>
S (ppm)	$\begin{array}{c} 97 \ (35) \\ 112 \ (32) \\ 59 \ (35) \end{array}$	$\begin{array}{c} 209 \ (40) \\ 456 \ (72) \\ 93 \ (27) \\ 270 \ (99) \end{array}$	$\begin{array}{c} 388 \ (67) \\ 139 \ (33) \\ 139 \ (43) \end{array}$	$\begin{array}{c} 95 \ (36) \\ 102 \ (31) \\ 44 \ (22) \end{array}$	$\begin{array}{c} 1005 \ (18\\ 514 \ (127\\ 493 \ (92)\\ 1258 \ (12\end{array}$	$\begin{array}{c} 215 \ (156 \\ 199 \ (103 \\ 48 \ (33) \end{array}$	$\begin{array}{c} 216 \ (90) \\ 177 \ (65) \\ 104 \ (80) \\ 74 \end{array}$	425 (153 87 (40) 158 (52) 150 (30) es are eive
$\rm P_2O_5$	$\begin{array}{c} 0.42 \\ 0.48 \\ 0.36 \end{array}$	$\begin{array}{c} 0.27\\ 0.48\\ 0.29\\ 0.28\end{array}$	$\begin{array}{c} 0.32 \\ 0.39 \\ 0.35 \end{array}$	$\begin{array}{c} 0.35 \\ 0.49 \\ 0.35 \end{array}$	$\begin{array}{c} 0.81\\ 0.78\\ 0.78\\ 0.80\end{array}$	$\begin{array}{c} 0.78 \\ 0.83 \\ 0.79 \end{array}$	$\begin{array}{c} 0.82 \\ 0.76 \\ 0.82 \\ 0.82 \\ 0.77 \end{array}$	0.79 0.93 0.77 0.79
$K_2O$	5.06 5.28 4.65	4.73 5.59 4.60 4.72	4.76 5.04 4.48	5.05 5.08 5.07	$\begin{array}{c} 1.55 \\ 1.60 \\ 1.62 \\ 1.65 \end{array}$	1.69 1.63 1.69	$   \begin{array}{c}     1.69 \\     1.62 \\     1.70 \\     1.52   \end{array} $	1.78 1.94 1.72 1.64 Analyse
$Na_2O$	8.45 8.50 7.99	8.33 8.23 8.29 8.20	8.52 8.57 8.40	8.59 8.35 8.52	3.59 3.51 3.74 3.66	3.68 3.78 3.87	3.95 3.72 3.69 3.65	3.94 4.34 3.71 3.74 ed fO2:
CaO	2.69 2.47 2.82	2.79 2.01 2.76 2.76	2.85 2.30 2.78	2.67 2.64 2.67	$\begin{array}{c} 10.97 \\ 10.90 \\ 10.83 \\ 10.93 \\ 10.93 \end{array}$	11.30 11.30 11.30	$\begin{array}{c} 11.37\\ 11.15\\ 10.90\\ 11.00\end{array}$	12.50 11.90 11.43 11.44 <u>11.44</u>
MgO	$\begin{array}{c} 0.86 \\ 0.83 \\ 0.89 \end{array}$	$\begin{array}{c} 0.99\\ 0.93\\ 0.92\\ 0.96\end{array}$	$\begin{array}{c} 0.95 \\ 1.12 \\ 0.95 \end{array}$	$\begin{array}{c} 0.90 \\ 0.95 \\ 0.92 \end{array}$	9.07 9.10 9.08 8.87	$\begin{array}{c} 9.41 \\ 9.38 \\ 9.35 \end{array}$	8.56 8.98 9.01 9.18	9.36 9.09 9.56 9.56 moeratur
MnO	$\begin{array}{c} 0.21 \\ 0.21 \\ 0.20 \end{array}$	$\begin{array}{c} 0.21\\ 0.21\\ 0.22\\ 0.22\end{array}$	$\begin{array}{c} 0.24 \\ 0.26 \\ 0.25 \end{array}$	$\begin{array}{c} 0.18 \\ 0.21 \\ 0.18 \end{array}$	$\begin{array}{c} 0.20\\ 0.20\\ 0.17\\ 0.19\end{array}$	$\begin{array}{c} 0.18 \\ 0.19 \\ 0.20 \end{array}$	$\begin{array}{c} 0.20\\ 0.20\\ 0.19\\ 0.19\end{array}$	0.19 0.17 0.18 0.18 0.17
FeO tot	3.31 3.84 3.77	2.34 4.26 3.22	3.46 4.84 4.39	$1.97 \\ 4.75 \\ 1.69$	12.20 12.20 12.34 12.09	9.09 8.83 8.47	9.34 11.27 11.39 11.88	4.02 4.77 7.39 7.51 1: run dur
$Al_2O_3$	20.49 20.06 20.25	20.60 19.33 20.40 20.58	20.08 19.61 20.08	20.92 19.97 20.97	$13.73 \\ 13.95 \\ 13.78 \\ 13.77 \\ 13.77$	$\frac{14.34}{14.25}$	$14.40\\14.04\\13.86\\13.84$	15.33 14.86 14.69 14.69
$TiO_2$	$\begin{array}{c} .1) \\ 0.98 \\ 0.98 \\ 0.98 \\ 1.06 \end{array}$	$\begin{array}{c} 7.13)\\ 1.12\\ 0.96\\ 1.08\\ 1.08\\ 1.10\end{array}$	$2.9) \\ 1.04 \\ 1.22 \\ 1.05$	$8.29) \\ 1.00 \\ 1.02 \\ 1.01$	4.37 4.36 4.32 4.41	4.59 4.58 4.59	4.62 4.55 4.48 4.48	4.90 4.87 4.64 4.67 startine
$SiO_2$	$\begin{array}{l} \text{; } \mathrm{PH}_2 = 0 \\ 57.49 \\ 57.34 \\ 57.88 \\ 57.88 \end{array}$	$\begin{array}{l} \text{;} \ \mathrm{PH}_2 = 1 \\ 58.47 \\ 57.73 \\ 58.47 \\ 58.47 \\ 57.81 \end{array}$	C; $PH_2 = 57.60$ 56.49 57.15	$\begin{array}{c} {}^{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_{\circ}_$	$= 0.5) \\ 43.28 \\ 43.27 \\ 43.27 \\ 43.35 \\ 43.35$	$= 12.94) \\ 44.89 \\ 45.15 \\ 45.28$	$\begin{array}{c} 2.27 \\ 44.98 \\ 43.65 \\ 43.82 \\ 43.46 \end{array}$	28.16) 47.07 47.11 46.21 45.73 mtheses as:
nS	; 1050°C 9 5	; 1030°C 8 3 4	5h; 1030° 6 4 4	; 1030°C 7 9 6	C; PH <sub>2</sub> = 7 5 9	C; PH <sub>2</sub> = 3 4	$egin{array}{c} { m PH_2} = \ 7 \ 4 \ 6 \ 2 \ 2 \end{array}$	$\begin{array}{c} \mathrm{PH_2} = \\ 6 \\ 6 \\ 4 \\ 3 \\ \mathrm{in \ \ parter} \end{array}$
n	018; 70h 10 10 5	018; 46h 9 8 4	018; 70.5 8 6	018; 72h 20 12 13	h; 1200°. 7 5 9	h; 1200°6 8 8 8	1200°C; 8 12 7	1200°C; 8 10 4 5 rre eiven
S added <sup>*</sup>	<b>1-1</b> (ERE-97 1 wt% 500 ppm 125 ppm	<ul> <li><b>1-3</b> (ERE-97</li> <li>1 wt%</li> <li>500 ppm</li> <li>125 ppm</li> <li>500 ppm</li> </ul>	1-4 (ERE-97 1 wt% 500 ppm 125 ppm	<b>1-5</b> (ERE-97 500 ppm 500 ppm 125 ppm	.B (KI-04; 5 2500 ppm Low S 500 ppm 1 wt%	; (KI-04; 5.5 Low S 2500 ppm 500 ppm	: (KI-04; 5h; 1 wt% 2500 ppm 500 ppm Low S	i (KI-04; 5h; 1 wt% 2500 ppm 500 ppm Low S conditions a
Experiment	PV PHON ERE_S01 ERE_S02 ERE_S03	<b>PV</b> PHON ERE_S07 ERE_S08 ERE_S08 ERE_S09 ERE_S10	PV_PHON ERE_S11 ERE_S12 ERE_S12	PV PHON ERE_S15 ERE_S16 ERE_S16 ERE_S17	<b>PV BAS-1</b> KI S02B KI S04 KI S05 KI S05 KI S06	<b>PV BAS-2</b> KI 503 KI 507 KI 507	<b>PV BAS-</b> 3 KI <u>S</u> 09 KI S10 KI S11 KI S11 KI S12	PV BAS-4 KI S13 KI S14 KI S14 KI S15 KI S16 Notes: Bun



Figure 5.3: Harker variation diagrams illustrating the evolution of experimental melts in ERE-97018 samples. Open square represents the composition of the starting material. Light blue bars spanning the width of each figure represent  $\pm 1$  standard deviation of the starting material analysis.



Figure 5.4: Harker variation diagrams illustrating the evolution of experimental melts in KI-04 samples. Open square represents the composition of the starting material. Pink bars spanning the width of each figure represent  $\pm 1$  standard deviation of the starting material analysis.

undersaturated. Thus, the model of O'Neill & Mavrogenes (2002) was used to estimate sulfur fugacities for fluid undersaturated runs (including those suspected of leaking their fluid phase during the run) with relatively reducing conditions.

Dissolved H<sub>2</sub>O and CO<sub>2</sub> contents in five samples could not be measured via FTIR (ERE\_S08, 15, 16, 17, and KI\_S08) due to glass chips extracted from the sample capsules being too small to prepare and polish for FTIR analysis. In these cases, melt H<sub>2</sub>O and CO<sub>2</sub> contents were calculated using the model of Papale et al. (2006) based on the total amount of H<sub>2</sub>O and CO<sub>2</sub> in the system. Samples ERE\_16 & 17 did not contain any CO<sub>2</sub>. Because the Papale et al. (2006) model does not consider the presence of sulfur, calculated melt H<sub>2</sub>O contents for these two samples are likely erroneously high, as the presence of sulfur will act to dilute the fluid with respect to H<sub>2</sub>O, thus lowering the fH<sub>2</sub>O, which would result in lower dissolved H<sub>2</sub>O contents. This, then, results in erroneously low XH<sub>2</sub>O<sup>fluid</sup> and high XStot values for these runs.

For samples ERE\_S11 & 12, the mass of sulfur locked in solid S-bearing phases (or ISL), and thus the mass of sulfur in the fluid, could not be reliably calculated. For these samples, the  $fH_2O$  was calculated using the model of Moore et al. (1998) based on the composition and concentration of  $H_2O$  dissolved in the melt.

### 5.5.4 Fluid/Melt Partitioning of Sulfur

In a sulfur-saturated magmatic system, sulfur will partition into three phases: solid (as pyrrhotite or anhydrite), liquid (as dissolved S in the melt  $\pm$  immiscible sulfide liquid) and gas or fluid. Unlike H<sub>2</sub>O and CO<sub>2</sub>, which account for the majority of volcanic volatiles, the partitioning of sulfur will largely depend on the presence of a solid S-bearing phase. With sufficient crystallization of pyrrhotite, for example, the fluid/melt partition coefficient ( $K_D^{fl/m}$ ) for sulfur will decrease to around 1, as pyrrhotite can store nearly all of the sulfur in a magmatic system (Scaillet et al., 1998). If no solid S-bearing phase is present, sulfur will partition between the fluid and melt only. In this case (as is the case for almost all of my experimental samples), the  $K_D^{fl/m}$  for sulfur is influenced by a number of factors including melt

		Table	5.8: Ec	quilibriu	m fluid	phase co	ompositior	ns of all ex	periments			
$\operatorname{Run}$	$\Delta$ NNO	$\Delta FFS$	$f\mathrm{H}_2$	$fH_2O$	$fCO_2$	$\log fS_2$	$log fSO_2$	$log f H_2 S$	$\rm XH_2O^{fl}$	$\mathrm{XCO}_2^{fl}$	$\mathrm{XSO}_2^{fl}$	$\mathrm{XH}_2\mathrm{S}^{fl}$
ERE-97018	Phonolite	Experim	ents									
$ERE_S01 \star$	-1.62	7.48	0.12	17.77	1077	-3.120	-10.26	-2.474	0.019	0.901	0.069	0.010
$ERE_S02\star$	-0.50	3.21	0.12	64.31	1104	-1.846	-8.488	-1.836	0.069	0.924	0.007	0.000
$ERE_S03$	1.68	1.54	0.12	790.5	0	-3.911	-7.341	-2.869	0.854	0	0.146	0.000
ERE_S07	-4.96	5.70	19.72	48.48	1119	-1.241	-13.07	0.700	0.045	0.800	0.000	0.156
ERE_S08	-5.21	5.70	19.72	36.73	1137	-1.285		0.678	0.034	0.811	0.000	0.155
$ERE_S09 \star$	-2.60	5.79	19.72	734.4	0	-4.423	-12.13	-0.892	0.797	0	0.000	0.203
$ERE_S10 \star$	-2.96	6.52	19.72	489.2	0	-3.916	-12.23	-0.638	0.531	0	0.000	0.469
$ERE_S11^{\dagger}$	-3.35	9.18	3.34	52.47					0.056			
$ERE_S12^{\dagger}$	-4.53	9.63	3.34	13.60					0.015			
ERE $S13 \star$	-0.90	5.70	3.34	885.2	0	-2.446	-9.435	-0.674	0.947	0	0.022	0.031
ERE S15	-4.88	2.95	21.05	56.65	1050	-1.367	-13.21	0.665	0.065	0.927	0.000	0.008
$ERE S16 \star$	-6.27	7.11	21.05	11.46	0	-8.381	-17.95	-2.842	0.013	0	0.000	0.989
$ERE_S17 \star$	-7.03	7.11	21.05	4.778	0	-9.363	-19.03	-3.333	0.005	0	0.000	0.995
C 10 171	F -											
NI-U4 Dasai	nue exper	iments										
$KI_{S02B}$	1.09	2.99	0.56	175.2	943.4	-0.934	-5.969	-1.120	0.181	0.805	0.014	0.000
$\mathrm{KI}_{\mathrm{S03}\star}$	-1.44	4.29	14.43	248.2	851.7	-2.597	-9.324	-0.383	0.257	0.727	0.000	0.016
$\mathrm{KI}_{-}\mathrm{S04}$	2.57	-4.09	0.56	967.7	0	-9.334	-8.684	-5.320	1.000	0	0.000	0.000
$\mathrm{KI}_{\mathrm{S05}}$	2.55	0.63	0.56	942.0	0	-4.625	-6.353	-2.965	0.973	0	0.027	0.000
$\mathrm{KI}$ S06	1.07	4.55	0.56	172.2	867.5	-0.311	-5.672	-0.808	0.178	0.740	0.081	0.001
$KI_S07\star$	-2.50	4.69	14.43	73.11	1053	-3.778	-10.98	-0.974	0.076	0.899	0.000	0.025
$\mathrm{KI}_{\mathrm{S08}\star}$	-2.35	3.73	14.43	86.85	1056	-4.789	-11.33	-1.480	0.090	0.902	0.000	0.008
$\mathrm{KI}_{\mathrm{S09}}$	-0.11	6.34	2.53	200.1	845.8	1.314	-6.044	0.816	0.207	0.722	0.042	0.029
$\mathrm{KI}_{-\mathrm{S10}}$	-0.32	5.49	2.53	158.2	955.1	1.153	-6.328	0.736	0.164	0.816	0.010	0.011
$\mathrm{KI}_{\mathrm{S11}\star}$	0.06	4.91	2.53	244.9	853.7	-1.839	-7.444	-0.760	0.253	0.729	0.012	0.006
$\mathrm{KI}_{\mathrm{S12}\star}$	1.24	2.91	2.53	948.9	0	-0.718	-5.708	-0.200	0.981	0	0.018	0.001
$\mathrm{KI}_{-\mathrm{S13}}$	-2.46	4.97	31.40	167.1	923.8	0.567	-8.761	1.536	0.166	0.759	0.000	0.074
$\mathrm{KI}_{-\mathrm{S14}\star}$	-2.47	3.94	31.40	164.9	989.1	-3.813	-10.96	-0.654	0.164	0.813	0.000	0.023
$\mathrm{KI}_{\mathrm{S15}\star}$	-1.07	5.15	31.40	821.8	107.8	-2.217	-8.769	0.144	0.818	0.089	0.001	0.092
$KI_S16\star$	-1.21	3.95	31.40	705.3	334.3	-2.423	-9.005	0.041	0.702	0.275	0.000	0.023
$\dagger$ indicates r using the me	uns where	$fH_2O w$ Neill & N	as calcu. Iavroger	lated usi res (2002	$\frac{1}{2}$	nodel of N	/loore et al.	. (1998). × i	ndicates r	ın where	fS <sub>2</sub> was c	alculated

composition, fluid composition, temperature, and oxygen fugacity.

 $K_D^{fl/m}$  values for sulfur of my experiments show a wide range, with ERE-97018 phonolite values from 22–1629 and KI-04 basanite values from <1–614. These ranges reflect the wide ranges of fluid composition and  $fO_2$  in my experiments. In addition, it is important to note that many of the charges contained very small amounts of fluid (particularly those experiments without  $CO_2$ ), which increases the error associated with the calculation of both fluid compositions and fugacities.

For both compositions, the  $K_D^{fl/m}$  for sulfur is correlated with melt composition (Figures 5.5 and 5.6). In particular, the  $K_D^{fl/m}$  in runs without CO<sub>2</sub> show a remarkably strong negative correlation with the total Fe content of the melt (Figure 5.5). Runs that contained CO<sub>2</sub> generally had a very high XCO<sub>2</sub><sup>fluid</sup> (average 0.76; maximum 0.96). Charges with CO<sub>2</sub>-bearing fluids, which had low fluid sulfur concentrations, therefore show markedly lower  $K_D^{fl/m}$  values. Although less pronounced, these experiments still show a negative correlation with XFeOtot, likely facilitated by the increased S solubility in melts with higher total Fe contents. Similarly,  $K_D^{fl/m}$  values from basanite experiments show a strong positive correlation with melt silica content, in agreement with the observations of previous studies (Figure 5.6, Scaillet et al., 1998).

#### 5.5.5 Sulfur Speciation

Sulfur speciation was determined using the wavelength shifts of SK $\alpha$  radiation peaks in experimental glasses relative to FeS ( $\Delta\lambda(SK\alpha)$ ), and those values are reported in Table 5.9. For many samples, a value of  $\Delta\lambda(SK\alpha)$  could not be obtained because a very low signal to noise ratio (typically resulting from very low S concentrations) prevented good Gaussian fits to the data.

Assuming a linear relationship between  $\Delta\lambda(SK\alpha)$  and the proportion  $S^{6+}/\Sigma S$ allows me to then relate the proportion of oxidized S in my melts to the prevailing



Figure 5.5: Partition coefficients  $(K_D^{fl/m})$  of sulfur in phonolite and basanite experiments as a function of XFeOtot.



Figure 5.6: Partition coefficients  $(K_D^{fl/m})$  of sulfur in basanite experiments as a function of melt silica content.

	$\Delta \rm QFM$	$\Delta\lambda$ (K $\alpha$ )	$\overline{X(S^{6+}/Stot)}$	S	$S^{6+}$	$S^{2-}$
		$(\text{Å x } 10^{3})$		(ppmw)	(ppmw)	(ppmw)
ERE-97018	8 phonolite	experiments				
$ERE\_S01$	-0.9220			97 (35)		
$ERE_{S02}$	+0.1952			112 (32)		
$ERE_{S03}$	+2.3745			59~(35)		
$ERE\_S07$	-4.2671	$1.26\pm0.29$	$0.35\pm0.08$	209(40)	129.58	79.42
$ERE_{S08}$	-4.5083	$3.15\pm0.08$	$0.85\pm0.02$	456(72)	396.72	59.28
$ERE_{S09}$	-1.9064			93(27)		
$ERE_{S10}$	-2.2592			270 (99)		
$ERE\_S11$	$-2.6567^{\dagger}$	$3.10\pm0.13$	$0.80\pm0.03$	388~(67)	310.4	77.6
$ERE_{S12}$	$-3.8296^{\dagger}$	$2.74 \pm 0.35$	$0.76\pm0.06$	139(33)	105.64	33.36
$ERE_{S13}$	-0.2026	$2.89 \pm 0.15$	$0.75 \pm 0.04$	139(43)	104.25	34.75
$ERE\_S15$	-4.1849			95 (36)		
$ERE_{S16}$	-5.5729	$3.02 \pm 0.13$	$0.78\pm0.03$	103 (31)	80.34	22.66
$ERE\_S17$	-6.3328			44(22)		
KI-04 basa	nite experii	nents	0.00 1 0.01	1005 (100)	2.62	6.10
KI_S02B	+1.7809	$1.36 \pm 0.25$	$0.36 \pm 0.01$	1005 (183)	362	643
KI_S03	-0.7426			215(156)	222	200
KI_S04	+3.2652	$1.30 \pm 0.1$	$0.36 \pm 0.03$	514(127)	226	288
KI_S05	+3.2417	$1.38 \pm 0.09$	$0.36 \pm 0.02$	493 (92)	177	316
KI_S06	+1.7659	$1.47 \pm 0.07$	$0.38 \pm 0.02$	1258(128)	478	780
KI_S07	-1.8042			199(103)		
KI_S08	-1.0540	0.01 + 0.05		48(33)	41	1.77
$KI_{S09}$	+0.5819	$0.31 \pm 0.25$	$0.09 \pm 0.06$	216(90)	41	175
KI_SI0	+0.3779			177(65)		
KI_SII	+0.7576			104(80)		
KI_S12	+1.9340			(4	70	959
$KI_{S13}$	-1.(040	$0.30 \pm 0.08$	$0.08 \pm 0.02$	425(153)	(2	303
$M_{015}$	-1.7759			07 (40) 159 (59)		
$M_{01}$	-0.3810			158(52)		
KI_S10	-0.5138			150 (30)		

Table 5.9: SK $\alpha$  peak shift determinations

Numbers in parentheses are standard deviations.

 $^\dagger \text{Oxygen}$  fugacities calculated based on water fugacities calculated with the model of Moore et al. (1998).

 $fO_2$ . This relationship is controlled by the reaction:

$$S_{(melt)}^{2-} + 2O_{2(fluid)} = SO_{4(melt)}^{2-}$$
(5.13)

The proportions of sulfate in my experimental glasses as a function of  $fO_2$ in terms of the FMQ (fayalite-magnatite-quartz) buffer are shown in Figure 5.7. Also plotted are the data of Carroll & Rutherford (1988), Wallace & Carmichael (1994), and Matthews et al. (1999). The curves are empirical fits determined by Wallace & Carmichael (1994, solid line; fit to the data of Carroll & Rutherford, 1988), Jugo et al. (2005, long dashed line; fit to EMP data from the literature), and Jugo et al. (2010, thin dashed line; fit to XANES data).

The basanite KI-04 samples show a reasonable agreement with other data sets and the empirical fits, but the phonolite ERE-97018 samples do not agree whatsoever with the literature data. This is likely due to beam damage (in this case, oxidation) of the samples during the EMP analysis. All samples were subjected to an electron beam for long durations (up to 260 s) at high beam current (40 nA) and accelerating voltage (20 keV). Although this is known to cause significant beam damage, especially to hydrous, alkaline, silica-rich glasses (Humphreys et al., 2006; Morgan & London, 2005), this analytical setup was necessary to increase the signal to noise ratio, particularly for samples with low sulfur contents. Unfortunately, that means that the oxidation state of sulfur in the ERE-97018 phonolite experiments could not be measured.

# 5.6 Discusion

# 5.6.1 Sulfur Carrying Capacity of Basanite and Phonolite Melts

Although the data presented here are insufficient to quantify any empirical relationships describing the sulfur carrying capacity of Erebus melts, I can use the overall trends seen in fluid/melt partitioning of sulfur as well as the sulfur "solubil-



Figure 5.7: Proportion of sulfate relative to total sulfur in our glasses as measured by EMP with  $\Delta\lambda(SK\alpha)$ . Phonolite ERE-97018 samples were likely oxidized during analysis (see text). Curves are empirical fits to EMP (Jugo et al., 2005; Wallace & Carmichael, 1994) and XANES data (Jugo et al., 2010).

ity" (whether at or below sulfide saturation) in phonolite and basanite experiments to broadly assess the sulfur degassing processes at Erebus volcano.

The dissolution, fluid/melt partitioning, and degassing of sulfur in silicate melts are principally influenced by sulfur fugacity, oxygen fugacity, temperature, and melt composition (Carroll & Rutherford, 1987; Clémente et al., 2004; Jugo et al., 2005; Keppler, 2010; Scaillet et al., 1998; Webster & Botcharnikov, 2011). In my experiments, this is best expressed as the concentration of S in the melt as a function of the sulfur fugacity, with points grouped based on oxygen fugacity. Figure 5.8 illustrates this for both basanite and phonolite experiments, grouped as a function of PH<sub>2</sub> added to the pressure vessel as a proxy for oxygen fugacity. The effect of temperature and composition are apparent when comparing the melt S concentration in 1200 °C basanite experiments and 1030 °C phonolite experiments with similar sulfur and oxygen fugacities. Sulfur dissolution is enhanced in the hotter basanite experiments by up to an order of magnitude under the most oxidizing conditions.

Using petrological constraints on the Erebus lavas, I can hypothesize as to the greatest influences upon sulfur degassing ( $fS_2$ ,  $fO_2$ , X, T) in various regions of the Erebus plumbing system. Table 5.10 lists relevant compositional and thermodynamic data for Erebus phonolite, phonotephrite, and basanite. In Erebus melt inclusions, sulfur contents range from <500 ppm in the most evolved phonolites to >2500 ppm in the most primitive basanites (Figure 5.9, Eschenbacher, 1998; Oppenheimer et al., 2011a).

Erebus phonotephrites (AW-82033) have about 50% dissolved S content relative to their basanite parent (DVDP3-295). The temperature does not change much between basanite and phonotephrite lavas. Extensive magma evolution (phonotephrite is a 45% residual melt of basanite) and change in  $fO_2$  are thus likely the main parameters controlling sulfur exsolution in the deep and intermediate regions of the plumbing system. Intermediate and evolved lavas have similar oxygen fugacities, and so changes in T and composition likely drive sulfur degassing in the shallow system.



Figure 5.8: Sulfur concentration in experimental melts as a function of sulfur fugacity. Points are grouped by PH<sub>2</sub>, which serves here as a proxy for oxygen fugacity.



Figure 5.9: Sulfur contents dissolved in melt inclusions from Erebus measured by electron microprobe. The degree of fractionation was determined by correlation of the melt inclusion silica content with the fractionation model compositions of (Kyle et al., 1992). Figure from Eschenbacher (1998) (data also published in Oppenheimer et al., 2011a).

Table 5.10: Average volatile concentrations in Erebus melt inclusions and estimates of temperature, sulfur fugacity, and oxygen fugacity based on analytical and experimental petrology

$XSiO_2$	XFeOtot	$\mathbf{S}^{melt}$ ppm	T ( $^{\circ}$ C)	$\log f S_2$	$fO_2$
Phonolite EA1 0.62	0.05	381	$1000^{1}$	$-2.75^2$	QFM–QFM-1 <sup>3</sup>
Phonotephrite 0.50	AW-82033 0.10	1330	$1081^{4}$	$-3.01^{5}$	$\rm QFM^4$
Basanite DVD 0.46	P3-295 0.10	2166.2	$1100^{6}$	$2.13^{7}$	$NNO+1^6$

Melt inclusion data from Oppenheimer et al. (2011a).

<sup>1</sup>Many studies have indicated a lava lake temperature of ~1000 °C (e.g., Caldwell & Kyle, 1994; Dunbar et al., . 1994; Kyle, 1977), although other studies suggest the temperature could be lower (923 °C, Calkins et al., 2008; 950  $\pm$  25 °C, Moussallam et al., 2013) or higher (1080 °C, Burgisser et al., 2012)

 $^{2}$ Based on the composition of pyrrhotite crystals in a phonolite bomb (Kyle, 1977)

 $^{3}$ Based on phase equilibrium experiments (Moussallam et al., 2013)

 $^{4}$ Based on oxide pairs (Kyle et al., 1992)

 $^5\mathrm{Based}$  on the composition of pyrrhotite crystals (Kyle et al., 1992)

 $^6\mathrm{Based}$  on phase equilibrium experiments (see Chapter 4)

 $^7\mathrm{Calculated}$  using the thermodynamic method described in this chapter

In Erebus Lineage lavas, magma differentiation must occur under a sustained high-temperature regime (>1075 °C; see Chapter 4) until very shallow depths ( $\sim$ 1000 °C in the lava lake), and so sulfur degassing throughout the majority of the plumbing system will be less influenced by changes in temperature than the DVDP lineage lavas, which decreases in temperature from >1075 °C to  $\sim$ 1000 °C or below early in the fractionation process.

#### 5.6.2 Implications for Degassing at Erebus

Erebus volcano is very well monitored, especially in terms of surface gas compositions and fluxes. Given the unique composition of Erebus lavas, however, linking the surface degassing to subsurface magmatic processes is nontrivial.  $SO_2$  is the most consistently monitored gas at Erebus (as is typical for volcanic gas monitoring), and emissions have been recorded each austral Summer season since 1983. This extensive data set is one of the most consistent records of degassing from an open-vent volcano and has been used to understand cyclic trends in degassing from the Erebus lava lake and to quantify total gas flux from the volcano. Recent studies have reported an SO<sub>2</sub> flux of  $61 \pm 27$  Mg d<sup>-1</sup> from Erebus (Sweeney et al., 2008). In the following analysis, I use my experimental results to place broad constraints on the amount of phonolite required to supply this flux each day.

Despite  $SO_2$  being the most widely measured species in the gas phase, sulfur is arguably the most complicated volatile component to model in the melt phase. The complexity arises from sulfur's multiple oxidation states, affinity to iron in the melt, poorly understood compositional dependencies, and its ability to heavily partition into solid phases (commonly pyrrhotite or anhydrite). In order to understand the origin of the Erebus sulfur emissions, we must consider three sources: sulfur dissolved within the melt, sulfur fluid in a co-existing pre-eruptive fluid phase, and sulfur stored in solid phases.

Using the partition coefficient of sulfur between the fluid and melt phases  $(K_D^{fl/m})$ , I can construct a relationship between the volumes of fluid and melt required to produce 61 Mg of SO<sub>2</sub> dependent upon  $K_D^{fl/m}$ . First, the extreme values for the volumes of melt and fluid can be constrained by calculating the volume of phonolite required given a  $K_D^{fl/m} = 0$  (i.e. all of the sulfur is derived from the melt). The SCSS for ERE-97018 phonolite has been experimentally determined over a range of oxygen fugacities. Given a lava lake  $fO_2 = \sim QFM$ , based on magnetite-ilmenite pairs in natural samples (Kyle, 1977) and phase equilibrium experiments (Moussallam et al., 2013), my experiments suggest a sulfur carrying capacity of  $\sim 200-400$  ppm in Erebus phonolite. This is consistent with the 381 ppm sulfur measured in Erebus phonolite melt inclusions (Oppenheimer et al., 2011a). To account for 61 Mg of  $SO_2$  per day, or ~30.5 Mg of S, a melt with 400 ppm dissolved S must have a mass of 76,250 Mg. Given a phonolite crystal content of  $\sim 30\%$  (Kelly et al., 2008), 57,188 Mg, or about  $5.72 \times 10^7$  kg, of phonolite magma is required. Assuming a density of  $2.5 \text{ g/cm}^3$ , a volume of  $22,880 \text{ m}^3$ phonolite magma each day is required to account for 61 Mg/day of  $SO_2$  given a  $\mathcal{K}_{D}^{fl/m} = 0$ . With this number, a general equation relating the volume of phonolite magma to the fluid/melt partition coefficient of sulfur can be derived:

Volume of Phonolite 
$$(m^3/day) = \frac{22880}{K_D^{fl/m} + 1}$$
 (5.14)

My experimental  $\mathcal{K}_D^{fl/m}$  values range from quite low (approaching 1) to ~650. The value of  $K_D^{fl/m}$  is influenced by melt composition (e.g. silica and total iron concentrations) and can be buffered by the presence of a solid S-bearing phase. If pyrrhotite formation is extensive enough, the  $K_D^{fl/m}$  of sulfur can be driven to very low values, as low as  $\sim 1$  (Scaillet et al., 1998). This is significant as it implies that pyrrhotite has the ability to store nearly all sulfur in a system. At Erebus, pyrrhotite is present as an accessory mineral in primitive, intermediate, and evolved lavas, but the extent to which pyrrhotite will buffer the sulfur  $K_D^{fl/m}$ is not known. For this analysis, I assume that the sulfur  $K_D^{fl/m}$  will fall somewhere between ~10–100. Equation 5.14 is plotted in Figure 5.10 for sulfur  $K_D^{fl/m}$  values ranging from 0–100 (a) and from 10–100 (b). Assuming that the range of partition coefficient values in Figure 5.10b is representative of the Erebus system, we can expect a volume of  $\sim 250-2100 \text{ m}^3/\text{day}$  of phonolite to degas in the lava lake. Because eruptions of magma from the lake are rare, the magma-derived gas flux at Erebus has been hypothesized to be driven by bi-directional core annular flow within the shallow conduit and lava lake (Oppenheimer et al., 2009), and so this volume of phonolite must be recycled daily within the shallow plumbing system.

## 5.7 Conclusions

In this chapter, I have used petrological and experimental data to constrain the fluid/melt partitioning and degassing of sulfur in primitive and evolved Erebus melts. In addition, I have demonstrated a thermodynamic approach that allows for the quantification of the composition of an equilibrium fluid phase given minimal information commonly known from petrological and mineralogical data in natural lavas.

An examination of the petrology and mineralogy of Erebus lavas has also al-



Figure 5.10: The volume of Erebus phonolite magma per day required to produce an SO<sub>2</sub> flux of 61 Mg day<sup>-1</sup> as a function of sulfur  $K_D^{fl/m}$  based on 5.14. The full range of sulfur  $K_D^{fl/m}$  values from 0–100 is shown on in (a). A  $K_D^{fl/m}$  range of 10–100, assumed here to be a reasonable range of estimates for Erebus, is shown in (b).

lowed me to place broad constraints on the main parameters controlling sulfur dissolution and degassing throughout the magmatic plumbing system. In the deepest part of the system, where basanite is evolving, sulfur degassing is primarily driven by chemical evolution of the melt and changes in the redox state. At shallower depths, where phonolite magma is stored, melt evolution (notably a steep drop in XFeO<sup>melt</sup>) and cooling are the dominant factors controlling the exsolution of S. Temperature change is likely a much stronger driving force for S degassing in DVDP lavas, as experiments in Chapter 4 demonstrated that a drop in temperature from >1075 °C to ~1000 °C or below must occur quite early in the fractionation process.
## Chapter 6

# The Last Stage: Modeling degassing at Erebus from the inside out

One of the grand desires of both petrologists and gas geochemists is to be able to combine what melt inclusions tell us about deep volatile processes with what is measured in the gases being emitted from volcanoes. Experimental petrology has historically lent a hand in making this connection, and this has equally been a goal of this thesis. As is common in science, however, my experimental data have posed new questions to ponder rather than simply explaining the gas budget of Erebus. In this concluding chapter, I will combine elements from Chapters 3, 4, and 5 with the suite of melt inclusions from Erebus lavas (Eschenbacher, 1998; Oppenheimer et al., 2011a) to try and understand the total gas budget of Erebus volcano and how mixtures of deeply and shallowly sourced gases may contribute to the surface measurements made of the Erebus plume (Oppenheimer et al., 2009).

Melt inclusions contain a record of the dissolved volatiles stored within magmas. Melt inclusions at Erebus cover the entire compositional range of its lavas (see Figure 1.10) and indeed tell the story of magma degassing at various depths within the conduit. Melt inclusions alone can rarely be successfully matched to surface gas emissions, however, as they do not directly record any information about the presence, amount, or composition of any coexisting fluid or gas phase. This has been widely acknowledged by petrologists and geochemists alike, and this "excess fluid" phase has been cited as the reason for discrepancies in S flux measured in gas emissions and based on melt inclusion concentrations at many volcanoes (see Shinohara, 2008), including Katmai (Lowenstern et al., 1991), the Bishop Tuff (Wallace et al., 1999), Nevado del Ruiz (Sigurdsson et al., 1990), Mount St. Helens (Gerlach & McGee, 1994), Redoubt (Gerlach et al., 1994), and famously at Mount Pinatubo (Wallace & Gerlach, 1994). Likewise, many studies have concluded that a coexisting fluid phase must be present at Erebus to account for the observed gas output.

An understanding of fluid-melt interactions at various relevant P-T-X conditions can allow for the estimation of such excess fluid in volcanic systems. Using essentially the same thermodynamic approach as outlined in Chapter 5 combined with petrologic data and constraints provided by the experimental results of this thesis, I have calculated the equilibrium fluids that would coexist with basanite, tephriphonolite, and phonolite melt inclusions, representing deep (5000 bars), intermediate (3000 bars) and shallow ( $\sim$ 2000 bars) magma reservoirs, respectively, as well as the whole-rock volatile concentrations of an anorthoclase phonolite representing the volatile concentration in the lava lake ( $\sim$ 4 bars). Pressure estimates have been calculated based on melt inclusion volatile contents using either the model from Chapter 3 or that of Papale et al. (2006). I also consider contributions from degassing melt, calculated as the difference between the average dissolved volatiles in a group and the average dissolved volatiles in the succeeding group (in the order basanite-tephriphonolite-phonolite melt inclusions-lava lake phonolite).

# 6.1 Application of the Thermodynamic Model to Natural Systems

In Chapter 5, I demonstrated a thermodynamic approach to modeling the C-O-H-S fluid phase composition in equilibrium with a melt given known melt volatile concentrations and amounts of  $H_2O$ ,  $CO_2$ , and  $S_{tot}$  (sum of oxidized and reduced S species) in the fluid phase. The same thermodynamic rules used in these calculations can also be used to calculate the mole fractions of all fluid species even when no information about the fluid composition is known. This latter approach

is more applicable to natural systems where mineralogy can be used to determine certain parameters such as oxygen and sulfur fugacity. As no direct information about a pre-eruptive fluid phase is stored in the rock record, this presents us with a quantitative way to relate pre-eruptive information (e.g. melt inclusions, petrology) to surface degassing.

In this alternative thermodynamic approach, I first calculate the fugacities and partial pressures of all species in the fluid and can subsequently calculate the mole fractions. A minimum of four parameters must be known: the temperature T, the pressure P, the  $fO_2$ , and either the  $fH_2O$  or the  $fH_2$ . Alternatively, if  $fH_2O$  or  $fH_2$  is not known, the pressure P and  $fH_2O$  can be modeled based on the melt volatile contents, assuming a compositionally relevant model exists for the magma of interest.

Firstly, given  $fO_2$  and  $fH_2O$ ,  $fH_2$  can be determined (or, if  $fH_2$  is known,  $fH_2O$  can be determined) by rearranging Equation 5.6 as:

$$fH_2 = \frac{fH_2O}{K_F^{H_2O} \cdot fO_2^{1/2}} \tag{6.1}$$

Here, the P and T must be known in order to determine the correct equilibrium constants  $K_F$  or fugacity coefficients,  $\gamma$ . If  $fS_2$  is not known, it can now be calculated using Equation 5.12. With  $fS_2$ ,  $fO_2$ , and  $fH_2$  known, the  $fSO_2$  and  $fH_2S$  can be calculated using same relationship expressed in Equation 5.10. The partial pressures of all species for which fugacity is known can now be calculated using the general relationship:

$$fi = \gamma i \cdot P_i \tag{6.2}$$

where *i* represents the species of interest. In magmatic systems, we can generally assume that the concentrations of CO,  $CH_4$ , OCS, and other S species are minimal, and so I assume that the total pressure of the system is equal to the sum

of the partial pressures of H<sub>2</sub>, O<sub>2</sub>, S<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S:

$$P_{tot} = P_{H_2} + P_{O_2} + P_{S_2} + P_{H_2O} + P_{CO_2} + P_{SO_2} + P_{H_2S}$$
(6.3)

Using this relationship, I can solve for  $P_{CO_2}$ . The final fugacity,  $fCO_2$ , can now be solved for using Equation 6.2. The fugacities of the pure species at the given P and T can be calculated as:

$$fi^{pure} = \gamma i \cdot P_{tot} \tag{6.4}$$

Finally, the mole fractions of all species in the fluid can be calculated using the general relation:

$$X_i^{fluid} = \frac{fi}{fi^{pure}} \tag{6.5}$$

If  $\text{XCO}_2^{fluid}$  or  $f\text{CO}_2$  is known (e.g. using a solubility model), Equation 6.4 can be used to solve for  $P_{CO_2}$  directly, and the total pressure of the system can then be calculated. In this case, only an *a* priori guess of  $P_{tot}$  is required, as this value can be solved for iteratively by calculating  $P_{tot}$ , calculating new  $\gamma$ i values based on this total pressure, and recalculating a new  $P_{tot}$ . This process can be iterated until the change in  $P_{tot}$  is on the order of 1 bar.

In the case of Erebus, all of the necessary information is known to calculate equilibrium fluid compositions for much of the system (primitive/deep, intermediate, and evolved/shallow).

#### 6.1.1 Ideal Mixing of Non-ideal Gases

The fluid phase of each experiment was modeled using a thermodynamic approach that assumes ideal mixing of species in the fluid (Henrian behavior). It has been demonstrated, notably by Holloway (1977), that for pressure-temperature conditions close to any reasonable geotherm, fluids will in fact mix in a non-ideal manner. In other words, the underlying assumption of my model is essentially demonstrably false. An alternative approach, which makes no *a priori* assumption of ideality, will be discussed here.

The most commonly applied non-ideal-mixing thermodynamic approach to modeling the fugacities and activities of species in supercritical fluids or fluid-melt systems relies upon an equation of state for mixtures (commonly, the Modified Redlich-Kwong Equation of state, or the MRK EoS; see Holloway, 1977 and Flowers, 1979). The (unmodified) Redlich-Kwong Equation itself, applicable to pure non-ideal fluids (my approach) is expressed as:

$$P_{tot} = \frac{RT}{V - b} - \frac{a}{(V^2 + bV) \cdot T^{1/2}}$$
(6.6)

where  $P_{tot}$  is total pressure, R is the gas constant (= 83.12 cm<sup>3</sup>· bar/deg·mol), Tis the temperature in Kelvin, V is the volume, and a and b are pressure-independent parameters for the attractive and repulsive potential energy terms from the Mie equation. Constants a and b can be calculated from critical data and have the same physical meaning as the van der Waals constants. The Redlich-Kwong (or some other EoS) forms the basis of almost every thermodynamic model of magmatic fluids in the literature and is, in fact, used in my model to calculate the fugacity coefficients of the pure fluid species. From this point forward, one must decide whether to treat the fluid as an ideal or non-ideal *mixture*. In my model, I assume ideal mixing of real (non-ideal) gases (i.e. the Lewis-Randall Rule). In this context, that means that calculations for the fugacity of each species were made independently, and then the mixture was calculated as the sum of the products of the fugacity of each species and the mole fraction of that species in the fluid.

In contrast, the Modified RK equation requires the calculation of the a and b parameters for mixing. The MRK for the fugacity coefficient of the *i*th component of a mixture consisting of both polar and non polar molecules is given by Prausnitz

et al. (1998) as:

$$ln\gamma_{i} = ln\left(\frac{V}{V-b}\right) + \frac{b_{i}}{V-b} - \frac{\sum_{j=1}^{\hat{i}} a_{i,j}X_{j}}{bRT^{3/2}} ln\left(\frac{V+b}{V}\right) + \frac{ab_{i}}{b^{2}RT^{3/2}} \left(ln\left(\frac{V+b}{V}\right) - \frac{b}{V+b}\right) - ln\frac{PV}{RT}$$

$$(6.7)$$

Here, individual values of a must be calculated for the interaction of each pair of species, i and j, in the fluid. The mixing rules used to determine the values of a and b are complex and must account for polar–polar, non-polar–non-polar and polar–non-polar molecular interactions. In addition, if the fluid contains both H<sub>2</sub>O and CO<sub>2</sub>, the value  $a_{H_2O-CO_2}$  must also account for the tendency of these two fluids to chemically react and form carbonic acid.

The thermodynamic properties required by the non-ideal mixing rules always come in the form of empirical data from experiments or laboratory measurements (or conservative extrapolations of these data sets). Unfortunately, data concerning the interactions of all species modeled in this work do not exist at relevant P-T conditions. Further, H<sub>2</sub>S and SO<sub>2</sub> are moderately polar species and will require specific functions to describe their mixing properties.

Both ideal and non-ideal mixing scenarios have been applied to similar studies seeking to model the fluid phase of sulfur-bearing experiments. Some have applied the non-ideal mixing rules assuming that polar species for which no P-V-T data are available will act as non-polar species and/or they have extrapolated or interpolated existing data sets (e.g., Clémente et al., 2004; Connolly & Cesare, 1993). Others have used an ideal mixing approach similar to my own (e.g., Burgisser et al., 2012; Scaillet & Macdonald, 2006) and/or empirical models (e.g., Scaillet & Pichavant, 2003). Because of the overwhelming uncertainties involved, it is difficult to say which of these approaches best approximates the natural system. Here, I prefer the simpler Lewis-Randall approach and argue that the more complicated treatment of the fluid as a non-ideal mixture is, in light of the lack of thermodynamic data necessary to constrain it, neither necessary nor justifiable in application to my data.

#### 6.1.2 Details of Equilibrium Fluid Phase Calculations

Appendix B contains the step-by-step results of all thermodynamic calculations including the equilibrium constants and fugacity coefficients used. The calculated compositions of the equilibrium fluids are given in Table 6.1 and are shown in Figure 6.1.



Figure 6.1: Ternary diagram showing the calculated compositions of equilibrium fluids (dots) and fluids from degassed melt inclusions (squares). The normalized surface gas composition is also shown (large red dot). Each dot represents the equilibrium fluid calculated for a single melt inclusion or glass analysis. The names correspond to those in Table 6.1.

The volatile budget of a deep magma reservoir is represented by olivine-hosted melt inclusions from basanite DVDP3-295 (Oppenheimer et al., 2011a). For the calculations we assume: T = 1100 °C (Chapter 4);  $fO_2 = NNO+1$  (one log unit

Table 6.1: Thermodynamically calculated average equilibrium fluids, degassed melt inclusions, possible gas mixtures, and composition of the Erebus plume as measured by FTIR

	$\rm CO_2$	$H_2O$	$SO_2$	$H_2S$
	$\mathrm{mol}\%$	$\mathrm{mol}\%$	$\mathrm{mol}\%$	$\mathrm{mol}\%$
Equilibrium fluids coexisting with n	nelt inclusio	ons and lave	a lake phone	olite
Lava lake phonolite	60.02	37.82	0.03	2.12
EA-1 (phonolite)	99.83	0.17	$<\!0.01$	$<\!0.01$
97009 (tephriphonolite)	98.41	1.59	$<\!0.01$	0.01
DVDP 3-295 (basanite)	80.39	4.42	14.86	0.33
Composition of fluid from degassed	melt inclus	sions		
$\Delta$ Phon MI to LL Phon	16.95	60.38	$12.06^{1}$	$10.61^{1}$
$\Delta$ Teph to Phon MI	15.84	80.52	1.85	1.79
$\Delta Bas$ to Teph	10.78	82.11	6.96	0.15
Composition of calculated mixtures				
Constant fluid/melt $(23.5-35-100)$	50.03	40.85	7.98	1.14
Surface gas chemistry as measured	by FTIR			
Surface gas	36.41	57.88	1.40	$0.03^{2}$
Normalized surface gas	38.04	60.47	1.46	$0.03^{2}$

Notes: Equilibrium fluids coexisting with melt inclusions (MI) and lava lake phonolite calculated using thermodynamic approach from Chapter 5, melt inclusion data from Oppenheimer et al. (2011a) and whole-rock data from Kyle (1977) representing the lava lake phonolite. Surface gas chemistry data are OP-FTIR measurements from Oppenheimer & Kyle (2008b). A step-by-step tabulation of the calculations can be found in Appendix B. Bas: basanite MI; Teph: tephriphonolite MI; Phon: Phonolite MI or lava lake (LL). \*Indicates S reported as total S (SO<sub>2</sub> + H<sub>2</sub>S). <sup>1</sup>Assuming complete S degassing. <sup>2</sup>H<sub>2</sub>S has not actually been measured in the Erebus plume. Oppenheimer & Kyle (2008b) suggest that the concentration of SO<sub>2</sub> must exceed that of H<sub>2</sub>S by at least a factor of 50 in order for its presence to go undetected by OP-FTIR. Values in this table represent that maximum amount (50x less than the amount of SO<sub>2</sub>).

above the Ni-NiO buffer; Chapter 4); and P = 5000 bars (Chapter 3).  $fH_2O$  and  $XCO_2^{fluid}$  were calculated for each melt inclusion using Equation 3.6 and isopleths from Chapter 3, respectively.

An intermediate magma reservoir is represented by olivine-hosted melt inclusions from tephriphonolite 97009 (Oppenheimer et al., 2011a). Here we assume: T = 1081 °C (Kyle et al., 1992); P = 3000 bars (Chapter 3);  $\log f S_2 = -3.01$  (Kyle et al., 1992, based on the composition of pyrrhotites); and  $\log f O_2 = -9.99$  (Kyle et al., 1992, based on oxide pairs).  $f H_2 O$  was calculated using Equation 3.6. PCO<sub>2</sub> was calculated as the difference between the total pressure and the sum of partial pressures of all other fluid species.

A shallow magma reservoir is represented by anorthoclase-hosted melt inclusions from phonolite bomb EA-1 (Oppenheimer et al., 2011a). This is the same reservoir postulated in Moussallam et al. (2013). Here we assume: T = 1000 °C (Caldwell & Kyle, 1994; Dunbar et al., 1994; Kyle, 1977);  $\log fS_2 = -2.7$  (Kyle, 1977, based on composition of pyrrhotites in similar phonolite bomb); and  $fO_2$ = QFM (quartz-fayalite-magnetite buffer; Moussallam et al., 2013). P and  $fH_2O$ were calculated for each melt inclusion using the models of Papale et al. (2006) and Moore et al. (1998), respectively. PCO<sub>2</sub> was calculated the same way as for tephriphonolite melt inclusions.

Finally, the dissolved volatile budget of the Erebus lava lake is represented by  $H_2O$  and  $CO_2$  concentrations reported for an anorthoclase phonolite (presumably a whole-rock analysis; sample #8 in Table 6 of Kyle, 1977). Here we assume: T = 1000 °C (Caldwell & Kyle, 1994; Dunbar et al., 1994; Kyle, 1977); P = 4.321 bars (modeled with Papale et al., 2006);  $\log fS_2 = -2.7$  (Kyle, 1977); and  $\log fO_2 = -12.2$  (Kyle, 1977).  $fH_2O$  was calculated using the model of Moore et al. (1998). PCO<sub>2</sub> was calculated the same way as for tephriphonolite and phonolite melt inclusions.

### 6.2 Interpretations

The thermodynamic calculations indicate that an equilibrium fluid coexisting with lava lake phonolite at 4.321 bars is more CO<sub>2</sub>-rich and H<sub>2</sub>O-poor than the gas measured coming from the Erebus lake via OP-FTIR (Lava lake phonolite:  $CO_2 =$  $60.02, H_2O = 37.82, SO_2 = 0.03, H_2S = 2.12 \text{ mol}\%$ ; Normalized surface gas:  $CO_2$  $= 38.04, H_2O = 60.47, SO_2 = 1.46, H_2S \le 0.03$ ; see Table 6.1). If we assume that the volatile concentrations in this phonolite bomb represent the actual dissolved volatile concentrations in the Erebus lava lake, we can thus conclude that the gases emitted from the lava lake are not in equilibrium with the lake itself. This finding has substantial implications for modeling degassing at Erebus via backward tracking of surface gas measurements, which often rely on an assumption of equilibrium (Burgisser et al., 2012). This conclusion is supported by a number of lines of evidence that suggest that surface gas at Erebus is sourced from very deep within the plumbing system: a) the equilibrium temperature calculated for the lava lake phonolite based on surface gas chemistry.g. (Burgisser et al., 2012) is about  $100 \,^{\circ}\mathrm{C}$  hotter than the equilibrium temperature constrained by the experiments of Moussallam et al. (2013); b) redox couples in the Erebus plume (e.g.  $CO-CO_2$ ) show significantly more oxidized signatures than the oxidation state of the lava lake as inferred from analytical and experimental petrology (Kyle et al., 1992; Moussallam et al., 2013; and c) the remarkably high C/H ratio in the Erebus plume (particularly during explosive degassing) is hypothesized to be caused by deep  $CO_2$  degassing (Oppenheimer et al., 2009, 2011a, and see Chapter 4).

In light of this initial conclusion, we can also then say that the Erebus plume must either consist purely of gas derived from depth or, more likely, that it is a mixture of gas derived from several places within the plumbing system. It is tempting to apply what is known from fractional crystallization modeling of the relative masses of Erebus magmas (Kyle, 1981; Kyle et al., 1992) to the proportions of fluid in the system that contribute to degassing. In other words, we know that the phonolite and tephriphonolite magmas are 23.5 and 35% residual melts generated from fractional crystallization of a parental basanite magma, respectively, and one might simply apply this 23.5-35-100 (or 15-22-63) ratio to our equilibrium fluids as:

$$0.15X_i^{Phon} + 0.22X_i^{Teph} + 0.63X_i^{Bas} = X_i^{gas}$$
(6.8)

Where X represents the mole fraction of the subscripted species i in the equilibrium fluid derived from the superscripted phase (*Phon* = Phonolite EA-1; *Teph* = Tephriphonolite 97009; *Bas* = Basanite DVDP 3-295; *gas* = Surface gas). In doing this, we assume that the relative proportions of equilibrium fluid coexisting with each magma are equal to the relative proportions of rock (i.e. the fluid/rock ratio is constant). We can also then also calculate the composition of a fluid made up of a 23.5-35-100 mixture of fluid from degassed melt inclusions. Results of these calculations are given in Table 6.1.

The surface gas composition cannot be adequately explained by any mixture of only equilibrium fluids or only melt inclusions. All of the equilibrium fluids are far too  $CO_2$ -rich and  $H_2O$ -poor. Conversely, the compositions of fluid from degassing melt (represented by the dissolved volatiles in melt inclusions and lava lake phonolite) are all too  $CO_2$ -poor and  $H_2O$ - and S-rich compared with the surface gas. Thus, we posit that the surface gas must be made up of some mixture of co-existing fluid phase plus volatiles from degassed melt.

#### 6.2.1 Modeling an Idealized Gas Mixture

I have attempted to constrain the proportional contributions of each fluid (equilibrium fluids and degassed melt inclusion fluids) that would result in the measured surface gas composition by using a simple gas mixing model. For this model, I allow for a contribution of all equilibrium fluids and degassed melt inclusion fluids in Table 6.1: Lava lake phonolite, EA-1, 97009, and DVDP 3-295 equilibrium fluids; and melt inclusion fluids from degassed basanite, tephriphonolite, and phonolite. The model runs on the assumption:

$$\Sigma F_i n = G_i \tag{6.9}$$

where  $F_i$  is the mol% of species *i* in contributing fluid *F*, and *n* is the propor-

tional contribution of fluid F to the surface gas composition G. Each contributing fluid can account for 0-100% of the surface gas. The composition of the surface gas G is a range of compositions defined as that measured by FTIR (i.e. the normalized values in Table 6.1)  $\pm 1$  mol%.

I have written a simple piece of code used to determine the idealized mixture of fluids that can account for the observed surface gas composition. The code was originally written in Python, but has been rewritten in C (translation from Python to C graciously provided by Nial Peters) to economize on computation time. The code is quite computationally expensive, even in C, and so is forked into four processes (i.e. the code utilizes all cores of a quad-core machine). The code works as follows:

- 1. Generates a list of one-dimensional arrays 7 values long where  $0 \le \text{value} \le 100$ . The sum of each array must be equal to 100 (e.g. [(100,0,0,0,0,0,0), (99,1,0,0,0,0,0), ..., (0,0,0,0,0,100)]). Each of these arrays represents a possible gas mixture where each value is a percentage of the total mixture.
- 2. The nth value from each array is then multiplied by the concentration of a species (either CO<sub>2</sub>, H<sub>2</sub>O, or S<sub>tot</sub>) in each of the 7 contributing fluids, in the order: EA-1 equilibrium fluid; 97009 equilibrium fluid; DVDP 3-295 equilibrium fluid; Lava lake equilibrium fluid; Bas-to-Teph MIs; Teph-to-Phon MIs; Phon-to-LL MIs.
- 3. Every array that satisfies the requirement in Equation 6.9 for all species is then saved to a file.

In the calculations, I assume only three gas species:  $CO_2$ ,  $H_2O$ , and  $S_{tot}$ . I use  $S_{tot}$  instead of the individual S species  $SO_2$  and  $H_2S$  for two main reasons. Firstly, the  $SO_2/H_2S$  ratio in the fluids from degassed melt inclusions is not constrained but has been estimated based on the oxygen fugacity of the host melt. Secondly, the fluid compositions as they have been estimated can never account for the surface gas if S speciation is taken into account. This is due to the fact that no  $H_2S$  has not been measured in the surface gas emissions. It has been difficult to explain the lack of reduced sulfur in the Erebus gas, especially given the reduced nature of the lava



Figure 6.2: Bright features that appear to be flames coinciding with a bubble burst in the Erebus lava lake in December, 2010. The long axis of the lake is  $\sim 40$  m, and the bubble diameter is  $\sim 5$  m. Photo credit: Clive Oppenheimer.

lake based on phase equilibrium experiments (Moussallam et al., 2013) and the presence of pyrrhotite in all Erebus rocks (again suggesting reducing conditions). It is possible that  $H_2S$  is present in the surface gas, but that it is not measured due to its destruction near the lake surface (Kyle et al., 1994). Oppenheimer & Kyle (2008b) suggested that the combustion of  $H_2S$  to  $SO_2$  at the lake surface is unlikely, given that CO is detected (i.e. all of the CO does not burn). Since the publication of that paper, however, bright features that appear to be flames coinciding with bubble bursts, which release visible gas, have been witnessed in the lava lake (Figure 6.2), suggesting some combustion is occurring just above the lake surface. For these reasons, our model does not attempt to reproduce the oxidation state of the surface gas, but merely the major gas composition. The actual code is shown in full in Appendix B.

38 possible fluid mixtures were found that satisfy Equation 6.9. All model

output values are given in Appendix B and are shown in Figure 6.3. Broadly, we can define two general fluid mixtures that can account for the observed gas output from Erebus volcano. In both mixtures, about 50% of the gas is made up of the fluid from degassed tephriphonolite melt inclusions. Another  $\sim 25\%$  is made up of fluid from degassed basanite melt inclusions. The remaining  $\sim 25\%$  is made up of either: mostly 97009 equilibrium fluid (model output numbers 1–28) or mostly EA-1 equilibrium fluid (numbers 29–38), with some small ( $\leq 3\%$ ) contribution from the equilibrium fluid coexisting with the lava lake.



Figure 6.3: All outputs from my simple gas mixing model that satisfy Equation 6.9. Fluids are stacked based on depth of origin from the most shallow (top) to deepest (bottom).

#### 6.2.2 Other considerations

It is important to note that the gas mixing scenarios presented in this chapter do not necessarily reflect the processes occurring in the natural Erebus system. Rather, the simplified approach presented here should be considered merely as a thought experiment that represents some possible mathematical solutions describing how the surface gas compositions at Erebus might be obtained based on the information that we have about the subsurface fluids. There is no direct evidence to support the conclusion that the surface gas is made up of one of the mixtures presented here. Instead, my approach is a first step toward a more rigorous model for understanding the total gas budget of Erebus.

My calculations only take into account the seven fluid compositions presented in Table 6.1. Other contributing factors may be adding to or subtracting from the final gas output measured at the Erebus crater. For example, the existence of active fumarolic ice caves and ice towers at Erebus (Figure 6.4) indicates that some gas escapes on the slopes of the volcano rather than from the lava lake (Curtis & Kyle, 2011). The total flux of gas from flank degassing is not known, but  $CO_2$ emissions from the ice towers constitute <2% of the total gas flux from Erebus (Wardell et al., 2003). Flank emissions where no ice tower has formed have not been estimated. Still, if a gas species is preferentially degassing through ice caves (i.e. the composition of the flank degassing is not the same as that of the lava lake degassing), then this must be taken into account when calculating the total gas budget.

Another possibility is that the fluids within the Erebus plumbing system are not in equilibrium with the melts. This would mean that the approach taken here is not valid, as I have used the equilibrium fluid compositions to calculate the total gas budget. Despite the fact that the composition of the Erebus surface gas is quite stable from year to year and the compositions of the lavas has been stable over the past several thousand years, many observations have suggested disequilibrium between the lava lake and the surface gas. The hypothesis that other parts of the Erebus plumbing system have not attained equilibrium is thus not implausible.



Figure 6.4: Ice tower "Harry's Dream" located  $\sim 1$  km north of the Erebus crater, seen actively degassing in December, 2010. Laura Jones and Jed Frechette for scale.

Even if the assumption of equilibrium is valid, it may be that the Erebus surface gas composition is not the result of simple mixing. In my model, I assume that all fluids contribute evenly across all species. It may be that some fluids contribute more of one species and less of another (i.e. the contribution of a fluid to the total gas budget is not equal to the equilibrium composition). For example, a fluid may contribute all of its  $CO_2$  and  $H_2O$ , but only a portion of its  $S_{tot}$  with the remaining S taken up by pyrrhotite crystals in subsequent melts or being lost from the fluid in some other way.

My approach represents a starting point for a more rigorous model that could be developed to constrain the total gas budget of Erebus. In addition, it highlights the complexity of volcanic degassing, and demonstrates that modeling the total gas budget of a volcano is difficult even for Erebus where subsurface gases are relatively well constrained and surface gas compositions are extremely well known.

## 6.3 Future work

The use of melt inclusions to constrain surface degassing and, thus, the use of surface gas measurements to constrain deep degassing has been a long-sought volcanological goal. The solubility data, phase equilibrium constraints, and thermodynamic approach of this thesis have served as a starting point to understanding the entire Erebus system. More data are needed to understand all of the discrete processes happening within the Erebus plumbing system, however, as well as to understand how those processes interact. Here I outline just a few possibilities for future work:

- Halogens: Erebus melt inclusions are very rich in halogens, notably F. Additionally, Erebus rocks contain F-rich crystal phases (e.g. fluoro-apatite). An experimental study into understanding the crystal-melt-fluid partitioning of F and Cl in Erebus lavas could give insights into the role of these species in degassing. Both HF and HCl are measured in the Erebus surface gas.
- 2. Mixed-volatile solubilities in phonolite: In Chapter 3, I established the mixed H<sub>2</sub>O-CO<sub>2</sub> solubility in Erebus phonotephrite. It is unknown how the saturation surface of these volatiles will change as melt composition changes. In order to better constrain the contribution of phonolite melts to the Erebus surface gas compositions, their volatile solubilities must be known. Currently, no mixed H<sub>2</sub>O-CO<sub>2</sub> solubility data in phonolites exist in the literature.
- 3. Development of a more rigorous degassing model: As stated previously, the model presented in this chapter is merely a first order approach to modeling the degassing behavior throughout the Erebus system. With the thermodynamic approach demonstrated here, a more rigorous model taking

more factors into consideration could be developed to simulate the contributions of various melts and fluids to the surface gas output at Erebus. For example, my model only calculates solutions for which the percentage of any particular contributing fluid is an integer. Given more time (and, perhaps, more computing resources), a more intelligent optimization algorithm could be developed allowing for more precise results.

### 6.4 Summary of this Thesis

Over the past several decades, Erebus, once considered a remote and barely reachable place, has become a rather well-studied volcano. Early work by Phil Kyle and others laid the groundwork for understanding the evolution of Erebus through petrological investigations of its lavas (e.g. Kyle, 1981; Kyle et al., 1992; Kyle, 1977). In the late 1990s, a large suite of melt inclusions representing the entire compositional range of Erebus lavas was analyzed for major element chemistry and volatile contents (Eschenbacher, 1998). At the time, however, the interpretation of those melt inclusions was hindered by the lack of experimental data on similar magmatic systems. The studies that followed focused largely on Erebus's most famous feature, its active phonolitic lava lake, as well as the gases being emitted from the crater. The work of Clive Oppenheimer and others established that the changes in gas flux and composition at Erebus are likely linked to subsurface magmatic processes, perhaps even those in the deepest part of the Erebus plumbing system (Oppenheimer & Kyle, 2008b). They proposed that the cyclical nature of the Erebus gas emissions is due to a pulsatory supply of volatile-rich magma from somewhere below the lava lake (Oppenheimer et al., 2009). Investigations into such cycles in the Erebus lava lake and gas emissions have been the focus of many recent studies (e.g. Moussallam, 2012, Peters et al., in prep; Ilanko et al., in prep). Together with infrasound, passive seismic, and terrestrial laser scanning studies, these works have contributed to numerical and conceptual models of the shallow plumbing system at Erebus ( $\sim 0-2$  km depth Burgisser et al., 2012; Molina et al., 2012). It has thus far remained unclear, however, how the intermediate  $(\sim 2-12 \text{ km})$  and deep  $(\sim 12-20 \text{ km})$  regions of the plumbing system contribute to

or influence surface behavior.

This thesis has provided the first experimental investigations into deep magmatic processes at Erebus and has complemented contemporary experimental studies of the shallow system (Moussallam et al., 2013). Together, these works represent an experimentally constrained model of the entire Erebus plumbing system, from mantle to surface. Using these new data, I have parameterized a thermodynamic approach to modeling the total gas budget at Erebus, which considers the influence of shallow, intermediate, and deep magmas. Here I briefly summarize the conclusions of the work carried out for this thesis:

- 1. Mixed volatile solubility in phonotephrite and non-Henrian behavior of volatiles in melts at high pressure: The results from Chapter 3 are among the first to demonstrate non-Henrian behavior (non-ideal mixing) of H<sub>2</sub>O and CO<sub>2</sub> dissolved in a silicate melt, which occurs at pressures above ~5000 bars. In addition, I have shown that current volatile solubility models do not reproduce my experimental results, reflecting a previous lack of experimental data on mafic alkaline melt compositions and indicating that none of these models is applicable to the deep Erebus system. An empirical model for mixed H<sub>2</sub>O-CO<sub>2</sub> solubility in mafic alkaline melt has been presented and is applicable to similar melt compositions at ~1200 °C and 4000–7000 bars.
- 2. CO<sub>2</sub>-dominated volcanism: When combined with the results of other phase equilibrium (Moussallam et al., 2013) and melt inclusion (Oppenheimer et al., 2011a) studies, the results from Chapter 4 make a strong case for the Erebus plumbing system being influenced largely by the fluxing of mantle-sourced carbon, which controls phase stability, fractional crystallization through dehydration, degassing, and possibly also provides the sustained energy input necessary for maintaining an active surface lava lake.
- 3. Mapping the plumbing system beneath Ross Island: Phase equilibrium experiments indicate that the two most prevalent lava lineages on Ross Island, the Erebus Lineage (EL) and the Dry Valley Drilling Project lineage (DVDP), may be derived from the same parental basanitic magma source,

as earlier suggested by Kyle et al. (1992). Kaersutites, which crystallize at low temperature, and apatites have decisive effects on the differentiation of basanitic magma and explain the divergence between these two lineages. I have inferred that each of these two lava lineages is produced via distinct magma evolution pathways: a low-temperature, short-lived pathway followed by the DVDP lavas; and a high-temperature, sustained pathway followed by the EL lavas.

- 4. Sulfur in fluid-saturated and undersaturated phonolite and basanite melts: Results of sulfur-bearing experiments presented in Chapter 5 have placed broad constraints on the behavior of sulfur in Erebus melts. In addition, a thermodynamic approach to quantifying the fluid phase compositions of experimental charges has been developed.
- 5. Thermodynamic approach to modeling fluids in natural volcanic systems: A thermodynamic approach has been presented as a first step toward quantifying the total gas budget of Erebus volcano. The thermodynamic relationships were adapted from the approach presented in Chapter 5. The equations were then parameterized using elements from all of the experimental work presented in this thesis plus those from other experimental (e.g. Moussallam et al., 2013), petrological (e.g. Kyle, 1981; Kyle et al., 1992; Kyle, 1977), and geochemical (e.g. Oppenheimer et al., 2009) works. I have presented two possible fluid mixtures that could explain the composition of surface gases being emitted from the Erebus lava lake.

## Appendix A

Table Appendix A.1: X-ray fluorescence bulk rock analyses for major (wt%) and trace (ppm) elements from Eschenbacher (1998)

Sample	DVDP 3-295	AW82033	7713	97009	97010A	97010B	97010C
$SiO_2$	38.85	45.92	47.41	50.69	51.01	50.38	51.21
$TiO_2$	3.08	3.01	2.79	1.97	1.95	1.93	1.97
$Al_2O_3$	11.06	17.05	18.53	18.59	19.51	19.39	19.51
$\mathrm{Fe}_2\mathrm{O}_3^T$	11.58	11.37	10.52	9.04	7.78	7.72	7.85
MnO	0.17	0.22	0.22	0.23	0.2	0.19	0.2
MgO	12.43	3.89	2.79	1.92	2.05	2.06	2.05
CaO	9.89	8.06	7.59	4.46	5.45	5.41	5.5
$Na_2O$	2.53	5.11	5.86	7.58	6.93	6.88	6.94
$K_2O$	1.14	2.54	2.75	4.27	3.36	3.3	3.42
$P_2O_5$	0.63	1.09	1.21	0.82	0.97	0.96	0.98
Loss on	6.5	1.03	-0.03	0.09	0	0	0
ignition							
Totals	98.14	99.59	99.99	99.96	99.55	98.56	99.98
V	253	137	79	26.6	42.7	46.7	45.1
$\operatorname{Cr}$	620	50	$< \! 10$	$< \! 10$	$< \! 10$	$< \! 10$	$< \! 10$
Ni	249	23.3	8.2	5.5	5.3	5.1	4.6
Cu	79.7	42	41	17.9	12.6	10.2	12.2
Zn	90	116	115	113	97	96	97
Ga	16.4	22.1	22	21.9	22.2	20.7	21.5
Rb	21.5	45	58	99	73	73	73
$\operatorname{Sr}$	720	1059	1316	812	1321	1321	1324
Y	26	43	42.3	45.4	39.8	38.5	39.9
Zr	286	470	486	749	636	633	634
Nb	62	129	146	234	168	168	168
Mo	3	4.9	6.5	10.4	7.4	8.2	7.9
Ba	360	672	773	900	833	817	829
Pb	4.1	5.9	6.4	7	5.7	6.2	4.9
Th	10.9	16.2	18	23.7	21.5	21.1	19.9
U	3.9	3.9	3.3	6.5	5.5	4.1	5

5	$1\sigma$	1.1	0.15	0.57	0.96	0.02	0.24	0.98	0.31	0.13	0.07	325	228	175	1.82	0.19		973		$N{=}10$
DP 3-20	Mean	41.03	4.14	14.56	10.26	0.16	5.85	12.85	3.69	1.63	0.92	1572	2166	875	95.55	1.5		5520		0.37
8) - DV.	r	41.53	4.11	14.47	11.18	0.15	6.21	13.4	3.75	1.69	0.9	1690	2007	1090	97.86	1.39		7270	1200	0.52
ter (199	q	41.74	4.29	14.95	9.8	0.17	5.72	13.18	3.59	1.6	0.86	1460	1927	670	96.3	1.25	0.14	5280	880	0.42
henbach	1	42.07	3.96	14.57	10.32	0.17	5.97	13.2	3.74	1.59	0.91	1260	1787	1070	96.9	1.57	0.17	4660	780	0.3
om Escl	j	41.81	4.1	14.57	9	0.15	6.01	13.55	3.51	1.58	0.97	1070	2448	610	95.66	1.26	0.14	4890	790	0.39
itions fr	i	40.18	4.05	14.05	9.34	0.15	5.8	13.51	3.46	1.53	0.87	2060	2352	1020	93.5	1.3	0.14	5670	940	0.44
composi	20	41.07	4.06	14.52	10.45	0.19	5.69	12.68	3.71	1.47	0.9	1740	2187	860	95.22	1.75		6750	1090	0.38
clusion e	q	39.26	4.09	13.31	10.1	0.18	5.44	13.29	3.15	1.5	0.86	2030	2267	1000	91.72	1.67	0.19	5040	850	0.3
Melt in	С	39.15	4.5	15.38	12.41	0.17	5.6	10.27	4.14	1.9	0.94	1680	2488	870	94.96	1.46		5950	1000	0.41
ix A.2:	р	41.7	4.12	14.67	9.8	0.12	6.12	13.15	3.61	1.62	1.09	1380	2062	890	96.42	1.67	0.18	4000	000	0.24
Append	a	41.79	4.1	15.11	10.19	0.15	5.97	12.3	4.2	1.8	0.92	1350	2137	670	96.93	1.66	0.19	5680	090	0.34
Table 1	Inclusion	$\mathrm{SiO}_2$	${\rm TiO_2}$	$\mathrm{Al}_2\mathrm{O}_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$\mathrm{Na_2O}$	$\rm K_2O$	$P_2O_5$	F(ppm)	S (ppm)	CI (ppm)	Total	$\rm H_2O$	error	$CO_2 (ppm)$	error	$\rm CO_2/H_2O$

A.3:	Melt	IIICIL		mendin				(000			
d e	e	υl		f	00	h	·	k	_	Mean	$1\sigma$
45.08 4	.08	J.	3.68	48.34	45.35	42.95	45	46.41	46.06	44.75	1.76
3.68 4	<b>38</b> 4	J.	1.18	2.22	3.71	4.25	3.73	3.03	3.54	3.56	0.55
16.67	.67		17.71	16.58	19.59	16.92	16.9	17.49	17.39	17.36	0.85
10.23	.23		11.57	11.86	9.66	11.63	11.92	10.93	10.57	10.83	1.02
0.2	$\sim$ 1	_	).18	0.31	0.16	0.21	0.33	0.26	0.25	0.23	0.06
3.52	52	~	4.15	3.06	3.8	4	3.58	2.83	3.37	3.59	0.45
11.22	.22		11.93	6.02	8.7	10.71	8.93	8.26	7.99	9.43	1.69
4.74	74	~	4.68	5.81	5.32	4.45	5	5.74	5.6	5.03	0.51
1.77	22		1.52	3.69	2.01	1.66	2.65	3.44	3.19	2.43	0.78
1.4	Ŧ		1.24	1.26	1.37	0.75	1.96	1.3	1.3	1.31	0.28
1860	60		1840	2720	2080	1590	2130	2790	2810	2133	713
1390	90		1290	1100	1085	1575	1730	1455	1145	1330	244
870	0	-	300	760	750	450	640	1000	1110	784	182
98.93	.93		101.23	99.6	100.05	97.88	100.43	100.22	99.75	98.94	1.65
0.11	[]		0.19	0.12	0.17	0.34	0.11	0.11	0.11	0.16	0.07
0.02	)2		0.03	0.02	0.02	0.05	0.02	0.02	0.02		
1240	40		1940	230	280	930	1330	430	240	825	623
240	0	-	340	00	110	470	270	120	300		
1.11	[]		1.03	0.18	0.17	0.27	1.16	0.39	0.22	0.5	N=11

731	$1\sigma$	0.39	0.17	0.31	0.28	0.03	0.29	0.32	0.63	0.07	0.15	480	247	170	0.94	0.02		149		N=8
998) - 7	Mean	47.72	2.7	17.81	10.43	0.25	2.31	6.71	6.21	3.49	1.3	2774	1109	1038	99.42	0.11		448		0.42
acher (1	l	47.74	2.75	17.88	10.44	0.3	2.04	7.19	6.25	3.58	1.44	3510	1310	1120	100.24	0.08	0.01	230	80	0.29
Eschenb	k	47.6	3.1	17.42	10.98	0.3	2.96	7.12	4.76	3.47	1.33	2610	1305	980	99.53	0.14	0.02	740	200	0.55
is from	j	47.91	2.58	17.6	10.68	0.24	2.42	6.62	6.1	3.52	1.54	2780	1440	980	99.73	0.11	0.01	510	120	0.45
npositior	i	48.51	2.71	18.24	10.22	0.26	2.31	6.82	6.72	3.41	1.27	3210	1095	820	100.98	0.09	0.01	420	100	0.48
sion cor	h	47.59	2.63	17.96	10.2	0.22	2.13	6.3	6.62	3.54	1.29	3080	825	1080	98.97	0.11	0.01	420	110	0.39
elt inclu	03	47.43	2.57	18.17	10.16	0.22	2.12	6.63	6.64	3.41	1.07	2160	1150	1350	98.89	0.12	0.01	490	160	0.4
A.4: $Me$	f	47.8	2.61	17.76	10.35	0.22	2.35	6.47	6.25	3.55	1.35	2680	1025	850	99.16	0.1	0.01	430	120	0.44
pendix .	е	47.16	2.66	17.47	10.43	0.26	2.12	6.5	6.31	3.45	1.11	2160	725	1120	97.86	0.12	0.01	340	110	0.29
Table Ap	Inclusion	$SiO_2$	$TiO_2$	$Al_2O_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$\rm Na_2O$	$\rm K_2O$	$P_2O_5$	F (ppm)	S (ppm)	Cl (ppm)	Total	$\rm H_2O$	error	$CO_2 (ppm)$	error	$\rm CO_2/H_2O$

	$1\sigma$	1.61	0.17	0.47	0.4	0.02	0.1	0.34	0.44	0.13	0.1	859	131	2053	2.55	0.07		707		$N{=}10$
7009	Mean	51.11	1.82	19.28	7.17	0.2	1.31	3.97	7.65	4.9	0.55	1386	671	2172	98.39	0.53	0.08	2421	378	0.46
998) - 9	j	51.48	2.01	19.38	7.35	0.2	1.38	3.78	7.21	4.88	0.38	2430	060	1610	98.51	0.65	0.1	3590	009	0.55
acher (1	i	52.65	1.78	19.75	7.41	0.22	1.26	3.89	7.67	4.79	0.56	2180	805	1630	100.45	0.49	0.07	2520	330	0.51
Eschent	h	52.29	1.96	19.65	7.5	0.17	1.42	3.67	8.14	4.97	0.5	940	610	1400	100.58	0.44	0.06	3090	470	0.7
ns from	ы	51.83	1.5	19.74	6.63	0.18	1.37	4.82	7.48	4.7	0.61	1720	545	1410	99.22	0.52	0.07	2040	310	0.39
$\operatorname{mpositic}$	f	50.75	2.01	19.51	7.15	0.19	1.28	3.86	7.65	4.93	0.62	2210	530	1580	98.38	0.52	0.08	2340	370	0.45
sion co	е	50.55	1.59	18.95	6.58	0.19	1.28	4.06	8.57	5.16	0.63	0	525	8000	98.41	0.47	0.06	1520	270	0.32
elt inclu	q	52.02	1.8	19.16	7.39	0.21	1.46	4.1	7.76	4.93	0.66	1410	915	1520	99.88	0.45	0.06	1490	260	0.33
A.5: Me	С	51.08	1.92	19.04	7.77	0.24	1.29	4.08	7.44	4.79	0.63	1680	790	1260	98.63	0.56	0.09	2650	430	0.47
pendix .	р	51.51	1.84	19.4	7.19	0.2	1.29	3.67	7.5	4.99	0.44	0	635	1510	98.25	0.58	0.08	1860	290	0.32
able Ap	a	46.92	1.79	18.2	6.74	0.24	1.11	3.82	7.07	4.87	0.44	1290	665	1800	91.56	0.59	0.09	3120	450	0.53
Ţ	Inclusion	$SiO_2$	${\rm TiO}_2$	$\mathrm{Al}_2\mathrm{O}_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$\rm Na_2O$	$\rm K_2O$	$P_2O_5$	F (ppm)	S (ppm)	Cl (ppm)	Total	$H_2O$	error	$CO_2 (ppm)$	error	$\rm CO_2/H_2O$

	$1\sigma$	0.62	0.17	0.54	0.49	0.02	0.11	0.19	0.35	0.12	0.11	672	157	154	0.57	0.01		507		N = 8
) - 97010	Mean	53.56	1.87	19.63	6.71	0.19	1.21	3.56	8.01	5.22	0.77	2406	616	1223	101.14	0.12		877		0.74
er (1998)	i	54.46	1.92	20.34	5.8	0.18	1.14	3.42	7.77	5.17	0.63	2250	695	1050	101.23	0.1	0.02	650	210	0.65
chenbach	h	53.88	1.86	19.92	6.57	0.18	1.05	3.53	7.76	5.34	0.88	2120	520	1150	101.34	0.11	0.02	460	140	0.42
from Ese	ß	53.49	1.75	19.49	6.75	0.17	1.26	3.31	8.27	5.27	0.83	2600	685	1200	101.03	0.12	0.02	850	300	0.68
ositions	f	53.3	1.86	19.97	6.81	0.19	1.31	3.51	8.05	5.25	0.83	2230	345	1250	101.45	0.13	0.02	740	270	0.57
ion comp	е	54.23	1.66	20.14	6.45	0.19	1.09	3.43	8.65	5.41	0.57	1290	550	1300	102.12	0.13	0.02	nd		
elt inclus	d	53.49	2.17	18.9	6.82	0.19	1.27	3.74	7.9	5.14	0.77	2320	840	1420	100.82	0.13	0.02	060	180	0.77
x A.6: M	С	52.53	1.69	19.15	7.55	0.22	1.24	3.92	7.51	5.15	0.76	2770	540	1000	100.14	0.11	0.02	510	240	0.48
Appendiz	р	53.11	2.04	19.1	6.93	0.23	1.36	3.6	8.16	5.03	0.87	3670	755	1410	101.01	0.12	0.02	1950	270	1.62
Table	Inclusion	$\mathrm{SiO}_2$	$TiO_2$	$Al_2O_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$\rm Na_2O$	$\rm K_2O$	$P_2O_5$	F(ppm)	S (ppm)	Cl (ppm)	Total	$\mathrm{H}_{2}\mathrm{O}$	error	$CO_2 (ppm)$	error	$\rm CO_2/H_2O$

	$1\sigma$	0.6	0.04	0.28	0.1	0.03	0.03	0.12	0.27	0.27	0.02	347	58	171	1.11	0.02		125		$N{=}10$
$\Xi A1$	Mean	54.83	0.95	19.79	4.98	0.25	0.81	1.81	8.82	6.29	0.3	2652	375	1502	99.27	0.17		690		0.41
1998) - I	k	55.62	0.98	19.98	5.14	0.23	0.84	1.86	9.03	6.12	0.27	2880	420	1490	100.53	0.18	0.02	580	270	0.31
bacher (	j	54.42	0.91	19.68	4.98	0.23	0.81	1.91	8.65	5.98	0.32	3180	260	1380	98.37	0.14	0.01	880	320	0.61
Eschenł	i	54.43	0.96	19.68	5.05	0.25	0.78	1.89	8.59	6.1	0.29	2390	375	1290	98.41	0.15	0.02	790	260	0.5
is from	h	54.82	0.94	19.46	4.99	0.25	0.85	1.59	8.66	6.83	0.32	2590	395	1810	99.18	0.18	0.02	760	300	0.42
npositior	ъ0	55.51	0.94	20.06	5.03	0.31	0.78	1.96	8.89	6.21	0.31	2190	405	1330	100.38	0.15	0.02	760	250	0.5
sion cor	f	54.55	0.93	19.81	5.01	0.28	0.83	1.69	9.1	6.49	0.33	3150	355	1650	99.52	0.2	0.02	640	300	0.31
elt inclu	е	55.14	0.93	20.01	4.87	0.22	0.82	1.92	8.92	6.23	0.29	2120	365	1700	99.76	0.18	0.02	430	190	0.24
A.7: Me	q	53.5	0.98	19.3	5.04	0.21	0.8	1.86	8.25	6.01	0.29	2540	430	1640	96.69	0.16	0.02	700	300	0.44
pendix .	р	54.79	0.91	20.01	4.99	0.21	0.8	1.66	8.73	6.59	0.28	2660	465	1420	99.43	0.17	0.02	730	250	0.42
[able Ap]	a	55.24	1.02	20.14	4.87	0.27	0.85	1.89	9.14	6.12	0.33	2610	335	1430	100.28	0.16	0.02	640	340	0.41
L '	Inclusion	$SiO_2$	${\rm TiO_2}$	$\mathrm{Al}_2\mathrm{O}_3$	$\mathrm{FeO}^{T}$	MnO	MgO	CaO	$\rm Na_2O$	$\rm K_2O$	$\mathrm{P}_{2}\mathrm{O}_{5}$	F (ppm)	S (ppm)	Cl (ppm)	Total	$H_2O$	error	$CO_2 (ppm)$	error	$\rm CO_2/H_2O$

	11		-
KI-01	26-NOV-10 3:37:03PM 77° 50' 57.35" S	KINX-02	27-NOV-10 10:16:08PM 77° 39.420' S
	166° 42' 56.10" E		166° 22.954' E
KI-02	26-NOV-10 5:02:08PM 77° 50' 40.86" S	KFANG-01	elev 2965m 77° 29.488' S
	166° 45' 49.42" E		$167^{\circ}$ 14.679' E
KI-03	26-NOV-10 5:44:11PM 77° 50' 39 80" S	KFANG-02	elev 2985m 77° 29 453' S
	166° 45' 47.12'' E		167° 14.569' E
KI-04	26-NOV-10 7:37:21PM	KFANG-03	elev 2988m 77° 29 438' S
	166° 41' 33.45" E		167° 14.526' E
KROY-01	27-NOV-10 7:39:23PM	KFANG-04	elev 2970m 77° 29.466' S
	166° 10.456' E		167° 14.594' E
KBRN-01	27-NOV-10 8:26:35PM	KFANG-05	77° 29.509' S
	166° 15.062' E		167° 14.009° E
KINX-01	27-NOV-10 9:42:45PM		
	166° 23.138' E		

Table Appendix A.8: GPS coordinates of sample locations

	KFANG-01	KFANG-02	KFANG-03	KFANG-04	KFANG-05	KROY-01	KI-01-112710
Major Oxi	des~(wt%)						
$SiO_2$	49.38	46.26	44.13	49.13	48.98	55.28	42.27
$Al_2O_3$	17.998	17.51	16.535	19.913	17.84	19.378	13.514
$Fe_2O_3tot$	10.054	11.28	12.573	9.013	10.123	5.672	13.447
FeOtot	6.08	5.61	8.01	5.72	5.37	3.35	9.72
MnO	0.2325	0.2213	0.2341	0.1941	0.2382	0.1974	0.1905
MgO	2.139	3.908	4.571	2.292	2.197	1.209	8.607
CaO	5.062	7.479	9.585	7.107	5.004	3.089	10.85
$Na_2O$	7.188	5.61	4.67	6.096	6.881	7.952	3.519
$K_2O$	4.072	2.714	2.075	2.929	3.947	4.039	1.726
$\mathrm{TiO}_2$	2.198	2.944	3.706	2.18	2.178	1.158	4.153
$P_2O_5$	1.03	1.21	1.55	1.06	1.07	0.47	0.81
$\mathbf{PF}$	0.48	0.72	-0.28	0.03	1	0.66	-0.51
Total	99.83	99.86	99.35	99.94	99.47	99.11	98.57
Volatiles (	wt%)						
$H_2Otot$	0.61	0.72	0.42	0.25	0.89	0.55	0.26
$\rm CO_2 tot$	0.12	0.04	$<\!\!0.04$	$<\!\!0.04$	$<\!\!0.04$	$<\!\!0.04$	0.09
$\operatorname{Stot}$	0.09	0.04	0.02	0.05	0.1	0.03	0.03
Trace Elen	nents (ppm)						
As	2.165	1.539	4.56	1.143	3.082	2.104	nd
Ba	859	618.8	621.8	737.2	876.6	858.4	441.5
Be	4.8	3.409	2.287	3.364	4.937	6.418	1.965
Cd	0.496	0.405	0.571	0.346	0.555	0.593	0.238
Ce	208.6	161.2	168	171.9	223.1	200	100.2
$\mathrm{Co}$	13.41	24.58	28.86	14.66	13.99	4.211	46.79
$\operatorname{Cr}$	6.996	23.49	23.44	7.952	6.285	4.4	298.6
$\mathbf{Cs}$	0.84	0.578	0.404	0.553	0.77	1.211	0.375
Cu	30.87	29.17	25.53	30	35.41	4.783	46.16
Dy	7.883	6.831	7.784	6.365	8.234	8.263	5.577
$\mathrm{Er}$	3.806	3.182	3.492	3.053	4.049	4.5	2.488
Eu	3.828	3.598	4.166	3.695	4.03	4.016	2.977
$\operatorname{Ga}$	25.28	22.87	22.92	23.46	26.4	27.74	20.44
$\operatorname{Gd}$	10.14	9.215	10.66	8.634	10.64	9.368	7.762
Ge	1.444	1.374	1.528	1.292	1.567	1.582	1.448
$_{ m Hf}$	10.73	8.375	7.055	7.702	11.27	17.01	5.914
Но	1.428	1.221	1.341	1.125	1.47	1.547	0.983
In	0.092	0.094	0.141	0.106	0.083	$\mathbf{nd}$	0.085
La	107.9	80.86	79.54	85.46	112.3	103.9	49.3
Lu	0.537	0.414	0.424	0.402	0.554	0.684	0.301
Mo	6.971	4.377	3.451	5.397	5.412	8.44	3.589
Nb	182.2	128.7	105	122.7	190.4	216.7	66.54
Nd	80.43	67.6	74.6	67.52	84.07	71.43	48.04
Ni	5.022	15.91	15.46	7.671	4.553	nd	108.9

Table Appendix A.9: Whole rock compositions of all samples collected during field-work on Ross Island in 2010 (Part 1)

	KFANG-01	KFANG-02	KFANG-03	KFANG-04	KFANG-05	KROY-01	KI-01-112710
Pb	4.9816	2.7599	4.1905	3.5492	6.2063	4.4963	2.5887
$\Pr$	21.6	18.14	18.96	18.3	22.47	20.02	12.02
$\operatorname{Rb}$	83.9	55.9	37.67	56.96	84.91	92.88	31.44
$\mathbf{Sb}$	0.173	0.121	0.119	0.144	0.188	0.278	nd
$\operatorname{Sm}$	13.37	12.02	13.41	11.26	13.86	12.07	9.329
$\operatorname{Sn}$	3.826	2.624	2.564	3.084	4.191	5.091	2.391
$\operatorname{Sr}$	838	1086	1292	1367	820.3	800.7	971.5
Ta	12.34	8.816	7.677	8.785	12.78	14.74	4.97
$\mathrm{Tb}$	1.456	1.274	1.456	1.202	1.532	1.444	1.074
$\mathrm{Th}$	12.7	9.511	7.147	9.848	12.48	18	5.152
Tm	0.543	0.437	0.463	0.43	0.571	0.671	0.337
U	3.105	2.656	2.007	2.797	2.533	4.853	1.548
V	31.96	124.5	164.9	49.93	30.73	14.11	308.8
W	2.185	1.448	1.475	1.457	1.588	2.914	1.013
Υ	39.58	33.54	36.92	31.89	40.61	43.02	26.78
Yb	3.614	2.823	2.877	2.754	3.626	4.475	2.028
Zn	125.9	117	125	105.4	132	106.4	101.8
$\operatorname{Zr}$	612.6	466.8	337.1	450	608	755.2	260.3
nd = not	detected (be	low the dete	ction limit);	XRF analys	ses were perf	ormed at t	he Centre de
Recherche	es Pétrograph	iques et Géo	chimiques (S	SARM) in N	ancy, France		

Table Appendix A.9: Whole rock compositions of all samples collected during field-work on Ross Island in 2010 (Part 1)



IGSN: IAC000003 Name: KFANG-03 Type: Individual Sample AKA: Not Provided



Name: KI-01-112710 Type: Individual Sample AKA: Not Provided



Name: KI-03-112710 Type: Individual Sample AKA: Not Provided



IGSN: IAC00000A Name: KINX-1 Type: Individual Sample AKA: Not Provided



1GSN: IAC00000D Name: KFANG-04 Type: Individual Sample AKA: Not Provided



Name: KFANG-02 Type: Individual Sample AKA: Not Provided



IGSN: IACKROY01 Name: KROY-01 Type: Individual Sample AKA: Not Provided



IGSN: IAC000004 Name: KFANG-05 Type: Individual Sample AKA: Not Provided



IGSN: IAC000007 Name: KI-02-112710 Type: Individual Sample AKA: Not Provided



IGSN: IAC000009 Name: KI-04-112710 Type: Individual Sample AKA: Not Provided



IGSN: IAC00000B Name: KINX-2 Type: Individual Sample AKA: Not Provided



IGSN: IACFANG01 Name: KFANG-01 Type: Individual Sample AKA: Not Provided



IGSN: IACKBRN01 Name: KBRN-1 Type: Individual Sample AKA: Not Provided

Figure Appendix A.1: International Geo Sample Numbers (IGSNs) and QR codes for samples collected during the G-081 Antarctic Expedition in 2010.

	KI-02-112710	KI-03-112710	KI-04-112710	KINX-1	KINX-2	KBRN-1
Major Oxid	les (wt%)					
$SiO_2$	42.21	42.36	42.13	57.44	49.3	43.76
$Al_2O_3$	13.424	13.422	13.502	18.213	19.473	16.723
$Fe_2O_3tot$	13.857	13.72	13.51	7.231	8.384	11.713
FeOtot	10.03	9.34	9.61	3	2.9	7.21
MnO	0.1899	0.1889	0.1898	0.271	0.1837	0.2339
MgO	9.194	9.112	8.728	0.629	2.559	3.878
CaO	10.845	10.908	10.833	2.614	6.771	8.882
$Na_2O$	3.413	3.43	3.567	7.797	6.234	4.49
$\overline{K_2O}$	1.576	1.601	1.595	4.173	2.848	1.903
$\overline{\text{TiO}_2}$	4.247	4.217	4.169	0.567	2.164	2.996
$P_2O_5$	0.79	0.79	0.81	0.18	0.97	1.48
PF	-0.61	-0.56	-0.43	0.7	0.75	3.9
Total	99.14	99.18	98.61	99.81	99.64	99.97
Volatiles (u	vt%)					
H <sub>2</sub> Otot	0.19	0.19	0.29	0.35	0.41	4.2
$\rm CO_2 tot$	0.05	0.05	0.08	$<\!\!0.04$	0.11	0.15
Stot	0.02	0.02	0.02	0.02	0.02	0.02
Trace Elem	ents (ppm)					
As	nd	nd	nd	2.85	1.522	1.174
Ba	420	446.6	472.4	980.1	700	526.7
Be	1.817	2.003	2.107	5.642	3.888	2.682
Cd	0.245	0.274	0.258	0.524	0.433	0.517
Ce	97.38	101.7	104.6	208.7	153.1	168.9
Co	49.06	49.98	49.07	2.455	14.36	21.07
$\operatorname{Cr}$	335	340.4	324.6	4.56	11.86	7.517
$\mathbf{Cs}$	0.311	0.364	0.377	0.893	0.597	0.329
Cu	29.43	39.29	36.57	4.949	17.36	13.37
Dy	5.613	5.712	5.907	6.088	6.288	6.922
Er	2.458	2.546	2.578	3.345	3.078	3.141
Eu	2.941	3.08	3.169	2.888	3.56	3.909
Ga	20.51	20.88	21.07	26.27	22.27	21.71
Gd	7.456	7.869	8.052	7.251	8.368	9.677
Ge	1.429	1.507	1.562	1.616	1.318	1.355
$_{ m Hf}$	5.868	5.98	6.022	14.41	8.236	7.204
Ho	0.938	0.997	1.008	1.149	1.124	1.213
In	0.101	0.103	0.105	nd	nd	0.104
La	47.47	49.67	51.07	113.2	79.41	79.67
Lu	0.284	0.294	0.308	0.569	0.423	0.403
Mo	2.981	3.983	3.714	8.558	5.239	2.945
Nb	63.72	67.23	69.79	171.4	138.8	101.3
Nd	46.97	49.68	50.81	66.06	62.81	73.33
Ni	111.4	121.2	115	nd	9.403	6.011

Table Appendix A.10: Whole rock compositions of all samples collected during field-work on Ross Island in 2010 (Part 2)

	KI-02-112710	KI-03-112710	KI-04-112710	KINX-1	KINX-2	KBRN-1				
$\operatorname{Pb}$	2.3527	2.5431	2.8541	6.5182	3.2065	3.4635				
$\Pr$	11.76	12.34	12.68	19.7	17.19	18.99				
$\operatorname{Rb}$	28.74	31.18	32.18	88.81	53.89	36.97				
$\mathbf{Sb}$	nd	nd	nd	0.315	0.201	0.148				
$\operatorname{Sm}$	9.226	9.714	9.896	9.87	10.78	12.77				
$\operatorname{Sn}$	2.739	2.63	2.738	5.265	3.019	2.486				
$\mathbf{Sr}$	938.3	988.7	1018	505.9	1306	1211				
Ta	4.835	4.965	5.154	12.32	9.108	7.484				
$\mathrm{Tb}$	1.063	1.091	1.121	1.088	1.171	1.327				
$\mathrm{Th}$	4.872	5.16	5.407	17.44	11.21	7.828				
Tm	0.327	0.332	0.35	0.534	0.439	0.433				
U	1.384	1.53	1.7	4.68	3.218	2.461				
V	320.8	325.3	327.3	0.759	68.04	126.4				
W	0.944	1.007	1.003	2.861	1.999	0.339				
Υ	25.92	27.48	28.12	33.34	31.67	33.66				
Yb	1.937	2.035	2.097	3.569	2.747	2.695				
Zn	103.1	108.2	108.9	130.4	93.61	116.7				
Zr	252.2	266.5	272.7	760.9	477.2	377.5				
nd = not	nd = not detected (below the detection limit); XRF analyses were performed at the Centre de									
Recherches Pétrographiques et Géochimiques (SARM) in Nancy, France.										

Table Appendix A.10: Whole rock compositions of all samples collected during field-work on Ross Island in 2010 (Part 2)

$Sample^1$	A <sub>1430</sub>	$A_{1510}$	$A_{4500}$	$A_{5200}$	$A_{1640}$	$A_{3500}$	$A_{2345}$	$d~(\mu m)$	$ ho~({ m g/L})$
AW 82038	phonote	phrite es	rperimer	nts					
AW-06-a	0.160	0.202			0.137	0.796		66	2538.93
AW-06-b	0.142	0.181			0.103	0.861		65	
AW-10-a					0.449	1.292		27.48*	2348.18
AW-10-b			0.010	0.014	0.520	1.446	0.004	31.61*	
AW-13-a	0.012				0.205	0.765		20.51*	2443.39
AW-13-b	0.041	0.048			0.176	0.654		$17.46^{*}$	
AW-13-c					0.202	0.594		$17.16^{*}$	
AW-13-d	0.029	0.029			0.250	0.953		$24.66^{*}$	
AW-14-a	0.056	0.073	0.019		0.776	2.131		124	2605.45
AW-14-b			0.020					124	
AW-17-a	0.049	0.060	0.011	0.008	0.372	1.785		63	2502.23
AW-17-b	0.052	0.061	0.011	0.008	0.358	1.739		61	
AW-17-c	0.049	0.071	0.012	0.008	0.395	1.739		65	
AW-19B-a						0.649	0.030	68	2438.59
AW-20B-a	0.036	0.043			0.105	0.353	0.028	23	2411.85
AW-21-a					0.136	0.494		$18.99^{*}$	2329.60
AW-21-b	0.021	0.032			0.158	0.533		$15.91^{*}$	
AW-22-a	0.093	0.093						73	2441.59
AW-22-b						1.657		81.2	
AW-22-c						1.623		84	
AW-22-d						1.566		70.5	
AW-23-a					0.488	1.248		27.40*	2270.11
AW-23-b					0.465	1.218		$27.71^{*}$	
AW-23-c					0.426	1.119		25.02*	
AW-24-a	0.676	0.676			0.287	1.850		174	2613.80
AW-24-b	0.758	0.758			0.316	1.805		174	
AW-24-c	0.808	0.808			0.349	1.839		174	
AW-25-a	0.247	0.273	0.014	0.008	0.351	1.948		92	2588.60
AW-25-b	0.266	0.295	0.015	0.010	0.385	2.103		96	
AW-25-c	0.194	0.205	0.010	0.007	0.272	1.623		82	
AW-25-d	0.182	0.191	0.010	0.006	0.256	1.512		76	
АW-25-е	0.191	0.200	0.012	0.008	0.275	1.646		80	
AW-25-f	0.216	0.239	0.011	0.007	0.317	1.785		86	
AW-26-a	0.103	0.111	0.009	0.010	0.505	1.809		57	2498.74
AW-26-b	0.116	0.116	0.009	0.010	0.520	1.832		57	
AW-26-c	0.125		0.010	0.009	0.520	1.855		59	
AW-26-d	0.116	0.129	0.010	0.010	0.520	1.855		58	
AW-27-a	0.207	0.224			1.395			89	2543.54

Table Appendix A.11: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 4

$Sample^1$	A <sub>1430</sub>	$A_{1510}$	$A_{4500}$	$A_{5200}$	A <sub>1640</sub>	$A_{3500}$	$A_{2345}$	$d~(\mu m)$	$ ho~({ m g/L})$
AW-27-b	0.263	0.267	0.009	0.016	1.412			93	
AW-27-c	0.321	0.344	0.016	0.027	1.576			94	
AW-28-a			0.005	0.015	0.592	1.278		23.69*	2328.66
AW-28-b					0.494	1.173		$24.92^{*}$	
AW-28-c					0.533	1.248		$22.89^{*}$	
AW-28-d					0.476	1.145		$17.86^{*}$	
AW-29-a	0.097	0.103				0.415		45	2657.97
AW-29-b						0.432		45	
AW-29-c	0.114	0.125				0.437		45	
AW-33-a	0.111	0.122			0.148	0.805		30	2520.20
AW-33-b	0.117	0.135			0.163	0.842		32	
AW-33-c	0.078	0.091			0.123	0.823		32	
AW-34-a			0.011	0.035	1.260			95	2414.79
AW-34-b			0.010	0.033	1.218			91.3	
AW-34-c			0.014	0.036	1.333			91	
AW-34-d			0.035	0.084				178	
AW-38-a					0.169	0.361		$6.05^{*}$	2224.75
AW-38-b					0.205	0.520		8.05*	
AW-38-c					0.151	0.454		$7.44^{*}$	
AW-39-a	0.372	0.336	0.009	0.032	1.341			110	2409.74
AW-39-b	0.190		0.013	0.037	1.297			110	
AW-39-c			0.015	0.033	1.218			110	
AW-39-d	0.518		0.018	0.032	1.484			110	
AW-40-a	0.427	0.419			0.746			89	2532.21
AW-40-b	0.268	0.268				1.600		89	
AW-40-c	0.341	0.345	0.013	0.011	0.545	1.691		89	
AW-40-d	0.390	0.405			0.630			89	
АШ-40-е	0.380	0.386				1.702		89	
AW-41-a	0.208	0.227			0.504			176	2537.76
AW-42-a	0.085	0.117			0.126	0.641		97	2550.42
AW-42-b	0.046	0.081			0.078	0.409		68	
AW-42-c						0.423		71.4	
AW-45-a	0.677	0.664	0.020	0.026	1.123			110	2332.19
AW-45-b	0.904	0.860	0.023	0.025	1.224			110	
AW-45-c	0.568	0.568	0.021	0.027	1.072			110	
AW-45-d	0.540	0.497			0.868			110	
АW-45-е			0.020	0.026				110	
AW-46-a	0.431		0.010	0.024	0.879			58	2093.46
AW-46-b	0.530		0.014	0.030	1.148			58	

Table Appendix A.11: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 4

Sample <sup>1</sup>	A <sub>1430</sub>	A <sub>1510</sub>	A <sub>4500</sub>	A <sub>5200</sub>	A <sub>1640</sub>	A <sub>3500</sub>	A <sub>2345</sub>	$d (\mu m)$	$ ho~({ m g/L})$
AW-40-C	0.505		0.014	0.030	1.059			58 05	0120 67
AW 47 h			0.008	0.055	1.739			90 100	2132.07
AW 47 o			0.011	0.054	1.609			109	
AW-47-C			0.010	0.055				109	
KI-04 basa	enite expe	eriments							
KI-07-a	0.130	0.166			0.257	1.563		52	2820.18
KI-07-b	0.117	0.143	0.008	0.006	0.227	1.496		52	
KI-07-c	0.126	0.154	0.009	0.006	0.247	1.546		55	
KI-07-d	0.149	0.175	0.008	0.006	0.267	1.576		54	
KI-09-a	0.050	0.055			0.041	0.239		44	2629.61
KI-09-b						0.289		44	
KI-09-c	0.012	0.031			0.056	0.250		41	
KI-09-d	0.065	0.068			0.029	0.404		45	
KI-10-a	0.067	0.082			0.212	0.533		37	2672.91
KI-10-b	0.034	0.044			0.174	0.571		37	
KI-10-c	0.047	0.069			0.197	0.491		37	
KI-15-a	0.631	0.631			0.230	1.412		75.64*	2778.91
KI-15-b	0.403	0.429			0.169	1.263		$66.67^{*}$	
KI-16-a	0.513	0.480			0.491	1.582		50	2682.22
KI-20-a	0.096	0.099			0.265	0.726		45	2798.31
KI-20-b	0.132				0.194	0.580		45	
KI-20-c	0.111	0.117			0.260	0.590		29.22*	
KI-21-a	0.325	0.314			0.202	0.906		40	2731.74
KI-21-b	0.186	0.188			0.134	0.779		40	
KI-21-c	0.113	0.117			0.129	0.601		20.26*	
KI-21-d	0.140	0.148			0.126	0.659		20.83*	
КІ-21-е	0.145	0.170			0.174	0.678		21.39*	
KI-23-a	0.553	0.559	0.017		0.032	0.908		78	2831.76
KI-23-b	0.494	0.501			0.013	0.886		78	
KI-23-c	0.432	0.443	0.009	0.007	0.032	0.851		78	
KI-23-d	0.481	0.501	0.012	0.006	0.078	0.833		78	
KI-32-a	0.119				0.399	0.944		34	2556.20
KI-32-b	0.117				0.398	0.950		34	
KI-32-c	0.132				0.397	0.950		34	
KI-32-d	0.107				0.357	0.917		34	
KI-33-a					0.202	0.494		32	2168.26
KI-33-b					0.146	0.421		32	
Notation th	e same as	s in Tabl	e Append	lix A 12				-	

Table Appendix A.11: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 4
Sample <sup>1</sup>	A1430	A1510	A4500	A5200	A1640	A3500	A2345	$d (\mu m)$	ρ (g/L)
ERE-97018 F	Phonolite	e experir	nents	0200	1040	5000	2040		1 (0/ /
ERE S01-a	0.122	*						195	2425
$\mathrm{ERE}^{-}\mathrm{S01-b}$	0.123		0.032			1.747		195	
$\mathrm{ERE}^{-}\mathrm{S01-c}$			0.032	0.011		2.437	0.054	195	
ERE S01-d			0.025	0.007				195	
$\text{ERE}\_\text{S02-a}$	0.110					0.531	0.017	75	2397
ERE S02-b	0.086					0.555	0.013	75	
$ERE_S02-c$						0.628		75	
$ERE_{S02-d}$			0.017	0.003		0.607		75	
$ERE\_S02-e$			0.017	0.004		0.625		75	
ERE_S03-a			0.014		0.055	1.164		113	2418
$ERE_{S03-b}$			0.016		0.047	1.164		113	
$ERE_S03-c$			0.013	0.003		1.302		113	
$ERE_{S03-d}$			0.013	0.003		1.288		113	
$ERE_S03-e$			0.014	0.003		1.284		113	
$ERE\_S07-a$			0.016	0.004		1.489		122	2408
$ERE_S08-a$							0.041	182	2510
$ERE_S08-b$							0.055	182	
$ERE\_S09-a$			0.025					190	2420
$ERE_S09-b$			0.023					190	
$ERE_S09-c$			0.033	0.013		2.023		190	
$ERE_S09-d$			0.024	0.006		2.077		190	
ERE_S10-a			0.028		0.351			165	2314
$ERE_{S10-b}$			0.031		0.322			165	
$ERE_S10-c$			0.013	0.011		2.655		165	
ERE_S10-d			0.041	0.009		2.851		165	
ERE_S11-a						0.708		83	2436
ERE_S11-b	0.065	0.063				0.696		83	
ERE_S11-c			0.008	0.003		0.753		83	
ERE_S11-d			0.009	0.004		0.787		83	
ERE_S12-a		0.047				0.443	0.015	133.22*	2468
ERE_S12-b	0.014	0.093				0.441	0.028	128	
ERE_S12-c						0.495		128	
ERE_S12-d			0.010			0.495		128	2.405
ERE_S13-a			0.012			0.949		111.47*	2407
ERE_S13-b						0.944		109.67*	
$ERE\_S13-c$			0.010	0.001		1.068		104	

Table Appendix A.12: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 5  $\,$ 

Sample <sup>1</sup> ERE_S13-d	A <sub>1430</sub>	A <sub>1510</sub>	A <sub>4500</sub> 0.010	A <sub>5200</sub> 0.003	A <sub>1640</sub>	A <sub>3500</sub> 1.068	A <sub>2345</sub>	$\begin{array}{c} d \ (\mu \mathrm{m}) \\ 104 \end{array}$	$ ho~({ m g/L})$
KI 0/ Basani	ite erner	imonte							
KI SO2B a	$\begin{array}{c} 0 331 \\ 0 331 \end{array}$	inieniis				1.068		196	2877
$KI_{S02B-a}$	0.001					1.000		120	2011
$KI_{S02B-0}$	0.030					1.000		120 126	
KI_502B-d	0.521		0.006	0.002		1.000		$120 \\ 126$	
KI_502B-q KI_\$02B-e			0.000	0.002		1.004 1.332		120	
KI_502B C KI_503-a	0.072	0.063	0.000	0.001	0 191	1.002		160	2764
KI_S03-b	0.083	0.000	0.010		0.191			160	2101
KI_S03-c	0.076	0.065	0.018		0.201			160	
KI_S03-d	0.010	0.000	0.015		0.201	2.482		160	
KI S04-a			0.010			0.653		60.39*	2798
KI S04-b						0.678		60.39*	
KI S04-c			0.003			0.729		60.39*	
KI <sup>-</sup> S05-a						0.699		76	2808
KI S05-b			0.004			0.794		76	
$\overline{\mathrm{KI}}$ S05-c						0.830		76	
KI_S06-a	0.290	0.278				0.861		96	2873
KI_S06-b	0.305					0.827		96	
$KI_S06-c$	0.304					0.827		$102.36^{*}$	
$KI_S06-d$						0.928		96	
$KI_S06-e$						0.944		96	
KI_S06-f						0.913		96	
$KI_S07-a$	0.249	0.240			0.096			166	2746
$KI_S07-b$	0.143	0.142			0.058			166	
$KI_S07-c$	0.263	0.263			0.108			166	
$KI_S07-d$			0.014			2.308		166	
$KI_S07-e$			0.012	0.004		2.411		166	
KI_S08-a			0.033					375	2847
KI_S08-d			0.029	0.008				375	
KI_S08-e			0.031					375	
KI_S09-a	0.349	0.352				0.969		214	2857
KI_S09-b	0.294	0.298				0.926		214	
KI_S09-c						0.745		214	
KI_S09-d	0.352	0.356				0.978		214	
KI_S09-e						0.958		214	
KI_S09-t	0.000	0.051	0.000			0.873		214	2010
KI_S10-a	0.290	0.251	0.009			1.458		161	2812

Table Appendix A.12: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 5  $\,$ 

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sample <sup>1</sup>	A <sub>1430</sub>	A <sub>1510</sub>	A <sub>4500</sub>	A <sub>5200</sub>	A <sub>1640</sub>	A <sub>3500</sub>	A <sub>2345</sub>	$d (\mu m)$	$\rho (g/L)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI S10-b	0.275	0.244	0.009	0200	1010	1.316	2010	161	, (0, )
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\overline{\mathrm{KI}}$ S10-c			0.008			1.736		161	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI S10-d			0.009			1.714		161	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI <sup>-</sup> S11-a	0.083				0.042	1.325		127	2832
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\overline{\mathrm{KI}}$ S11-b	0.091	0.085			0.063	1.056		127	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI S11-c			0.008	0.002		1.754		127	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S11-d			0.010	0.003		1.893		127	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S12-a			0.013			1.570		170	2797
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$KI_S12-b$			0.022			2.156		170	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S12-c			0.014			2.174		170	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S13-a			0.014			1.523		271	2681
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$KI_S13-b$			0.015			1.604		271	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S13-c			0.020			1.958		271	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$KI_S13-d$						1.797		271	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S14-a	0.070	0.050						178	2827
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$KI_S14-b$	0.066	0.072						178	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S14-c			0.010			1.458		178	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S14-d			0.009			1.378		178	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	KI_S15-a	0.031	0.032	0.022		0.271			160	2705
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$KI_S15-b$	0.027	0.271	0.023		0.273			160	
KI_S15-d       0.022       0.008       2.333       160         KI_S15-e       0.019       0.009       2.333       160         KI_S16-a       0.028       0.021       0.030       0.014       0.252       239       2681         KI_S16-b       0.296       0.025       0.030       0.011       0.257       239       2681         KI_S16-b       0.296       0.025       0.030       0.011       0.257       239         KI_S16-c       0.027       0.013       2.716       239         KI_S16-d       0.027       0.013       2.826       239         KI_S16-e       0.026       0.012       2.967       239	$KI_S15-c$						2.269		160	
KI_S15-e0.0190.0092.333160KI_S16-a0.0280.0210.0300.0140.2522392681KI_S16-b0.2960.0250.0300.0110.257239KI_S16-c0.0270.0132.716239KI_S16-d0.0270.0132.826239KI_S16-e0.0260.0122.967239	$KI_S15-d$			0.022	0.008		2.333		160	
KI_S16-a       0.028       0.021       0.030       0.014       0.252       239       2681         KI_S16-b       0.296       0.025       0.030       0.011       0.257       239         KI_S16-c       0.027       0.013       2.716       239         KI_S16-d       0.027       0.013       2.826       239         KI_S16-e       0.026       0.012       2.967       239	$KI_S15-e$			0.019	0.009		2.333		160	
KI_S16-b       0.296       0.025       0.030       0.011       0.257       239         KI_S16-c       0.027       0.013       2.716       239         KI_S16-d       0.027       0.013       2.826       239         KI_S16-e       0.026       0.012       2.967       239	KI_S16-a	0.028	0.021	0.030	0.014	0.252			239	2681
KI_S16-c0.0270.0132.716239KI_S16-d0.0270.0132.826239KI_S16-e0.0260.0122.967239	$KI_S16-b$	0.296	0.025	0.030	0.011	0.257			239	
KI_S16-d0.0270.0132.826239KI_S16-e0.0260.0122.967239	$KI_S16-c$			0.027	0.013		2.716		239	
KI_S16-e 0.026 0.012 2.967 239	$KI_S16-d$			0.027	0.013		2.826		239	
	KI_S16-e			0.026	0.012		2.967		239	

Table Appendix A.12: Thicknesses, densities, and FTIR absorbance measurements of experimental glasses from Chapter 5  $\,$ 

<sup>1</sup>Capital letters and numbers refer to experiment type and number. Lowercase letter refers to individual FTIR measurement. \*Refers to sample thicknesses measured by interference fringes. d = sample thickness;  $\rho =$  density

## Appendix B

This appendix contains tables illustrating step-by-step how the thermodynamic calculations in Chapter 6 were performed in order to determine the compositions of equilibrium fluid co-existing with Erebus melt inclusions. All equations and references used are given in the table captions, and details of those equations can be found in Chapter 6. Also included in this appendix is the code used to model an idealized gas mixture and the output of model runs using this code. Details are given in Chapter 6.

	$\log KSO_2$	$\log KH_2O$	$\log KH_2S$	
Phon-8	10.71	7.06	1.06	
EA-1	10.71	7.06	1.06	
97009	9.68	6.35	0.8	
DVDP3-295	9.68	6.35	0.8	
	$\gamma H2O$	$\gamma SO2$	$\gamma H2S$	$\gamma \text{CO2}$
Phon-8	0.9983	0.9992	0.9998	1
EA-1	0.9108	1.139	1.129	1.013
97009	1.018	1.959	1.7	1.813
DVDP3-295	1.305	3.574	2.671	2.857

Table Appendix B.1: Equilibrium constants of formation and fugacity coefficients

Equilibrium constants of formation from Robie et al. (1978). Fugacity coefficients calculated with a modified Redlich-Kwong equation of state.

	$H_2O^{melt}$	$\mathrm{CO}_2^{melt}$	$\mathbf{S}^{melt}$	$T (^{\circ}C)^1$	$\log f S_2^2$	$\log f O_2^3$	Р
	$\overline{\mathrm{wt}}\%$	ppm	ppm				$(bars)^4$
Phon-8	0.11	300	n.d.	1000	-2.7	-12.2	4.321
EA1 a	0.16	640	225	1000	9.7	11 91	9524
EAI-a	0.10 0.17	040 720	330 465	1000	-2.1	-11.01 11.01	2004
	0.17	730	400	1000	-2.1	-11.01	2195
EAI-a	0.10	100	430 265	1000	-2.1	-11.31	2080
EA1-e	0.18	430 640	303 255	1000	-2.1	-11.31	2002
EAI-I	0.2	040 700	399 405	1000	-2.1	-11.31	2020
EAI-g	0.15	760	405	1000	-2.7	-11.31	2775
EAI-h	0.18	760	395	1000	-2.7	-11.31	2938
EAI-1	0.15	790	375	1000	-2.7	-11.31	2851
EA1-j	0.14	880	260	1000	-2.7	-11.31	2998
EA1-k	0.18	580	420	1000	-2.7	-11.31	2450
Average	0.167	691	380.5	1000	-2.7	-11.31	2671.3
97009-a	0.59	3120	655	1081	-3.01	-9.99	3000
97009-b	0.58	1860	635	1081	-3.01	-9.99	3000
97009-c	0.56	2650	790	1081	-3.01	-9.99	3000
97009-d	0.45	1490	915	1081	-3.01	-9.99	3000
97009-е	0.47	1520	525	1081	-3.01	-9.99	3000
97009-f	0.52	2340	530	1081	-3.01	-9.99	3000
97009-g	0.52	2040	545	1081	-3.01	-9.99	3000
97009-h	0.44	3090	610	1081	-3.01	-9.99	3000
97009-i	0.49	2520	805	1081	-3.01	-9.99	3000
97009-j	0.65	3590	690	1081	-3.01	-9.99	3000
Average	0.527	2422	670	1081	-3.01	-9.99	3000
DVDP3_205a	1.66	5860	9137	1100	2.04	-7.28	5000
DVDP3_205h	1.00 1.67	4000	2107	1100	2.04	-7.20	5000
DVDP3 205c	1.07	4000 5050	2002	1100	2.00 2.10	7.20	5000
DVDP3 205d	1.40 1.67	5040	2400	1100	2.10	7.20	5000
DVDD2 205g	1.07	6750	2207	1100	2.29 1.71	7.00	5000
DVDF 3-295g	1.70	6750 5670	2107	1100	1.71	-1.20	5000
DVDF 3-2951	1.0	4800	2002	1100	1.90	-1.20	5000
DVDD2 2051	1.20 1.57	4090 4660	244ð 1797	1100	2.34	-1.28	5000
DVDP3-2951	1.07	4000	1/8/	1100	2.40	-1.28	5000
DVDP3-295q	1.25	528U	1927	1100	2.10	-1.28	5000 5000
DVDP3-295r	1.39	(270	2007	1100	1.00	-7.28	5000
Average	1.498	5537	2166.2	1100	2.13	-7.28	5000

Table Appendix B.2: Measured or modeled variables considered known

Phon-8: whole rock analysis of phonolite from Kyle (1977); EA1: Anorthoclase-hosted phonolite melt inclusions (Oppenheimer et al., 2011a); 97009 & DVDP3-295: Olivine-hosted tephriphonolite and basanite melt inclusions, respectively (Oppenheimer et al., 2011a); <sup>1</sup>Based on phase equilibrium experiments (this thesis; DVDP3-295), oxide compositions (Kyle et al., 1992, 97009), or estimates of lava lake T (Caldwell & Kyle, 1994; Dunbar et al., 1994; Kyle, 1977, EA-1, Phon-8). <sup>2</sup>Based on pyrrhotite compositions from (Kyle, 1977, Phon-8, EA-1) and (Kyle et al., 1992, 97009) or calculated using method in Chapter 5 (DVDP3-295). <sup>3</sup>Based on oxide compositions (Kyle, 1977, Phon-8; and Kyle et al., 1992, 97009) or phase equilibrium experiments (Moussallam et al., 2013, EA-1; and Chapter 4, DVDP3-295). <sup>4</sup>Modeled with (Papale et al., 2006, Phon-8, EA-1) or Chapter 3 (97009, DVDP3-295).

	$\log f SO_2$	$\log f H_2 O^1$	$\log f \mathbf{H}_2$	$\log f H_2 S$	$\log f \mathrm{CO}_2^2$
Phon-8	-2.84	0.21	-0.75	-1.04	0.41
	-	-		-	-
EA1-a	-1.95	0.56	-0.84	-1.13	3.41
EA1-b	-1.95	0.63	-0.78	-1.07	3.45
EA1-d	-1.95	0.58	-0.82	-1.11	3.43
EA1-e	-1.95	0.65	-0.76	-1.05	3.32
EA1-f	-1.95	0.73	-0.68	-0.97	3.42
EA1-g	-1.95	0.53	-0.88	-1.17	3.45
EA1-h	-1.95	0.66	-0.74	-1.03	3.47
EA1-i	-1.95	0.53	-0.87	-1.16	3.46
EA1-j	-1.95	0.48	-0.92	-1.21	3.48
EA1-k	-1.95	0.65	-0.76	-1.05	3.39
Average	-1.95	0.60	-0.81	-1.10	3.43
97009-a	-1.82	1.77	0.42	-0.29	3.73
97009-b	-1.82	1.76	0.40	-0.30	3.73
97009-с	-1.82	1.73	0.37	-0.33	3.73
97009-d	-1.82	1.55	0.20	-0.51	3.73
97009-е	-1.82	1.59	0.23	-0.47	3.73
97009-f	-1.82	1.67	0.31	-0.39	3.73
97009-g	-1.82	1.67	0.31	-0.39	3.73
97009-h	-1.82	1.54	0.18	-0.52	3.73
97009-i	-1.82	1.62	0.27	-0.44	3.73
97009-j	-1.82	1.85	0.49	-0.21	3.73
average	-1.82	1.67	0.32	-0.39	3.73
DVDP3-295a	3.42	2.60	-0.11	1.71	4.12
DVDP3-295b	3.72	2.61	-0.10	2.02	4.10
DVDP3-295c	3.45	2.50	-0.21	1.64	4.13
DVDP3-295d	3.55	2.61	-0.10	1.84	4.12
DVDP3-295g	3.25	2.64	-0.07	1.59	4.12
DVDP3-295i	3.39	2.40	-0.31	1.49	4.13
DVDP3-295j	3.57	2.38	-0.33	1.64	4.13
DVDP3-2951	3.60	2.56	-0.15	1.84	4.12
DVDP3-295q	3.45	2.37	-0.34	1.51	4.13
DVDP3-295r	3.23	2.46	-0.25	1.38	4.13
Average	3.46	2.51	-0.20	1.67	4.12

Table Appendix B.3: Calculated or modeled fugacities

 $^1 \rm Calculated$  using the model of Moore et al. (1998) for Phon-8 & EA-1 or Equation 3.6 from Chapter 3 for 97009 & DVDP3-295.  $^2 \rm Calculated$  with Equation 6.2 (Phon-8, EA-1, 97009) or Equations 6.4 & 6.5.

	$\mathrm{PCO}_2^1$	$\rm PH_2O$	$PSO_2$	$\rm PH_2S$	$\rm XCO_2^2$	$\rm XH_2O$	$XSO_2$	$\rm XH_2S$
Phon-8	2.59	1.63	0.00	0.09	0.6002	0.3782	0.0003	0.0212
	9590.01	4.01	0.01	0.07	0.0094	0.0016	0.0000	0.0000
EAI-a	2029.91	4.01	0.01	0.07	0.9984	0.0010	0.0000	0.0000
EAI-D	2188.28	4.04	0.01	0.08	0.9983	0.0017	0.0000	0.0000
EAI-a	2081.71	4.22	0.01	0.07	0.9984	0.0010	0.0000	0.0000
EAI-e	2007.03	4.88 E 97	0.01	0.08	0.9970	0.0024	0.0000	0.0000
EAI-I	2020.02 2771.94	0.87 2.60	0.01	0.10	0.9977	0.0022	0.0000	0.0000
EAI-g	2111.24	5.09 5.06	0.01	0.00	0.9980	0.0015 0.0017	0.0000	0.0000
	2932.83	3.00	0.01	0.08	0.9982	0.0017	0.0000	0.0000
EAI-I	2847.18	3.70 2.22	0.01	0.06	0.9987	0.0013	0.0000	0.0000
EAI-J	2994.00	3.33 4.09	0.01	0.05	0.9989	0.0011	0.0000	0.0000
LAI-K	2444.99	4.92	0.01	0.08	0.9980	0.0020	0.0000	0.0000
Average	2000.78	4.44	0.01	0.07	0.9965	0.0017	0.0000	0.0000
97009-a	2941.76	57.93	0.01	0.30	0.9806	0.0193	0.0000	0.0001
97009-b	2943.57	56.13	0.01	0.29	0.9812	0.0187	0.0000	0.0001
97009-с	2947.11	52.61	0.01	0.27	0.9824	0.0175	0.0000	0.0001
97009-d	2964.69	35.11	0.01	0.18	0.9882	0.0117	0.0000	0.0001
97009-е	2961.74	38.05	0.01	0.20	0.9872	0.0127	0.0000	0.0001
97009-f	2953.88	45.87	0.01	0.24	0.9846	0.0153	0.0000	0.0001
97009-g	2953.88	45.87	0.01	0.24	0.9846	0.0153	0.0000	0.0001
97009-h	2966.13	33.69	0.01	0.18	0.9887	0.0112	0.0000	0.0001
97009-i	2958.68	41.10	0.01	0.21	0.9862	0.0137	0.0000	0.0001
97009-j	2930.34	69.29	0.01	0.36	0.9768	0.0231	0.0000	0.0001
Average	2952.18	47.57	0.01	0.25	0.9841	0.0159	0.0000	0.0001
	1005 00	205 04	796.96	10.00	0.0194	0.0520	0 1005	0.0024
DVDP3-295a	4025.00	305.84	1470.84	19.20	0.8134	0.0538	0.1295 0.9257	0.0034
DVDP3-2950	4430.00	309.23 941 99	14/9.84	39.14 16 20	0.7000 0.9172	0.0495 0.0491	0.2337 0.1279	0.0002
DVDP3-295C	4085.00	241.23	790.10 096.91	10.30	0.8173	0.0421	0.1378 0.1672	0.0028
DVDP3-2950	4575.00	309.25	980.81	26.10	0.7758	0.0524	0.1073	0.0044
DVDP3-295g	4625.00	337.19	503.11 coo.04	14.51	0.8440	0.0015	0.0918	0.0026
DVDP3-2951	4750.00	194.05	090.24 1041.74	11.49	0.8412	0.0345	0.1222	0.0020
DVDP3-295j	4700.00	183.72	1041.74	10.37	0.7910	0.0309	0.1753	0.0028
DVDP3-2951	4585.00	275.89	1107.74	20.14	0.7048	0.0460	0.1848	0.0044
DVDP3-295q	4750.00	181.04	(85.49 474.04	12.10	0.8292	0.0310	0.13/1	0.0021
DVDF3-295r	4750.00	220.29	474.94	ð.90 10.04	0.8709	0.0404	0.08/1	0.0010
Average	4649.50	255.83	859.63	19.04	0.8039	0.0442	0.1486	0.0033

Table Appendix B.4: Calculated or modeled partial pressures and mole fractions of equilibrium fluids

 $^1$ Calculated using Equation 6.3 for Phon-8, EA-1 & 97009 or with Equation 6.2 for DVDP3-295.  $^2$ Calculated using Equation 6.5 for Phon-8, EA-1 & 97009 or based on isobars from Chapter 3 for DVDP3-295.

## Code for the simple fluid mixing model used in Chapter 6.

```
#include <stdio.h>
  #include <unistd.h>
2
  #include <stdlib.h>
3
  #include <sys/wait.h>
4
  //All compositions are given in mol%
6
  //The below values are given in the order: EA-1 equilibrium fluid;
      97009 equilibrium fluid; DVDP 3-295 equilibrium fluid; Lava Lake
      euqilibrium fluid; Bas-to-Teph MIs; Tehp-to-Phon MIs; Phon-to-LL
      MIS
  float co2_vals[] = {99.83/100.0, 98.41/100.0, 80.39/100.0,
      60.02/100.0, 10.78/100.0, 15.84/100.0, 16.95/100.0};
  float h2o_vals[] = {0.17/100.0, 1.59/100.0, 4.42/100.0, 37.82/100.0,
9
      82.11/100.0, 80.52/100.0, 60.38/100.0};
  float so2_vals[] = {0.0, 0.0, 14.86/100.0, 0.03/100.0, 6.96/100.0,
      1.85/100.0, 12.06/100.0;
  float h2s_vals[] = {0.0, 0.1/100.0, 0.33/100.0, 2.12/100.0,
      0.15/100.0, 1.79/100.0, 10.61/100.0};
  float total_s_vals[] = {0.0, 0.1/100.0, 15.19/100.0, 2.15/100.0,
      7.11/100.0, 3.64/100.0, 22.67/100.0};
13
  //The below values are all for the surface gas, given in the order: x
14
      ; x-1; x+1, where x = measured value
  float surface_gas_co2[] = {38.04, 37.0, 39.0};
15
16 float surface_gas_h2o[] = {60.47, 59.47, 61.47};
 float surface_gas_so2[] = {1.46, 0.0, 3.46};
17
18 float surface_gas_h2s[] = {0.03, 0.0, 1.0};
```

```
float surface_gas_total_s[] = {1.49, 0.0, 2.49};
19
20
  //Defines an inline function that multiplies the possible percentage
21
      values a,b,c,d,e,f, and g by the concentration of some species (
      CO2, H2O, or Stot) in each contributing fluid
  inline float getVals(int a, int b, int c, int d, int e, int f, int g,
22
       float *ptr) {
    return (a*ptr[0])+(b*ptr[1])+(c*ptr[2])+(d*ptr[3])+(e*ptr[4])+(f*
23
      ptr[5])+(g*ptr[6]);
24
  }
25
  //Define the variables to be used
26
  int main(void) {
27
    register int a,b,c,d,e,f,g;
28
    double x=0;
29
    float val;
30
    int i;
31
    int start_val, end_val;
32
    char s[200];
33
    FILE *ofp;
34
35
    pid_t pid;
36
37
    //Generates a list of tuples, each tuple 7 values long, where the
38
      sum of each tuple is 100
    for (i = 0; i < 4; i++) {
39
      if ((pid = fork()) == 0) {
40
         sprintf(s,"iter_out_%d",i);
41
         ofp = fopen(s, "w");
42
```

```
start_val = i*25;
43
         end_val = start_val + 26;
44
         for (a=start val;a<end val;a++) {</pre>
45
           printf("proc%d: i = %d\n",i,a);
46
           for (b=100-a; b>-1; b--) {
47
             for (c=100-a-b; c>-1; c--) {
48
               for (d=100-a-b-c; d>-1; d--) {
49
                 for (e=100-a-b-c-d; e>-1; e--) {
50
                   for (f=100-a-b-c-d-e; f>-1; f--) {
51
                     for (q=100-a-b-c-d-e-f; q>-1; q--) {
52
53
               //If G - 1 >= the sum of the proportioned fluid
54
      contributions >= G+1, exclude that tuple from the final list. G =
      measured surface gas value of each species.
                       val = getVals(a,b,c,d,e,f,g,co2_vals);
55
                        if ((val < surface_gas_co2[1]) || (val >
56
      surface_gas_co2[2])){
                          continue;
                        }
58
                        val = getVals(a,b,c,d,e,f,g,h2o_vals);
60
                        if ((val < surface_gas_h2o[1]) || (val >
61
      surface_gas_h2o[2])) {
                          continue;
62
                        }
63
64
                        val = getVals(a,b,c,d,e,f,g,so2_vals);
65
                        if ((val < surface_gas_so2[1]) || (val >
66
      surface_gas_so2[2])) {
```

```
67
                           continue;
                         }
68
69
                         val = getVals(a,b,c,d,e,f,g,h2s_vals);
70
                         if ((val < surface_gas_h2s[1]) || (val >
71
      surface_gas_h2s[2])){
                           continue;
72
                         }
73
                         //Prints all tuples where G - 1 <= sum of the
74
      proportioned fluid contributions <= G + 1 is true for all gas
      species. Output is saved to four files: one file for each forked
      process.
                         fprintf(ofp,"%d %d %d %d %d %d %d %d \n",a,b,c,d,e,f,
75
      g);
76
                       }
77
                    }
78
                  }
79
                }
80
              }
81
            }
82
         }
83
84
         fclose(ofp);
85
       }
86
87
     }
     wait(NULL);
88
89
     wait(NULL);
     wait(NULL);
90
```

91 wait(NULL); 92 return 0; 93 }

No.	$EA-1^1$	$97009^{1}$	$\mathbf{D}\mathbf{V}\mathbf{D}\mathbf{P}^1$	Lava Lake <sup>1</sup>	$\Delta Bas^2$	$\Delta \text{Teph}^2$	$\Delta Phon^2$
1	0	27	0	0	22	51	0
2	0	27	0	0	21	52	0
3	0	26	0	2	23	49	0
4	0	26	0	2	22	50	0
5	1	26	0	0	22	51	0
6	1	26	0	0	21	52	0
7	1	25	0	2	23	49	0
8	1	25	0	2	22	50	0
9	2	25	0	0	22	51	0
10	2	25	0	0	21	52	0
11	2	24	0	2	24	48	0
12	2	24	0	2	23	49	0
13	3	24	0	0	23	50	0
14	3	24	0	0	22	51	0
15	3	24	0	0	21	52	0
16	3	23	0	2	24	48	0
17	4	23	0	0	23	50	0
18	4	23	0	0	22	51	0
19	4	23	0	0	21	52	0
20	5	22	0	0	23	50	0
21	5	22	0	0	22	51	0
22	5	22	0	0	21	52	0
23	6	21	0	0	24	49	0
24	6	21	0	0	23	50	0
25	6	21	0	0	22	51	0
26	7	20	0	0	24	49	0
27	7	20	0	0	23	50	0
28	8	19	0	0	24	49	0
29	22	3	0	3	22	50	0
30	23	3	0	1	21	52	0
31	23	3	0	3	22	50	0
32	24	2	0	1	21	52	0
33	24	1	0	3	22	50	0
34	25	1	0	1	21	52	0
35	25	0	0	3	22	50	0
36	26	0	0	1	22	51	0
37	26	0	0	1	21	52	0
38	26	0	0	1	20	53	0

Table Appendix B.5: Output from the simple gas mixing code (Chapter 6)

All values are percentages. Each row represents a tuple generated by the code given in Chapter 6 that satisfies Equation 6.9. <sup>1</sup>Equilibrium gas coexisting with listed melts. <sup>2</sup>Degassed melt inclusions:  $\Delta$ Bas to Teph;  $\Delta$ Teph to Phon MI;  $\Delta$ Phon MI to LL Phon.

## References

- Allard, P. (2010). A CO<sub>2</sub>-rich gas trigger of explosive paroxysms at Stromboli basaltic volcano, Italy. Journal of Volcanology and Geothermal Research, 189(3), 363–374. 117
- Andújar, J., Costa, F., & Martí, J. (2010). Magma storage conditions of the last eruption of Teide volcano (Canary Islands, Spain). Bulletin of volcanology, 72(4), 381–395. 22, 66
- Asimow, P. D., & Ghiorso, M. S. (1998). Algorithmic modifications extending MELTS to calculate subsolidus phase relations. *American Mineralogist*, 83, 1127–1132. 16
- Aster, R., Zandomeneghi, D., Mah, S., Mcnamara, S., Henderson, D. B., Knox, H., & Jones, K. (2008). Moment tensor inversion of very long period seismic signals from Strombolian eruptions of Erebus Volcano. *Journal of Volcanology* and Geothermal Research, 177(3), 635–647. 1
- Barclay, J., Rutherford, M., Carroll, M., Murphy, M., Devine, J., Gardner, J., & Sparks, R. (1998). Experimental phase equilibria constraints on pre-eruptive storage conditions of the Soufriere Hills magma. *Geophysical Research Letters*, 25(18), 3437–3440. 22
- Behrendt, J., LeMasurier, W., Cooper, A., Tessensohn, F., Trehu, A., & Damaske, D. (1991). Geophysical studies of the West Antarctic rift system. *Tectonics*, 10(6), 1257–1273. 2
- Behrens, H., & Jantos, N. (2001). The effect of anhydrous composition on water solubility in granitic melts. American Mineralogist, 86(1-2), 14–20. 19
- Behrens, H., Misiti, V., Freda, C., Vetere, F., Botcharnikov, R. E., & Scarlato, P. (2009). Solubility of H<sub>2</sub>O and CO<sub>2</sub> in ultrapotassic melts at 1200 and 1250 °C and pressure from 50 to 500 MPa. *American Mineralogist*, 94(1), 105–120. 21, 37, 47, 50, 51, 53, 69, 76, 129

- Behrens, H., Ohlhorst, S., & Holtz, F. (2004).  $CO_2$  solubility in dacitic melts equilibrated with  $H_2O-CO_2$  fluids: implications for modeling the solubility of  $CO_2$  in silicic melts. *Geochimica et Cosmochimica Acta*. 19
- Berndt, J. (2002). Differentiation of MOR Basalt at 200 MPa: Experimental techniques and influence of  $H_2O$  and  $fO_2$  on phase relations and liquid line of descent. Master's thesis, Universitätsbibliothek u. Technische Informationsbibliothek. 108
- Berresheim, H., & Jaeschke, W. (1983). The contribution of volcanoes to the global atmospheric sulfur budget. *Journal of Geophysical Research: Oceans* (1978–2012), 88 (C6), 3732–3740. 24
- Bindschadler, R., Vornberger, P., Fleming, A., Fox, A., Mullins, J., Binnie, D., Paulsen, S. J., Granneman, B., & Gorodetzky, D. (2008). The Landsat image mosaic of Antarctica. *Remote Sensing of Environment*, 112(12), 4214–4226. xiii, 5
- Boichu, M., Oppenheimer, C., Tsanev, V., & Kyle, P. R. (2010). High temporal resolution SO<sub>2</sub> flux measurements at Erebus volcano, Antarctica. *Journal of Volcanology and Geothermal Research*, 190(3), 325–336. 4, 20
- Botcharnikov, R., Behrens, H., & Holtz, F. (2006). Solubility and speciation of C–O–H fluids in andesitic melt at T = 1100-1300 ° C and P = 200 and 500 MPa. *Chemical Geology*. 19
- Botcharnikov, R., Behrens, H., Holtz, F., Koepke, J., & Sato, H. (2004). Sulfur and chlorine solubility in Mt. Unzen rhyodacitic melt at 850 °C and 200 MPa. *Chemical geology*, 213(1), 207–225. 24
- Botcharnikov, R., Freise, M., Holtz, F., Behrens, H., et al. (2005). Solubility of COH mixtures in natural melts: new experimental data and application range of recent models. *Annals of Geophysics*. 53
- Botcharnikov, R. E., Holtz, F., & Behrens, H. (2007). The effect of  $CO_2$  on the solubility of H<sub>2</sub>O–Cl fluids in andesitic melt. *European Journal of Mineralogy*, 19(5), 671–680. 19
- Brooker, R., Kohn, S., Holloway, J., & McMillan, P. (2001). Structural controls on the solubility of CO<sub>2</sub> in silicate melts Part I: bulk solubility data. *Chemical Geology*. 19, 37
- Burgisser, A., Oppenheimer, C., Alletti, M., Kyle, P. R., Scaillet, B., & Carroll, M. R. (2012). Backward tracking of gas chemistry measurements at Erebus

volcano. Geochemistry Geophysics Geosystems, 13(11). 2, 20, 21, 59, 117, 154, 163, 167, 175

- Burgisser, A., & Scaillet, B. (2007). Redox evolution of a degassing magma rising to the surface. *Nature*, 445(7124), 194–197. 22, 107
- Caldwell, D., & Kyle, P. (1994). Mineralogy and geochemistry of ejecta erupted from Mount Erebus, Antarctica, between 1972 and 1986. Volcanological and Environmental Studies of Mount Erebus, Antarctica, (pp. 147–162). 154, 166, 198
- Calkins, J., Oppenheimer, C., & Kyle, P. (2008). Ground-based thermal imaging of lava lakes at Erebus volcano, Antarctica. Journal of Volcanology and Geothermal Research, 177(3), 695–704. 1, 154
- Carroll, M., & Rutherford, M. (1985). Sulfide and sulfate saturation in hydrous silicate melts. Journal of Geophysical Research: Solid Earth (1978–2012), 90(S02), C601–C612. 24
- Carroll, M. R., & Blank, J. G. (1997). The solubility of H<sub>2</sub>O in phonolitic melts. American Mineralogist, 82(5), 549–556. 19, 129
- Carroll, M. R., & Rutherford, M. J. (1987). The stability of igneous anhydrite: experimental results and implications for sulfur behavior in the 1982 El Chichon trachyandesite and other evolved magmas. *Journal of Petrology*, 28(5), 781–801. 151
- Carroll, M. R., & Rutherford, M. J. (1988). Sulfur speciation in hydrous experimental glasses of varying oxidation state; results from measured wavelength shifts of sulfur X-rays. *American Mineralogist*, 73(7-8), 845–849. 126, 149
- Chen, Y., Provost, A., & Schiano, P. (2011). The rate of water loss from olivinehosted melt inclusions. Contributions to Mineralogy and Petrology. 59
- Church, B., & Johnson, W. (1980). Calculation of the refractive index of silicate glasses from chemical composition. Geological Society of America Bulletin, 91(10), 619–625. 75
- Cioni, R. (2000). Volatile content and degassing processes in the AD 79 magma chamber at Vesuvius (Italy). Contributions to Mineralogy and Petrology, 140(1), 40–54. 76, 129
- Clémente, B., Scaillet, B., & Pichavant, M. (2004). The solubility of sulphur in hydrous rhyolitic melts. *Journal of Petrology*, 45(11), 2171–2196. 24, 133, 151, 163

- Cocheo, P. (1993). The solubility of water in basanitic melts at low pressures. Masters thesis, Arizona State University. 21, 46, 76, 129
- Connolly, J., & Cesare, B. (1993). C–O–H–S fluid composition and oxygen fugacity in graphitic metapelites. *Journal of metamorphic geology*, 11(3), 379–388. 163
- Cooper, A., Cochrane, G., Zhang, J., Brancolini, G., Pellis, G., & Egloff, F. (1994). The antarctic crustal profile seismic project, Ross Sea, Antarctica. Antarctic Journal. 4
- Cooper, A. F., Adam, L. J., Coulter, R. F., Eby, G. N., & McIntosh, W. C. (2007). Geology, geochronology and geochemistry of a basanitic volcano, White Island, Ross Sea, Antarctica. *Journal of Volcanology and Geothermal Research*, 165(3), 189–216. xiii, 6
- Curtis, A., & Kyle, P. (2011). Geothermal point sources identified in a fumarolic ice cave on Erebus volcano, Antarctica using fiber optic distributed temperature sensing. *Geophysical Research Letters*, 38(16), L16802. 117, 172
- Dasgupta, R. (2013). Ingassing, storage, and outgassing of terrestrial carbon through geologic time. *Reviews in Mineralogy and Geochemistry*, 75(1), 183– 229. 19
- Devine, J. D., Gardner, J. E., Brack, H. P., Layne, G. D., Rutherford, M. J., et al. (1995). Comparison of microanalytical methods for estimating H<sub>2</sub>O contents of silicic volcanic glasses. *American Mineralogist*, 80(3), 319–328. 77
- Di Carlo, I., Pichavant, M., Rotolo, S. G., & Scaillet, B. (2006). Experimental crystallization of a high-K arc basalt: the golden pumice, Stromboli volcano (Italy). Journal of Petrology, 47(7), 1317–1343. 82, 108
- Di Carlo, I., Rotolo, S. G., Scaillet, B., Buccheri, V., & Pichavant, M. (2010). Phase equilibrium constraints on pre-eruptive conditions of recent felsic explosive volcanism at Pantelleria Island, Italy. *Journal of Petrology*, 51(11), 2245–2276. 22, 66
- Dixon, J. (1997). Degassing of alkalic basalts. American Mineralogist. 20, 37, 38, 39
- Dixon, J., & Pan, V. (1995). Determination of the molar absorptivity of dissolved carbonate in basanitic glass. *The American mineralogist*, 80(11-12), 1339–1342. 14, 46, 76, 129

- Dixon, J., Stolper, E., & Holloway, J. (1995). An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part I: Calibration and solubility models. *Journal Of Petrology*. 19, 51, 52, 53, 55
- Duan, X. (2014). A general model for predicting the solubility behavior of  $H_2O-CO_2$  fluids in silicate melts over a wide range of pressure, temperature and compositions. *Geochimica et Cosmochimica Acta*, 125, 582–609. 18
- Dunbar, N. W., Cashman, K. V., & Dupré, R. (1994). Crystallization processes of anorthoclase phenocrysts in the Mount Erebus magmatic system: evidence from crystal composition, crystal size distributions, and volatile contents of melt inclusions. Volcanological and environmental studies of Mount Erebus, Antarctica, (pp. 129–146). 154, 166, 198
- Eggler, D., & Rosenhauer, M. (1978). Carbon-dioxide in silicate melts 2. Solubilities of CO<sub>2</sub> and H<sub>2</sub>O in CaMgSi<sub>2</sub>O<sub>6</sub> (diopsode) liquids and vapors at pressures to 40 kb. *American Journal Of Science*, 278(1), 64–94. 37
- Eggler, D. H. (1974). Application of a portion of the system CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>– NaAlSi<sub>3</sub>O<sub>8</sub>–SiO<sub>2</sub>–MgO–Fe–O<sub>2</sub>–H<sub>2</sub>O–CO<sub>2</sub> to genesis of the calc-alkaline suite. *American Journal of Science*, 274(3), 297–315. 4
- Eschenbacher, A. (1998). Pre-eruptive volatile contents of fractionating, alkaline magma, Mount Erebus, Ross Island, Antarctica. Unpublished MSc thesis, New Mexico Institute of Mining and Technology. xiv, xviii, xxi, 13, 15, 17, 59, 98, 151, 153, 158, 175, 178, 179, 180, 181, 182, 183, 184
- Esser, R. P., Kyle, P. R., & McIntosh, W. C. (2004). <sup>40</sup>Ar/<sup>39</sup>Ar dating of the eruptive history of Mount Erebus, Antarctica: volcano evolution. Bulletin of Volcanology, 66(8), 671–686. xiii, xiv, 4, 7, 8
- Feig, S. T., Koepke, J., & Snow, J. E. (2010). Effect of oxygen fugacity and water on phase equilibria of a hydrous tholeiitic basalt. *Contributions to Mineralogy* and Petrology, 160(4), 551–568. 82, 86
- Fine, G., & Stolper, E. (1986). Dissolved carbon dioxide in basaltic glasses: concentrations and speciation. Earth And Planetary Science Letters, 76(3-4), 263–278. 38, 47, 76
- Finotello, M., Nyblade, A., Julia, J., Wiens, D., & Anandakrishnan, S. (2011). Crustal Vp–Vs ratios and thickness for Ross Island and the Transantarctic Mountain front, Antarctica. *Geophysical Journal International*, 185(1), 85–92. 4, 12

- Flowers, G. C. (1979). Correction of Holloway's (1977) adaptation of the modified Redlich-Kwong equation of state for calculation of the fugacities of molecular species in supercritical fluids of geologic interest. *Contributions To Mineralogy* And Petrology, 69(3), 315–318. 50, 51, 85, 132, 162
- Foley, S. F. (1988). The genesis of continental basic alkaline magmasNan interpretation in terms of redox melting. *Journal of Petrology*, (1), 139–161. 109
- Freise, M., Holtz, F., Koepke, J., Scoates, J., & Leyrit, H. (2003). Experimental constraints on the storage conditions of phonolites from the Kerguelen Archipelago. *Contributions to Mineralogy and Petrology*, 145(6), 659–672. 22, 66
- Furman, T., & Graham, D. (1999). Erosion of lithospheric mantle beneath the East African Rift system: geochemical evidence from the Kivu volcanic province. *Developments in Geotectonics*, 24, 237–262. 4
- Galer, S., & O'nions, R. (1989). Chemical and isotopic studies of ultramafic inclusions from the san carlos volcanic field, arizona: A bearing on their petrogenesis. *Journal of Petrology*, 30(4), 1033–1064. 3
- Gates, D. S., & Thodos, G. (1960). The critical constants of the elements. AIChE Journal, 6(1), 50–54. 132
- Gee, L. L., & Sack, R. O. (1988). Experimental petrology of melilite nephelinites. Journal of Petrology, 29(6), 1233–1255. 109
- Gerke, T. L., Kilinc, A. I., & Sack, R. O. (2005). Ti-content of high-Ca pyroxenes as a petrogenetic indicator: an experimental study of Mafic alkaline rocks from the Mt. Erebus volcanic region, Antarctica. *Contributions to Mineralogy and Petrology*, 148(6), 735–745. 4
- Gerlach, T., & McGee, K. (1994). Total sulfur dioxide emissions and pre-eruption vapor-saturated magma at Mount St. Helens, 1980–88. Geophysical Research Letters, 21(25), 2833–2836. 159
- Gerlach, T. M., Westrich, H. R., Casadevall, T. J., & Finnegan, D. L. (1994). Vapor saturation and accumulation in magmas of the 1989–1990 eruption of Redoubt Volcano, Alaska. *Journal of Volcanology and Geothermal Research*, 62(1), 317–337. 159
- Giordano, D., Russell, J. K., & Dingwell, D. B. (2008). Viscosity of magnatic liquids: a model. Earth and Planetary Science Letters, 271(1), 123–134. 16

- Graf, H.-F., Feichter, J., & Langmann, B. (1997). Volcanic sulfur emissions: Estimates of source strength and its contribution to the global sulfate distribution. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 102(D9), 10727– 10738. 24
- Green, D. (1973). Conditions of melting of basanite magma from garnet peridotite. Earth and planetary science letters, 17(2), 456–465. 4
- Gupta, S., Zhao, D., & Rai, S. (2009). Seismic imaging of the upper mantle under the Erebus hotspot in Antarctica. Gondwana Research, 16(1), 109–118. 2
- Halmer, M., Schmincke, H.-U., & Graf, H.-F. (2002). The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years. *Journal of Volcanology and Geothermal Research*, 115(3), 511–528. 24
- Harris, A., Valade, S., Sawyer, G., Donnadieu, F., Battaglia, J., Gurioli, L., Kelfoun, K., Labazuy, P., Stachowicz, T., Bombrun, M., et al. (2013). Modern multispectral sensors help track explosive eruptions. *Eos, Transactions Ameri*can Geophysical Union, 94 (37), 321–322. 23
- Harrison, T. M., & Watson, E. B. (1984). The behavior of apatite during crustal anatexis: equilibrium and kinetic considerations. *Geochimica et Cosmochimica* Acta, 48(7), 1467–1477. 99, 105
- Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C., & Welch, M. D. (2012). Nomenclature of the amphibole supergroup. *American Mineralogist*, 97(11-12), 2031–2048. 91
- Holloway, J. R. (1971). Internally heated pressure vessels. In G. C. Ulmer (Ed.) Research techniques for high pressure and high temperature, (pp. 217–258). Berlin, Heidelberg, and New York (Springer-Verlag): Research for high pressure and temperature. 68
- Holloway, J. R. (1977). Fugacity and activity of molecular species in supercritical fluids. In *Thermodynamics in geology*, (pp. 161–181). Springer. 50, 51, 85, 132, 161, 162
- Humphreys, M. C., Kearns, S. L., & Blundy, J. D. (2006). SIMS investigation of electron-beam damage to hydrous, rhyolitic glasses: Implications for melt inclusion analysis. *American Mineralogist*, 91(4), 667–679. 149
- Iacono-Marziano, G., Gaillard, F., Scaillet, B., Pichavant, M., & Chiodini, G. (2009). Role of non-mantle CO<sub>2</sub> in the dynamics of volcano degassing: The Mount Vesuvius example. *Geology*, 37(4), 319–322. 118

- Iacovino, K. (2014a). Electronic appendix 2: Supplementary data file: Individual electron microprobe analyses of experimental and natural phases. URL http://dx.doi.org/10.6084/m9.figshare.913460 72
- Iacovino, K. (2014b). FTIR Background Subtract Program. URL http://dx.doi.org/10.6084/m9.figshare.928142 77
- Iacovino, K., Moore, G., Roggensack, K., Oppenheimer, C., & Kyle, P. (2013a). H<sub>2</sub>O–CO<sub>2</sub> solubility in mafic alkaline magma: applications to volatile sources and degassing behavior at Erebus volcano, Antarctica. *Contributions to Mineralogy and Petrology*, (pp. 1–16). 70
- Iacovino, K., Peters, N., & Oppenheimer, C. (2013b). Toward a unified method for the quantification of volatiles in magmas via FTIR. *Mineralogical Magazine*, 77(5), 1352. 77
- Ihinger, P. D., Hervig, R. L., & McMillan, P. (1994). Analytical Methods for Volatiles in Glasses. *Reviews in Mineralogy and Petrology*, 69. 46, 75, 128
- Jakobsson, S. (1997). Solubility of water and carbon dioxide in an icelandite at 1400 °C and 10 kilobars. *Contributions To Mineralogy And Petrology*. 19, 46
- Jendrzejewski, N., Trull, T., Pineau, F., & Javoy, M. (1997). Carbon solubility in mid-ocean ridge basaltic melt at low pressures (250–1950 bar). *Chemical Geology*. 19
- Johnson, J., Aster, R., Jones, K. R., Kyle, P., & McIntosh, B. (2008). Acoustic source characterization of impulsive Strombolian eruptions from the Mount Erebus lava lake. *Journal of Volcanology and Geothermal Research*, 177(3), 673–686. 4
- Jones, K. R., Johnson, J. B., Aster, R., Kyle, P. R., & McIntosh, W. (2008). Infrasonic tracking of large bubble bursts and ash venting at Erebus volcano, Antarctica. Journal of Volcanology and Geothermal Research, 177(3), 661–672.
- Jones, L., Frechette, J., Okal, M., Kyle, P., & Oppenheimer, C. (2011). Observing the dynamics of Mount Erebus using a terrestrial-based LiDAR (abstract). Polar Technology Conference, Albuquerque 24 Mar 2011. 1
- Jugo, P. J., Luth, R. W., & Richards, J. P. (2005). Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. *Geochimica* et Cosmochimica Acta, 69(2), 497–503. xxi, 126, 149, 150, 151

- Jugo, P. J., Wilke, M., & Botcharnikov, R. E. (2010). Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity. *Geochimica et Cosmochimica Acta*, 74(20), 5926–5938. xxi, 149, 150
- Kaszuba, J. P., & Wendlandt, R. F. (2000). Effect of carbon dioxide on dehydration melting reactions and melt compositions in the lower crust and the origin of alkaline rocks. *Journal of Petrology*, 41(3), 363–386. 67
- Kelly, P., Kyle, P., Dunbar, N., & Sims, K. (2008). Geochemistry and mineralogy of the phonolite lava lake, Erebus volcano, Antarctica: 1972–2004 and comparison with older lavas. *Journal of Volcanology and Geothermal Research*, 177(3), 589–605. xv, 9, 31, 32, 35, 117, 155
- Keppler, H. (2010). The distribution of sulfur between haplogranitic melts and aqueous fluids. *Geochimica et Cosmochimica Acta*, 74(2), 645–660. 24, 151
- Koepenick, K., Brantley, S., Thompson, J., Rowe, G., Nyblade, A., & Moshy, C. (1996). Volatile emissions from the crater and flank of Oldoinyo Lengai volcano, Tanzania. *Journal of geophysical research*, 101(B6), 13819–13. 109
- Kress, V., & Carmichael, S. (1991). The compressibility of silicate liquids containing Fe<sub>2</sub>O<sub>3</sub> and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contributions To Mineralogy And Petrology*, 108, 82–92. 50
- Kuryaeva, R., & Kirkinskii, V. (1997). Influence of high pressure on the refractive index and density of tholeiite basalt glass. *Physics and chemistry of minerals*, 25(1), 48–54. 75
- Kyle, P. (1981). Mineralogy and geochemistry of a basanite to phonolite sequence at Hut Point Peninsula, Antarctica, based on core from Dry Valley Drilling Project Drillholes 1, 2 and 3. *Journal Of Petrology*, 22(4), 451. xiv, xviii, xix, 3, 4, 9, 10, 12, 22, 32, 87, 100, 104, 110, 167, 175, 177
- Kyle, P., & Cole, J. (1974). Structural control of volcanism in the McMurdo Volcanic Group, Antarctica. Bulletin volcanologique, 38(1), 16–25. 3, 110
- Kyle, P., Moore, J., & Thirlwall, M. (1992). Petrologic evolution of anorthoclase phonolite lavas at Mount Erebus, Ross Island, Antarctica. *Journal Of Petrology*, 33(4), 849. xiv, xv, xviii, xxi, 2, 3, 8, 9, 10, 11, 12, 22, 29, 31, 32, 33, 70, 86, 96, 99, 107, 110, 122, 153, 154, 166, 167, 175, 177, 198

- Kyle, P. R. (1977). Mineralogy and glass chemistry of recent volcanic ejecta from Mt Erebus, Ross Island, Antarctica. New Zealand journal of geology and geophysics, 20(6), 1123–1146. 107, 117, 154, 155, 165, 166, 175, 177, 198
- Kyle, P. R., & Rankin, P. C. (1976). Rare earth element geochemistry of Late Cenozoic alkaline lavas of the McMurdo Volcanic Group, Antarctica. *Geochimica* et Cosmochimica Acta, 40(12), 1497–1507. 3, 4
- Kyle, P. R., Sybeldon, L. M., Mcintosh, W. C., Meeker, K., & Symonds, R. (1994). Sulfur dioxide emission rates from mount erebus, antarctica. Antarctic Research Series, 66, 69–82. 170
- Lange, R., & Carmichael, I. (1987). Densities of Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub> liquids - New measurements and derived partial molar properties. *Geochimica Et Cosmochimica Acta*, 51(11), 2931–2946. 46, 75, 128
- Lange, R. A. (1994). The effect of  $H_2O$ ,  $CO_2$  and F on the density and viscosity of silicate melts. *Reviews in Mineralogy and Geochemistry*, 30(1), 331-369. 19
- Le Bas, M., Le Maitre, R., Streckeisen, A., Zanettin, B., et al. (1986). A chemical classification of volcanic rocks based on the total alkali-silica diagram. *Journal* of petrology, 27(3), 745–750. 32
- Lesne, P., Kohn, S. C., Blundy, J., Witham, F., Botcharnikov, R. E., & Behrens, H. (2011a). Experimental simulation of closed-system degassing in the system basalt-H<sub>2</sub>O-CO<sub>2</sub>-S-Cl. Journal of Petrology, 52(9), 1737–1762. 19, 126
- Lesne, P., Scaillet, B., Pichavant, M., & Beny, J.-M. (2011b). The carbon dioxide solubility in alkali basalts: an experimental study. *Contributions To Mineralogy And Petrology*, (pp. 1–16). xv, xvi, 19, 21, 37, 39, 40, 52, 53, 54, 55, 63
- Lesne, P., Scaillet, B., Pichavant, M., Iacono-Marziano, G., & Beny, J.-M. (2011c). The H<sub>2</sub>O solubility of alkali basaltic melts: an experimental study. *Contributions To Mineralogy And Petrology*, 162(1), 133–151. xv, xvi, 19, 21, 39, 40, 52, 53, 55, 63
- Lowenstern, J. (2001). Carbon dioxide in magmas and implications for hydrothermal systems. *Mineralium Deposita*, 36(6), 490–502. 57
- Lowenstern, J. B., Mahood, G. A., Rivers, M. L., & Sutton, S. R. (1991). Evidence for extreme partitioning of copper into a magmatic vapor phase. *Science*, 252 (5011), 1405–1409. 159

- Marianelli, P., Sbrana, A., Métrich, N., & Cecchetti, A. (2005). The deep feeding system of Vesuvius involved in recent violent strombolian eruptions. *Geophysical* research letters, 32(2). 117
- Martí, J., Andújar, J., Costa, F., Wolff, J., & Carroll, M. (2008). Pre-eruptive conditions of the phonolitic magma from the El Abrigo caldera-forming eruption (Las Cañadas caldera, Tenerife, Canary Islands). In *IOP Conference Series: Earth and Environmental Science*, vol. 3, (p. 012013). IOP Publishing. 22, 66
- Matthews, S., Jones, A., & Beard, A. (1994). Buffering of melt oxygen fugacity by sulphur redox reactions in calc-alkaline magmas. *Journal of the Geological Society*, 151(5), 815–823. 127
- Matthews, S., Moncrieff, D., & Carroll, M. (1999). Empirical calibration of the sulphur valence oxygen barometer from natural and experimental glasses: method and applications. *Mineralogical Magazine*, 63(3), 421–421. 126, 127, 149
- Menzies, M., Kempton, P., & Dungan, M. (1985). Interaction of continental lithosphere and asthenospheric melts below the geronimo volcanic field, arizona, usa. *Journal of Petrology*, 26(3), 663–693.
- Merrill, R., & Wyllie, P. (1975). Kaersutite and kaersutite eclogite from kakanui, new zealandÑwater-excess and water-deficient melting to 30 kilobars. *Geological* Society of America Bulletin, 86(4), 555–570. 4
- Métrich, N., & Clocchiatti, R. (1996). Sulfur abundance and its speciation in oxidized alkaline melts. Geochimica Et Cosmochimica Acta, 60(21), 4151–4160. 126
- Métrich, N., & Wallace, P. J. (2008). Volatile abundances in basaltic magmas and their degassing paths tracked by melt inclusions. *Reviews in Mineralogy and Geochemistry*, 69(1), 363–402. 112
- Molina, I., Burgisser, A., & Oppenheimer, C. (2012). Numerical simulations of convection in crystal-bearing magmas: A case study of the magmatic system at Erebus, Antarctica. Journal of Geophysical Research: Solid Earth (1978–2012), 117(B7). 2, 175
- Moore, G. (2008). Interpreting  $H_2O$  and  $CO_2$  contents in melt inclusions: constraints from solubility experiments and modeling. *Reviews in Mineralogy and Geochemistry*, 69(1), 333–362. 16, 38
- Moore, G., & Carmichael, I. (1998). The hydrous phase equilibria (to 3 kbar) of an andesite and basaltic andesite from western Mexico: constraints on water

content and conditions of phenocryst growth. Contributions to Mineralogy and Petrology, 130(3-4), 304–319. 22, 66, 108

- Moore, G., Roggensack, K., & Klonowski, S. (2008). A low-pressure-hightemperature technique for the piston-cylinder. *American Mineralogist*, 93(1), 48–52. 41, 42
- Moore, G., Vennemann, T., & Carmichael, I. (1998). An empirical model for the solubility of H<sub>2</sub>O in magmas to 3 kilobars. *American Mineralogist*, 83(1), 36–42. 19, 143, 144, 148, 166, 199
- Morgan, G. B., & London, D. (2005). Effect of current density on the electron microprobe analysis of alkali aluminosilicate glasses. American Mineralogist, 90(7), 1131–1138. 149
- Morimoto, N. (1988). Nomenclature of pyroxenes. *Mineralogy and Petrology*, 39(1), 55–76. 91
- Morizet, Y., Brooker, R. A., & Kohn, S. C. (2002). CO<sub>2</sub> in haplo-phonolite melt: solubility, speciation and carbonate complexation. *Geochimica Et Cosmochimica Acta*, 66(10), 1809–1820. 19, 76, 129
- Moune, S., Holtz, F., & Botcharnikov, R. E. (2009). Sulphur solubility in andesitic to basaltic melts: implications for Hekla volcano. *Contributions to Mineralogy* and Petrology, 157(6), 691–707. 24
- Moussallam, Y. (2012). Hydrogen emissions from Erebus volcano, Antarctica. Bulletin of Volcanology, 74(9), 2109–2120. 175
- Moussallam, Y., Oppenheimer, C., Scaillet, B., & Kyle, P. R. (2013). Experimental phase-equilibrium constraints on the phonolite magmatic system of Erebus volcano, Antarctica. *Journal Of Petrology*. 1, 4, 24, 104, 107, 110, 112, 117, 123, 154, 155, 166, 167, 170, 176, 177, 198
- Mysen, B. (1990). Effect of pressure, temperature, and bulk composition on the structure and species distribution in depolymerized alkali aluminosilicate melts and quenched melts. *Journal Of Geophysical Research-Solid Earth And Planets*, 95(B10), 15733–15744. 37
- Mysen, B. O. (1977). The solubility of  $H_2O$  and  $CO_2$  under predicted magma genesis conditions and some petrological and geophysical implications. *Reviews of Geophysics*, 15(3), 351-361. 4
- Mysen, B. O. (1988). Structure and properties of silicate melts, vol. 354. Elsevier Amsterdam. 37

- Mysen, B. O., Virgo, D., & Seifert, F. A. (1982). The structure of silicate melts: implications for chemical and physical properties of natural magma. *Reviews of Geophysics*, 20(3), 353–383. 37
- Newhall, C., & Dzurisin, D. (1989). Historical unrest at large calderas of the world. Journal of Geology; (USA), 97(5). 4
- Newman, S., & Lowenstern, J. (2002). VolatileCalc: a silicate melt-H<sub>2</sub>O-CO<sub>2</sub> solution model written in Visual Basic for excel. *Computers and Geosciences*. xv, 38, 39, 40, 53, 63
- Nichols, A., & Wysoczanski, R. (2007). Using micro-FTIR spectroscopy to measure volatile contents in small and unexposed inclusions hosted in olivine crystals. *Chemical geology*, 242(3), 371–384. 75
- Ochs, F., & Lange, R. (1999). The density of hydrous magmatic liquids. *Science*, 283, 1314–1317. 46, 75, 128
- O'Neill, H. S. C., & Mavrogenes, J. A. (2002). The sulfide capacity and the sulfur content at sulfide saturation of silicate melts at 1400 C and 1 bar. *Journal of Petrology*, 43(6), 1049–1087. 143, 144
- Oppenheimer, C., Burton, M. R., Durieux, J., & Pyle, D. M. (2002). Open-path Fourier transform spectroscopy of gas emissions from Oldoinyo Lengai volcano, Tanzania. Optics and lasers in engineering, 37(2), 203–214. 109
- Oppenheimer, C., & Kyle, P. (2008a). Volcanology of Erebus volcano, Antarctica. Journal of Volcanology and Geothermal Research. 1, 2, 4, 20, 59, 61, 63, 110, 112, 117
- Oppenheimer, C., & Kyle, P. R. (2008b). Probing the magma plumbing of Erebus volcano, Antarctica, by open-path FTIR spectroscopy of gas emissions. *Journal* of Volcanology and Geothermal Research, 177(3), 743–754. 165, 170, 175
- Oppenheimer, C., Lomakina, A., & Kyle, P. (2009). Pulsatory magma supply to a phonolite lava lake. *Earth And Planetary Science Letters*. 20, 110, 156, 158, 167, 175, 177
- Oppenheimer, C., Moretti, R., Kyle, P. R., Eschenbacher, A., Lowenstern, J. B., Hervig, R. L., & Dunbar, N. W. (2011a). Mantle to surface degassing of alkalic magmas at Erebus volcano, Antarctica. *Earth And Planetary Science Letters*, 306(3-4), 261–271. xv, xvii, xviii, xxi, 1, 2, 4, 9, 13, 18, 20, 21, 24, 29, 31, 40, 41, 58, 59, 60, 61, 62, 64, 98, 99, 108, 110, 112, 113, 117, 151, 153, 154, 155, 158, 164, 165, 166, 167, 176, 198

- Oppenheimer, C., Scaillet, B., & Martin, R. S. (2011b). Sulfur degassing from volcanoes: source conditions, surveillance, plume chemistry and earth system impacts. *Reviews in Mineralogy and Geochemistry*, 73(1), 363–421. 23, 24
- Pandya, N., Muenow, D. W., & Sharma, S. K. (1992). The effect of bulk composition on the speciation of water in submarine volcanic glasses. *Geochimica et Cosmochimica Acta*, 56(5), 1875–1883. 75
- Papale, P., Moretti, R., & Barbato, D. (2006). The compositional dependence of the saturation surface of H<sub>2</sub>O + CO<sub>2</sub> fluids in silicate melts. *Chemical Geology*. xv, xvi, 16, 18, 20, 39, 40, 50, 53, 55, 63, 135, 143, 159, 166, 198
- Pawley, A. R., Holloway, J. R., & McMillan, P. F. (1992). The effect of oxygen fugacity on the solubility of carbon-oxygen fluids in basaltic melt. *Earth and Planetary Science Letters*, 110(1), 213–225. 50
- Peters, N. (2014). Avoplot: An extensible scientific plotting tool based on matplotlib. *Journal of Open Research Software*. 77
- Peters, N., Oppenheimer, C., & Kyle, P. (2014). Autonomous thermal camera system for monitoring the active lava lake at Erebus volcano, Antarctica. *Geo*scientific Instrumentation Methods and Data Systems, 3, 13–20. 1
- Popp, R. K., & Taras Bryndzia, L. (1992). Statistical analysis of Fe<sup>3+</sup>, Ti, and OH in kaersutite from alkalic igneous rocks and mafic mantle xenoliths. *American Mineralogist*, 77, 1250–1250. 106
- Popp, R. K., Virgo, D., & Phillips, M. W. (1995). H deficiency in kaersuitic amphiboles: Experimental verification. American Mineralogist, 80(11), 1347– 1350. 106
- Portnyagin, M., Almeev, R., & Matveev, S. (2008). Experimental evidence for rapid water exchange between melt inclusions in olivine and host magma. *Earth* and Planetary Science Letters. 59
- Prausnitz, J. M., Lichtenthaler, R. N., & de Azevedo, E. G. (1998). Molecular thermodynamics of fluid-phase equilibria. Pearson Education. 132, 162
- Robie, R. A., Hemmingway, B., & Fisher, J. R. (1978). Thermodynamic properties of minerals and related substances at 298.15 k and 1 bar pressure and at higher temperature. *Geol. Surv. Bull., vol., p. 1452-1452 (1978).*, 1, 1452–1452. 50, 85, 132, 197
- Roux, J., & Lefevre, A. (1992). A fast-quench device for internally heated pressure vessels. European journal of mineralogy, 4(2), 279–281. 68, 139

- Rutherford, M., Sigurdsson, H., Carey, S., & Davis, A. (1985). The May 18, 1980, eruption of Mount St. Helens: 1. Melt composition and experimental phase equilibria. *Journal of Geophysical Research: Solid Earth (1978–2012)*, 90(B4), 2929–2947. 22
- Rutherford, M. J. (1993). Experimental petrology applied to volcanic processes. Eos, Transactions American Geophysical Union, 74(5), 49–55. 16
- Sack, R. O., Walker, D., & Carmichael, I. S. (1987). Experimental petrology of alkalic lavas: constraints on cotectics of multiple saturation in natural basic liquids. *Contributions to Mineralogy and Petrology*, 96(1), 1–23. 66
- Scaillet, B., Clemente, B., Evans, B. W., & Pichavant, M. (1998). Redox control of sulfur degassing in silicic magmas. Journal of Geophysical Research: Solid Earth (1978–2012), 103 (B10), 23937–23949. 133, 143, 145, 151, 156
- Scaillet, B., & Macdonald, R. (2006). Experimental and thermodynamic constraints on the sulphur yield of peralkaline and metaluminous silicic flood eruptions. *Journal of Petrology*, 47(7), 1413–1437. 163
- Scaillet, B., & Pichavant, M. (2003). Experimental constraints on volatile abundances in arc magmas and their implications for degassing processes. *Geological Society, London, Special Publications*, 213(1), 23–52. 163
- Scaillet, B., Pichavant, M., Roux, J., Humbert, G., & Lefevre, A. (1992). Improvements of the Shaw membrane technique for measurement and control of fH<sub>2</sub> at high temperatures and pressures. *American Mineralogist*, 77, 647–655. 123
- Scaillet, B., Pichavant, M., et al. (2005). A model of sulphur solubility for hydrous mafic melts: application to the determination of magmatic fluid compositions of Italian volcanoes. Annals of Geophysics. 24
- Schnetzer, C. (1993). The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations. *Nature.*, 366, 327–329. 24
- Shaw, H. R., & Wones, D. R. (1964). Fugacity coefficients for hydrogen gas between 0 degrees and 1000 degrees C, for pressures to 3000 atm. American Journal of Science, 262(7), 918–929. 85
- Shinohara, H. (2008). Excess degassing from volcanoes and its role on eruptive and intrusive activity. *Reviews of Geophysics*, 46(4). 122, 159
- Shinohara, H., Aiuppa, A., Giudice, G., Gurrieri, S., & Liuzzo, M. (2008). Variation of H<sub>2</sub>O/CO<sub>2</sub> and CO<sub>2</sub>/SO<sub>2</sub> ratios of volcanic gases discharged by continuous

degassing of Mount Etna volcano, Italy. Journal of Geophysical Research: Solid Earth (1978–2012), 113(B9). 117

- Sigurdsson, H., Carey, S., Palais, J., & Devine, J. (1990). Pre-eruption compositional gradients and mixing of andesite and dacite magma erupted from Nevado del Ruiz Volcano, Colombia in 1985. Journal of Volcanology and Geothermal Research, 41(1), 127–151. 159
- Sisson, T., & Grove, T. (1993). Experimental investigations of the role of  $H_2O$  in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology*, 113(2), 143–166. 108
- Sisson, T., Ratajeski, K., Hankins, W., & Glazner, A. (2005). Voluminous granitic magmas from common basaltic sources. *Contributions to Mineralogy and Petrol*ogy, 148(6), 635–661. 108
- Späth, A., Le Roex, A. P., & Opiyo-Akech, N. (2001). Plume–lithosphere interaction and the origin of continental rift-related alkaline volcanismÑthe Chyulu Hills Volcanic Province, southern Kenya. *Journal of Petrology*, 42(4), 765–787. 4
- Spera, F. J. (1984). Carbon dioxide in petrogenesis III: role of volatiles in the ascent of alkaline magma with special reference to xenolith-bearing mafic lavas. *Contributions to Mineralogy and Petrology*, 88(3), 217–232. 67
- Spera, F. J., & Bergman, S. C. (1980). Carbon dioxide in igneous petrogenesis: I. Contributions to Mineralogy and Petrology, 74(1), 55–66. 57
- Spilliaert, N., Allard, P., Métrich, N., & Sobolev, A. (2006). Melt inclusion record of the conditions of ascent, degassing, and extrusion of volatile-rich alkali basalt during the powerful 2002 flank eruption of Mount Etna (Italy). Journal of Geophysical Research: Solid Earth (1978–2012), 111 (B4). 117
- Stoiber, R. E., Williams, S. N., & Huebert, B. (1987). Annual contribution of sulfur dioxide to the atmosphere by volcanoes. Journal of Volcanology and Geothermal Research, 33(1), 1–8. 24
- Sun, S. S., & Hanson, G. N. (1975). Origin of Ross Island basanitoids and limitations upon the heterogeneity of mantle sources for alkali basalts and nephelinites. *Contributions to Mineralogy and Petrology*, 52(2), 77–106. 3
- Sweeney, D., Kyle, P. R., & Oppenheimer, C. (2008). Sulfur dioxide emissions and degassing behavior of Erebus volcano, Antarctica. *Journal of Volcanology and Geothermal Research*, 177(3), 725–733. 4, 23, 155

- Tagliani, S. M., Nicotra, E., Viccaro, M., & Gianfagna, A. (2012). Halogendominant mineralization at Mt. Calvario dome (Mt. Etna) as a response of volatile flushing into the magma plumbing system. *Mineralogy and Petrology*, 106(1-2), 89–105. 117
- Thibault, Y., & Holloway, J. (1994). Solubility of CO<sub>2</sub> in a Ca-rich leucitite: Effects of pressure, temperature, and oxygen fugacity. *Contributions To Mineralogy And Petrology*, 116(1-2), 216–224. 19
- USGS (2001/2000). ASTER scenes AST\_ L1A.003:2004567740; AST\_L1A.003:2004567742; AST\_L1A. 003:2005468113; AST\_L1A.003:2003371731. USGS, Sioux Falls, (p. 10/20/2001; 10/20/2001; 09/03/2001; 10/23/2000). xiii, 5
- Vetere, F., Botcharnikov, R. E., Holtz, F., Behrens, H., & De Rosa, R. (2011). Solubility of H<sub>2</sub>O and CO<sub>2</sub> in shoshonitic melts at 1250° C and pressures from 50 to 400 MPa: Implications for Campi Flegrei magmatic systems. *Journal of Volcanology and Geothermal Research*. 19
- Walker, J. A., Roggensack, K., Patino, L. C., Cameron, B. I., & Matías, O. (2003). The water and trace element contents of melt inclusions across an active subduction zone. *Contributions to Mineralogy and Petrology*, 146(1), 62–77. 117
- Wallace, P. (2005). Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanology* and Geothermal Research. 59
- Wallace, P., & Carmichael, I. (1994). S speciation in submarine basaltic glasses as determined by measurements of SK $\alpha$  X-ray wavelength shifts. *The American mineralogist*, 79(1-2), 161–167. xxi, 126, 127, 149, 150
- Wallace, P. J., Anderson Jr, A. T., & Davis, A. M. (1999). Gradients in H<sub>2</sub>O, CO<sub>2</sub>, and exsolved gas in a large-volume silicic magma system: interpreting the record preserved in melt inclusions from the Bishop Tuff. *Journal of Geophysical Research*, 104 (B9), 20097–20. 159
- Wallace, P. J., & Gerlach, T. M. (1994). Magmatic vapor source for sulfur dioxide released during volcanic eruptions: evidence from Mount Pinatubo. *Science*, 265(5171), 497–499. 122, 159
- Wardell, L., Kyle, P., & Campbell, A. (2003). Carbon dioxide emissions from fumarolic ice towers, mount erebus volcano, antarctica. *Geological Society, Lon*don, Special Publications, 213(1), 231–246. 172

- Wardell, L., Kyle, P., & Chaffin, C. (2004). Carbon dioxide and carbon monoxide emission rates from an alkaline intra-plate volcano: Mt. Erebus, Antarctica. *Journal of volcanology and geothermal research*, 131(1), 109–121.
- Webster, J. D., & Botcharnikov, R. E. (2011). Distribution of sulfur between melt and fluid in SOHC-Cl-bearing magmatic systems at shallow crustal pressures and temperatures. *Reviews in Mineralogy and Geochemistry*, 73(1), 247–283. 151
- Williams, S. N., Schaefer, S. J., Marta Lucia Calvache, V., & Lopez, D. (1992). Global carbon dioxide emission to the atmosphere by volcanoes. *Geochimica et Cosmochimica Acta*, 56(4), 1765–1770. 24
- Winther, K. T., Watson, E. B., & Korenowski, G. M. (1998). Magmatic sulfur compounds and sulfur diffusion in albite melt at 1 GPa and 1300-1500 °C. *American Mineralogist*, 83, 1141–1151. 127
- Witham, F., Blundy, J., Kohn, S. C., Lesne, P., Dixon, J., Churakov, S. V., & Botcharnikov, R. (2012). SolEx: A model for mixed COHSCl-volatile solubilities and exsolved gas compositions in basalt. *Computers & Geosciences*, 45, 87–97. xv, 16, 24, 39, 40, 53, 63
- Wright, R., & Pilger, E. (2008). Satellite observations reveal little inter-annual variability in the radiant flux from the Mount Erebus lava lake. Journal of Volcanology and Geothermal Research, 177(3), 687–694. 4
- Zandomeneghi, D., Aster, R., Kyle, P., Barclay, A., Chaput, J., & Knox, H. (2013). Internal structure of Erebus volcano, Antarctica imaged by high-resolution active-source seismic tomography and coda interferometry. *Journal of Geophysical Research: Solid Earth.* 1
- Zimmer, M. M., Plank, T., Hauri, E. H., Yogodzinski, G. M., Stelling, P., Larsen, J., Singer, B., Jicha, B., Mandeville, C., & Nye, C. J. (2010). The role of water in generating the calc-alkaline trend: new volatile data for Aleutian magmas and a new tholeiitic index. *Journal of Petrology*, 51(12), 2411–2444. 108